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ON ORIGINS OF THE REGION C AND THE CORE OF THE EARTH —IONIC-INTERMETALLIC-METALLIC— TRANSITION HYPOTHESIS

BY

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1. Introducton

In any discussion concerened with the structure of the earth's interior, the problem of origins of the region C and the core plays the most important roll and attracts attention of geophysists, geochemists, mineralogists and geologists. Several hypotheses have been proposed on the region C or the core. There is, however, nothing that can explain both the origins of the region C and the core by such an idea, that one of both origins is inevitably related with another. Ramsey's hypothesis, for example, concerns with the core but not with the region C, although it seems to me that he supports the Jeffreys-Bernal's hypothesis regarding the origin of the region C, and believes that the pressure-induced changes paly the important roll on the structure of the earth's interior. Olivine-spinel transition hypothesis suggested by Jeffreys and Bernal implies no direct information for the origin of the core, and iron-core hypothesis is not directly connected with the origin of the region C. We should recognize the existence of a close relation between both origins, which may be connected with the evolution of the earth.

Though it is true that the structure of the earth's interior is so complicated for us to need a great deal of knowledge on physics, chemistry, cosmology and the other, the principal ideas contained in the hypotheses proposed hitherto are not so many as these hypotheses. The following two principal ideas are current according to the present writer's opinion ; (1) differenciation by chemical reaction or gravitational force, or both, and (2) pressure-induced change in cohesive properties.

The layered structure in the earth's interior, found by seismologists, attracted attention of the researchers, mainly geochemists, who gave many contributions based upon the idea (1) through an analogy with a smelting furnace. Unfortunately the knowledge on the thermal states within the earth's interior, one of the most difficult problems to be solved, is indispensable in the investigation based upon the idea (1). On the other hand, the idea (2) was developed mainly by physists comparatively later than the idea (1), who were stimulated by astrophysical investigations. One of the characteristic features in the idea (2) is that the physical state under considerably high pressure is independent of temperature in the first approximation, as whithin a white dwarf in an extreme case. This feature of the idea (2) has an adventage in comparison with idea (1), since anyone taking a part in each of the ideas, whether it is (1) or (2), muse fact the effect caused by high pressure.

The fact that the pressure of order of 1,000 *kbars* prevails the earth's central part prevents the investigators from applying simply the results established under low pressure region. Moreover it is noted that in any discussion concerning with the structure of the earth's interior are the two unknown parameters, "constituent materials and physical properties". Thus one attempts to find what kinds of materials can be there examining equation of state with some parameters demonstrating the materials, and it results often that ambiguities due to extrapolation of equation of state to high pressure are replaced by variaty of materials. There is, however, no evidence that simple extrapolation of physical relations to high pressure has necessarily the tendency such that they contain some real quantities in their approximation ranges. One wants to apply such a method that is possible to examine itself and alter itself according to given conditions. On this point of view, it seems that the microscopic treatments are able to possess the ability, because all studies on physical properties stand on the microscopic points of view. In the case, for example, to apply Thomas-Fermi-Dirac or Thomas-Fermi method for the state of the core, one can examine the validities under high pressure, as will be described later.

Of course, the microscopic treatments are much more complicated than the macroscopic one, so that labourous calculations are required in order to obtain some quantitative results. There is another weak-point, that is, the crystal structure and the bonding force must be set up and thus one

can not help to assume the constituent material. This difficulty, however, would be covered by many informations from cosmology, geochemistry, and mineralogy, to be restricted within the selection of relatlvely small number of compounds regarding the composition of the upper mantle. And, though the binding forces in these materials are unknown under high pressure range, there are many kinds of compounds, each of which is a characteristic of bond type under normal condition, and they are considered as the expressions of various types of bonding characters, some of which might be corresponding to the bonding characters induced by the effect of pressure. Therefore, we can investigate the bonding characters of many compounds under normal condition in laboratory, to estimate these deformed characters under the effect of pressure. The present paper originates in such a standpoint that the structure of the earth's interior is dependent on pressure-effect in the first approximation and the origins of the region C and the core are due to essentially same pressure-induced changes.

2. The region B

Jeffreys (1939a, b) computed values of the P-velocity throughout the earth. and of the S-velocity down to a depth of 2,900 *km*, using the Jeffreys-Bullen travel-times. This led to a division of the earth, with respect to depth, into several regions, each characterized by the type of velocity variation in it. The nomenclature A, B, C, D, E, F and G to denote the regions was introduced in the course of subsequent work (Bullen, 1940; 1942) on the problem of the earth's density variation. At a later stage (Bullen, 1949), it appeared that the lowest 200 *km* of the region D were sufficiently

Table 1. Regions of the earth's interior.

region	range of depth (*km*)	p-velocity (*km/sec*)	s-velosity (*km/sec*)
A	0-33	(widely varying)	(widely varying)
B	33-410	7.8- 9.0	4.4-5.0
C	410-1000	9.0-11.4	5.0-6.4
D′	1000-2700	11.4-13.6	6.4-7.3
D″	2700-2900	13.6	7.3
E	2900-4980	8.1-10.4	(not observed)
F	4980-5120	10.4- 9.5	(not observed)
G	5120-6370	11.2-11.3	(not observed)

different in a significant physical respect from the rest of D to warrant the subdivision of D into the regions D′ and D″. Table 1 summarizes the velocity distributions in these layers.

Williamson and Adams (1923) used hydrostatic relation with seismic data in examining the denity variation in the outer mantle, and Bullen also (1936) in an attack on the density variation in the whole earth. He gave the distributions of density, elastic constants and pressure in the two model, A and B, which are used widely in discussions of the earth's interior (Bullen 1953). These values well be used in the present paper. Also the present writer as well as many authors, will exclude the region A from the problem considered, because of its complicated character and less importance for the present study of deeper parts.

From Jeffreys-Bullen table, it had appeared that the P- and S-velocities increases with depth, starting a value of 7.8 *km/sec.* in the case of the P-velocity just below Mohorovičić discontinuity, at a very uniform rate to a depth near 410 *km.*

2.1. Materials composing the region B.

Dunite, a fairly pure form of olivine, $(Mg, Fe)_2SiO_4$, has been favoured as the rock in the region B by a large number of authors. Williamson and Adams first stated that there are no measurements which conflict seriously with the conclusion that the mantle consists of ultra-basic rock. Modern aspect of the internal composition that the relative abundances of the chemical elements in the earth may be found by suitable weighting of the analysis of meteorites. Washington concluded by analysis of the average stony meteorite that it corresponds to olivine, 35, pyroxene, 42, anorthosite, 4, troilite, 5, nickel-iron, 13 per cent. From his result the silicates of the average stony meteorite is considered to be fairly evenly divided between olivines and pyroxenes.

Attempting to reconcile the seismic data with respect to the region B with the meteoritic mineralogy, Birch (1952) stated that the ratio of incompressibility to denity in the region B agrees with only that of forsterite (Mg_2SiO_4), not with that of peridotite or the average stony meteorite, even without allowance for the effect of temperature. As in Table 2 are shown the ratios of incompressibilities to densities of several silicates and oxides,

Table 2. $\phi=(K_T/d)$ of some oxides and silicates.
(room temperature, one atmosphere)

substance	$\phi_0=(K_T/d)$ $(km/sec)^2$	substance	$\phi_0=(K_T/d)$ $(km/sec)^2$
oxides ;		$CaO\cdot Al_2O_3 2SiO_2$	33
MgO	47	$CaO\cdot MgO\cdot 2SiO_2$	28
Al_2O_3	69	$MgO\cdot SiO_2$	29
$MgO\cdot Al_2O_3$		(Mg, Fe)$O\cdot SiO_2$	28
$FeO\cdot Fe_2O_3$	37	$2MgO\cdot SiO_2$	36
Fe_2O_3	32	$2FeO\cdot SiO_2$	26
TiO_2	50	$3CaO\cdot Fe_2O_3\cdot 3SiO_2$	43
SiO_2-quartz	14	$3CaO\cdot Al_2O_3\cdot 3SiO_2$	45
Silicates :		$3MgO\cdot Al_2O_3\cdot 3SiO_2$	44
$Na_2O\cdot Al_2O_3\cdot 6SiO_2$	20	$3FeO\cdot Al_2O_3\cdot 3SiO_2$	40
$K_2O\cdot Al_2O_3\cdot 6SiO_2$	18	$3BeO\cdot Al_2O_3\cdot 6SiO_2$	67
$Na_2O\cdot Al_2O_3\cdot 4SiO_2$	39		
$Li_2O\cdot Al_2O_3\cdot 4SiO_2$	45		

there are a number of possibilities which don't so greatly strain the data. These minerals are garnets and the pyroxene mineral, jadite and spodumene, some of which are examined by several authors as the composition of the region B. For example, the eclogite was considered by Birch (1952) and some petrologists. Yoder (1950) and Robertson, Birch and MacDonald (1957) proposed the possibility of jadite composing the region B. There is, however, no evidence that these minerals are more adequate for the composition in the region B than olivine. At any rate one may conclude that the examination whether olivine has physical properties compatible with those in the region B should be first made. Olivine is generally composed of 90% forsterite (Mg_2SiO_4) and 10% fayalite (Fe_2SiO_4). Therefore the physical properties of olivine are demonstrated mainly by those of forsterite.

2.2. Changes of incompressibility and density of forsterite with pressure.

The structure of forsterite (olivine-structure) is found by Bragg (1937) as shown in Fig. 1. The unit cell has the following three axes ; $a=4.755\,A$, $b=10.21\,A$ and $c=5.985\,A$.

In order to obtain the lattice energy of forsterite, though exact quantum mechanical treatment is essentially required, this treatment is not applicable to such a complicated crystal structure as olivine structure, and therefore, the semi-empirical formula deviced by Born and Mayer (see, Born and Huang, 1954) is adopted, since forsterite is regarded, in the first approximation, as an ionic crystal (see, Verhoogen, 1958). Using Born and Mayer's formula, the lattice energy $U(v)$ of an ionic crystal is expressed by

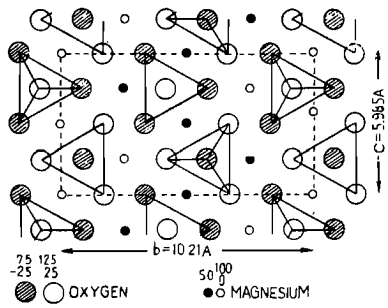

Fig. 1. Olivine-structure of Mg_2SiO_4. Si atom of which position is the center of O-tetrahedral, is not shown in the figure.

$$U(v) = -A/(v/v_0)^{1/3} + B\exp\{-(v/v_0)^{1/3}/\rho\} \qquad (2.1)$$

where v denotes volume per molecule, A, B and ρ constants, and suffix 0 refers zero pressure ((2.1) can be used only when temperature is absolute zero). (2.1) can be applied to the crystal containing somewhat covalent bonds, through the constants B and ρ modified suitably by semi-empirical treatment, and is proved to be deduced from quantum mechanical foundation. The first term in (2.1) exhibits the electrostatic potential energy and the second term the repulsive energy due to overlapping of electron clouds.

Магницкий (1953) applied already (2.1) to forsterite. He, however, used an uncorrect value of A, that is, the Madelung constant of olivine structure. The writer (1958, 1959a) evaluated the Madelung constant for olivine structure, using Bertaut's method (1952), which is suitable to treat such a complicated structure as olivine structure. The result is given by

$$A/(v/v_0) = 155.22e^2/b, \qquad (2.2)$$

where e is electronic charge ($=4.8029\cdot10^{-23}$ *esu*), and b is the length of b-axes.

By differentiating once and twice (2.1), pressure p and incompressibility (isothermal) K_T are expressed by

$$p = -dU/dv = (1/3v)[-A/(v/v_0)^{1/3} + B\{(v/v_0)^{1/3}/\rho\}\exp\{-(v/v_0)^{1/3}/\rho\}] \qquad (2.3)$$

$$K_T = -vdp/dv = (1/9v)[-A/(v/v_0)^{1/3} + B\{(v/v_0)^{1/3}/\rho\}\exp\{-(v/v_0)^{1/3}/\rho\} + B\{(v/v_0)^{2/3}/\rho^2\}\exp\{-(v/v_0)^{1/3}/\rho\}] + p. \qquad (2.4)$$

Using the experimental value of incompressibility under normal condition, $1.22 \cdot 10^{12}$ *dynes/cm*^{2}, from the condition $p=0$, the unknown parameters B and ρ are determined. Using these values (2.1) becomes

$$U = -350.709185/(v/v_0)^{1/3} + 5890.08736 \exp\{-4.2735(v/v_0)^{1/3}\} \quad (\cdot 10^{-12}\ ergs/molecule) \tag{2.5}$$

From (2.3), (2.4) and (2.5), one can evaluate pressure p and incompressibility K_T as functions of volume. Using the density under normal condition, 3.3 *gr/cm*^{3}, density d also is evaluated as a function of volume. If one uses the atomic weights of Mg, Si and O and the lattice constants given by Bragg, the density under normal condition becomes 3.216 *gr/cm*^{3}. Those values of pressure p, incompressibility K_T and density d thus obtained are listed in Table 3, and shown in Fig. 2, in comparison with those of Bullen.

Table 3. Variation of density, incompressibility and pressure of Mg_2SiO_4 versus (v/v_0).

(v/v_0)	pressure p ($\cdot 10^{12}$ *dynes/cm*^{2})	incompressibility ($\cdot 10$ *dynes*^{12}*/cm*^{2})	density (g/cm^3)
1	0.000	1.22	3.30
0.99	0.039	1.32	3.40
0.98	0.082	1.45	3.51
0.97	0.129	1.56	3.62
0.96	0.180	1.70	3.73

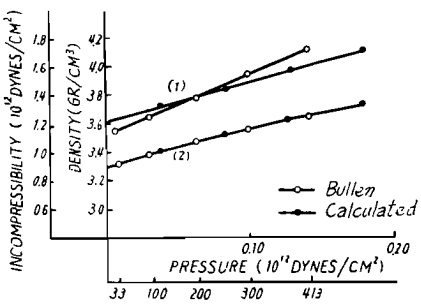

Fig. 2. Distribution of incompressibility (curve 1) and density (curve 2) within the region B.

In Fig. 2 one can see that the calculated density- and incompressibility-distributions are in well accordance with those of Bullen. Comparing the calculated value of the ratio of incompressibility to density, denoted by $\phi = K_T/d$, with that of Bullen, one can see that the maximum discrepancy is about 8%, that is due to the followings: (1) the calculated denotes the

isothermal values and Bullen's the adiabatic values, (2) (2.1) or (2.3) tends to exhibit somewhat poor approximation under higher pressure region, and (3) Bullen's value contains the error due to uncertainty in seismic velocities, especially in S-wave. Therefore we may conclude that the elastic properties deduced from olivine model are compatible with those in the region B. Also the expression (2.1) is regarded as a good approximation to the pressure range corresponding to the region B. The existence of about 10% fayalite together with forsterite in olivine may make the incompressibility a little lower, since fayalite is more compressible than forsterite.

2.3. Electric conductivity of forsterite

The electric conductivity of the earth's mantle can be inferred from a study of geomagnetic transient variation.

The periodic solar-daily variations and the aperiodic magnetic storms can be separated by a Gaussian analysis into induced and exciting components. A knowledge of the total field at the earth's surface enables one to compute the maximum depth penetrated by the induced currents. Knowing the depth of penetration of the induced currents over a wide range of frequency, one can calculate the distribution of the conductivity. A knowledge of the electric conductivity of the materials that make up the earth's mantle is important in discussion of the thermal state of the earth.

Lahiri and Price (1939) estimated the conductivity to a depth of about 800 *km.* They showed that a number of distributions are compatible with the magnetic variations, but there is a very rapid increase in conductivity somewhere within the outer few hundred kilometers of the earth. Considering the shielding effect of the oceans, Rikitake (1951) supports the conclusion of Lahiri and Price that the conductivity rises sharply some-

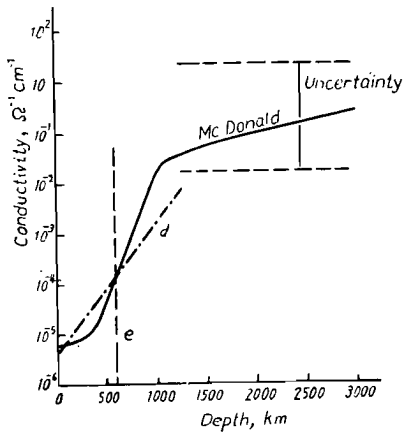

Fig. 3. Distribution of electrical conductivity within the mantle, according to Lahiri and Price, or McDonald.

where in the outer few hundred kilometer of the earth. McDonald (1957), extending the analysis to long-period variation of internal origin of magnetic field and was thus able to estimate the conductivity at the core-mantle boundary. These values are shown in Fig. 3.

Coster (1948) showed experimentally that the electric conductivities of silicates obey the relation

$$\sigma = \sigma_0 \exp(-E/kT) \tag{2.6}$$

where E is called activation energy and σ_0 is a constant proportionallity with the interpolation of conductivity at infinite temperature. Hughes (1953) confirmed Coster's results and further showed that the electrical conduction in olivine can be interpreted in terms of three different conductions. The numerical values for three mechanisms are listed in Table 4.

Table 4. Electric conductivity of olivine.

type of conduction	$ohm^{-1}\ cm^{-1}$	*E. ev.*	range of dominance, °C
Impurity	10^{-4}	1	<600
Intrinsic	10	3.2	600-1,1000
Ionic	10^{-5}	3.0	>1,100

On examining the Table 4, one can conclude that ionic conduction is predominant within the region B, because the temperature within the regin B is between about 1,000 and 2,000°*C*. To estimate the thermal state of the region B, the variation of σ_0 and E versus pressure, especially of E must be established. Hughes' laboratory study (1956) reported that dE/dp of peridot is $4.8 \cdot 10^{-6}$ *ev/bar* and the temperature at 100, 600, 1,000 *km* depth are 1,480, 2,200 and 3,180°*K*. His experiment, however, was done below a pressure of about 9.0 *kbars* and hence its extrapolation induced the overestimation of temperature within the mantle, due to a larger effect of temperature on E than of pressure under comparatively low pressure region (see, Wada, 1958, 1959a). Rikitake (1952) estimated theoretically the variation E versus pressure in the case of ionic conduction. The assumption made by him are as follows: the variation of E versus pressure is affected only by the variation of attractive potential, neglecting the repulsive potential of an ion pair, the effect of polarization energy due to ion-vacancy,

and the effect of potential barrier for a moving ion or hole. The present writer (Wada, 1958, 1959a) evaluated the activation energy E in ionic conduction of forsterite due to Schottky defects of Mg^{2+} and O^{2-}, to give the value of 3.2 *ev.* as in well accordance with Hughes' results of 3.0 *ev.*. His evaluation, based upon Mott and Littleton's method (1938), includes the effects of repulsive energy and polarization energy. Moreover, he estimated the variation of E versus pressure. It is, however, noted that, because the changes of some parameters, such as the dielectric constant and the polarizabilities of ions, versus pressure are unknown, he adopts the plausible assumptions as follows :

(1) the variation of polarization energy is considered for the three cases; independent of v (case 1), in proportion to $(v)^{-1/6}$ (case 2) and $(v)^{-1/3}$ (case 3),

(2) the potential barrier varys in propotion to $(v)^{-4}$, because the repulsive potential, as considered generally as mainly effective in this case, varys in proportion to $(r)^{-12}$, where r denotes the nearest neighbour interionic distance,

(3) the temperature-dependency of E is evaluated by equation of state of Mie and Grüneisen (see, Born and Huang, 1953).

The values of E thus obtained are listed in Table 5. He concluded as follows :

(I) Under a pressure range between 0 and 10.0 *kbars*, the temperature-dependency of E is appreciably effective in comparison with the pressure-dependency, and hence, if one extrapolates the resuls to higher pressure,

Table 5. Pressure-dependence of activation energy at 1,500°K.

P	$E(ev.)$		
($\cdot 10^{12}$ *dynes/cm*^{2})	Case I	Case II	Case III
0.000	3.250	3.265	3.296
0.010	3.290	3.290	3.290
0.049	3.405	3.370	3.260
0.092	3.516	3.420	3.210
0.137	3.620	3.480	3.150
0.187	3.720	3.570	3.100

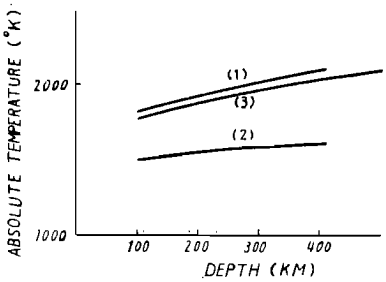

Fig. 4. Distribution of temperature within the region B. (1) calculated value based upon Lahiri and Price's d-curve, (2) based upon Rikitake's model, and (3) Cutenberg's results.

one should overestimate E, and hence, also temperature, as seen in the estimation made by Hughes, (II) dE^2/dP^2 can not be disregarded, as suggested already by Verhoogen (1956), and (III) the monotone-increase of E versus pressure is mainly due to the variation of potential barrier, whereas the residual part of E rather appears to decrease, as noted by Tozer (1959), too.

Based upon the estimation of E as a function of pressure or volume, the temperature-distribution within the region B was estimated by the writer, adopting the electric conductivity-distributions given by Lahiri and Price' d-curve and Rikitake's curve, where σ_0 was assumed as a constant, 10^6 $ohm^{-1}cm^{-1}$. His result is shown in Fig. 4, with the temperature distribution given by Gutenberg (1949). It is noted that the pressure-dependency of σ_0 was disregarded in his evaluation, whereas Rikitake and Hughes considered it. According to Tozer's opinion (1959), the effect is rather so small that the change of σ_0 of less than 50% throughout the mantle would be cosidered as a negligibly small contribution on the estimation of temperature within the mantle, in comparison with the effect due to the change of E.

From the description made hitherto, the assumption that the region B is composed mainly of olivine (almost forsterite) appears to have no serious objection. Namely the electric and elastic properties of forsterite agree well with those obtained from seismic and geomagnetic observations within the region B.

3. The region C.

Jeffreys (1936) reported the existence of a second-order discontinuity (change of gradient) in the seismic wave travel time at the depth corresponding to the epicenter distance of 20°. Since then many authors have discussed the nature and origin of this discontinuity. Jeffreys (1939a)

pointed out that there are sharp increases in the velocity gradients at a depth of 413 *km.*, the gradients then steady diminishing until normality is recovered near 1,000 *km.* Because of the smoothness of the changes near 1,000 *km*, the depth selected for the base of region C is somewhat arbitrary, but this arbitrariness is of no significance.

Gutenberg (1951) has not found evidence of the 20° discontinuity, and his gradients run fairly steady from a depth of 150 *km.* to about 1,000 *km.*, where, however, there is a sharp reduction in the gradients. Though the discussion on the seismological evidence has not yet been confirmed, the existence of some kind of abnormality in the region C should not be overlooked.

We have, moreover, another important facts concerning the peculiarities of the region C. As mentioned in sec. 2.3., the existence of an abrupt increase in the electric conductivity is deduced at a depth corresponding approximately to the region C from short-period variation in the geomagnetic field. The sharp change in the conductivity means a sharp change in the activation energy E which will be related to a change in the physical or chemical state.

To account for the change of ϕ in the region C, Jeffreys and Bernal (1936) suggested a transition from orthorhombic to cubic olivine brought about by the high pressure. Bridgeman (1951) has incidentally found a discontinuous changes in the shearing strength of olivine at a pressure of 84.0 *kbars*, which corresponds to a depth of 250 *km* below the earth's outer surface.

Birch (1952) discussed the question of uniformity in the region C. Uniformity means that the variations of density and compressibility are caused by compression alone, as contrasted to variation resulting from chemical or physical change of state. He assumed the following equations to hold in the region C:

(A) hydrostatic equilibrium $dp/dr=-dg$,

(B) uniform composition $dp/da=K/d=\phi$,

and (C) adiabatic temperature gradient $dT/dr=(Ta/\rho C_p)dp/dr$,

where r is the radial distance, T, a and C_p the temperature, thermal expansion coefficient and specific heat. From these conditions, dK/dp can be evaluated directly from a knowledge of ϕ, which are deduced from seismic data. On the other hand, Birch used an equation of state deduced

from finite strain theory, to obtain a theoretical curve of the expression dK/dp as a function of depth. This theoretical curve disagrees the observed values deduced from ϕ in the region C, whereas in the region B and D both curves are in well accordance. This shows that at least one of the three assumptions, (A), (B) and (C), is not satisfied in the region C. Birch considered that the region C may be associated with a change of proportion of MgO, FeO and SiO_2 regarded as distinct phases. Miki (1955) discussed the possibility of a non-hydrostatic state in the region C.

Shimazu (1958) stated that there are two types of ideas on the origin of the region C.

(I) the material composing the region C is chemically as same as in the region B and D, but has crystallographical difference, which is related to some change of the cohesive properties.

(II) the region C is composed of any different material from those in the region B and D.

Regarding (1), olivine-spinel transition was first suggested. Магницкий (1956) and Магницкий and Калинин (1959) suggested the possibility that the chemical bond of Mg-O in Mg_2SiO_4 crystal transforms from ionic to covalent bond. Though in the transformation the possibility of crystallographic change was stated by no mean, his idea is regarded as belonging to (1). Holser and Schneer (1957) examined the possibility of (1) in the point of view of crystallographic investigation.

Regarding (II), the decomposition of Mg_2SiO_4 to two oxides, MgO and SiO_2, was suggested by Магницкий (1953) and Shimazu (1958). MacDonald (1956) also examined the same idea. Simazu's idea is different from the other in concern with considering a "squeezing process" to exclude SiO_2 produced in the decomposition out the region C.

3.1. Olivine-spinel transition

Since the suggestion of Jeffreys and Bernal, a little contribution to olivine-spinel transition hypothesis was made until Ringwood's papers were published. (Ringwood, 1956a, b, c, 1958a, b, c, 1959). Miki (1956) and Shima (1956) examined whether the change of ϕ in some polyorphic transition is likely to be positive. Miki concluded that the changes of ϕ in several transitions between each pair of typical crystal structures are likely

to be negative. He used the simplest formula of ionic crystal energy, which has an inverse power form as repulsive potential, using the repulsive coefficient n unchanged at each transition.

On the other hand, Ringwood investigated sub-phase equilibrium in the system Ni_2GeO_4-Mg_2SiO_4. Ni_2GeO_4 possesses a spinel structure and the ions Ni^{2+} and Mg^{2+} are similar in crystal-chemical properties and then able to replace each other in a many crystals and minerals. A similar resemblance occurs between Si^{4+} and Ge^{4+}. Studying the properties of this solid solution, he deduced their equilibrium relationship to coexisting olivine-spinel solid solution, through thermodynamical consideration. The p-v diagram obtained by him is shown in Fig. 5.

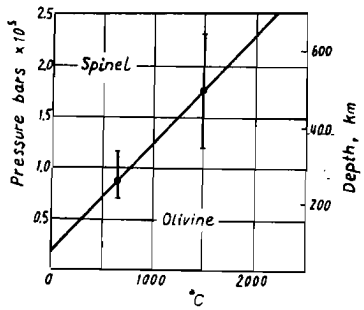

Fig. 5. Calculated equilibrium curve for the olivine-spinel transition in Mg_2SiO. Vertical lines indicates ranges of possible error due to experimental uncertainty (after Ringwood).

The present writer (Wada, 1958, 1959a) examined the possibility of olivine-spinel transition, comparing their lattice energies. The electrostatic potential energy of olivine structure is already given in section 2.2, and the Madelung constant for spinel structure was evaluated by Verwey, de Boer and van Santen (1948), who considered the change of oxygen parameter u, which is often used in the form $u=(3/8)+\delta$. When $\delta=0$ or $u=0.375\,A$, oxygen ions are situated in the most closely packed structure. There are the two kinds of arrangements of constituent ions in spinel structure, normal spinel and inverse spinel. If one exchanges a half of positive ions situated in octahedral sites with all of positive ions situated in tetrahedral sites in a normal spinel, a inverse spinel will be expressed.

Let the lattice energy be expressed by

$$U=-A/r+B/r^n \tag{3.1}$$

If the transition from olivine to spinel occurs at a pressure p, the thermodynamical equilibrium condition is expressed by

$$U+pv=U'+pv' \tag{3.2}$$

where the quantities with prime are refered to the high pressure modifica-

tion. Let us write (3.2) as

$$p=(U'-U)/(v-v') \tag{3.3}$$

The right hand side of (3.3) is, of course, a function of pressure. As an approximation, however, one can simply ignore the pressure dependence of the expression on the right and use its value corresponding to zero pressure.

$$p=(U_0'-U_0)/(v_0-v_0'), \tag{3.4}$$

where the suffix 0 signifies the value at zero pressure. It follows from the equilibrium condition and (3.5) that the nearest neighbour distance at zero pressure is given by

$$r_0=(nB)^{n-1}/(A)^{n-1} \tag{3.5}$$

and the energy per molecule can be writen as

$$U(r_0)=-A(n-1)/r_0 n \tag{3.6}$$

Since the volume per molecule is proportional to the third power of the nearest neighbour distance, let us denote the volume per molecule by sr^3 and $s'r^3$, respectively, for the two structures. Thus using (3.5) and (3.6) in (3.3), one can obtain the following approximation for the transition pressure :

$$p=AF_n/sr_0^4 \tag{3.7}$$

with F_n defined by

$$F_n=\frac{(n-1)}{n}\frac{\{1-(A'/A)^{n/(n-1)}(B/B')^{1/(n-1)}\}}{\{1-(s'/s)(B'A/BA')^{3/(n-1)}\}} \tag{3.8}$$

where the quantities with and without prime refer respectively to the high and low pressure modifications of the crystal.

The condition that a transition is possible, is expressed by $F_n>0$, since $p>0$ in (3.8) is necessary. Hence let us consider the possibility of tran-

Table 6. Electrostatic potential energy of spinel (normal and inverse) for several values of oxygen parameter u (unit : $(e^2/b)/molecule$).

type	$u=0.375$	$u=0.380$	$u=0.385$	$u=0.390$
normal spinel	168.9	166.1	163.5	190.9
inverse spinel	157.3	160.8	163.9	167.0

sition from olivine to spinel (normal or inverse), with the change of oxygen parameter u. Table 6 shows the Madelung constants for spinel structure, in which we adopt the length of b-axes of olivine, b, as an unit in length, whereas the values given by Verwey et al. are expressed by the lattice constant a as an unit in length. Therefore it is resulted in $s'/s=1$. Comparing the Madelung constant A for olivine structure with the Madelung constant A' for spinel structure with the change of oxygen parameter u, we know that A' is larger than A in the following range of u: $0.372<u<0.401$, whether spinel is normal or inverse (see Fig. 6).

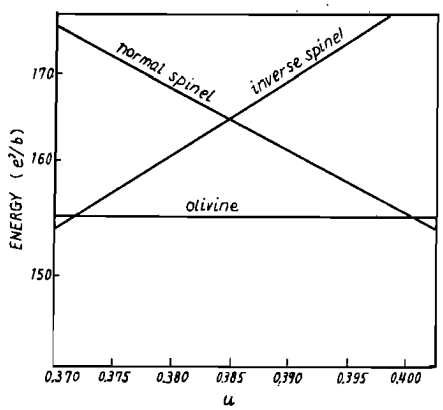

Fig. 6. Comparision of electrostatic potential energies of spinel and olivine forms in Mg_2SiO_4.

When $A'/A>1$, the condition of $F_n>0$ is satisfied in the two cases,

(i) $(A'/A)^n(B/B')<1$ and $(B'/B)(A/A')<1$

and (ii) $(A'/A)^n(B/B')>1$ and $(B'/B)(A/A')>1$

If we write $(B'A/BA')\equiv C$, (i) is expressed by $(A'/A)^{n-1}/C<1$ and $C<1$, one of which is not compatible with the other, because of the condition of $(A'/A)>1$. On the other hand, (ii) is satisfied, but this case means $r_0'>r_0$, namely, that corresponds to the transition from spinel to olivine. Thus it is concluded that the transition from olivine to spinel is impossible in the range of u, $0.372<u<0.402$. In the case of $u>0.402$, the transition to normal spinel is regarded as possible, but the spinel structure of $u>0.402$ is unlikely to be realized, because the tetrahedral site is too large. In the case of $u<0.372$, the transition to inverse type is regarded as possible, but the spinel structure having $u<0.372$ appears to be not found in usual compounds. The spinel structure having $u<0.372$ may be rather similar to olivine structure. Then we can conclude that the transition from olivine to spinel may be possible under the severe condition above described, on other words, impossible in the usual condition. Regarding this conclusion, it may be noted that Holser and Schneer (1957) suggested the possibility of the transition to the *inverse olivine* structure.

Recently Wentorf (1959) reported that no spinel form of forsterite was obtained at pressure as high as 130 *kbars.*

Regarding the olivine-spinel transition hypothesis, there is another question whether the spinel form possesses or not the elastic properties corresponding to those in the region C, even if the possibility of transition is allowed. Generally speaking, the second phase deduced from such a polymorphic transition as found in alkali halide, is likely to have rather less ϕ than the first phase, whereas Ringwood considered that the spinel form of forsterite may have the ϕ similar to that of corundum.

3.2. $Mg_2SiO_4 \rightleftarrows 2MgO + SiO_2$ hypothesis

Recently Магницкий (1953, 1955) and Shimazu (1958) suggested the hypothesis that in the region C is taken place the decomposition of Mg_2SiO_4, that is,

$$Mg_2SiO_4 \rightleftarrows 2MgO + SiO_2. \qquad (3.9)$$

At normal pressure the volume change in reacton (3.9) is positive. Due to a highly compressible property of normal quartz the molar volume of the right hand side of (3.9) reduces rapidly and the molar volume change becomes negative with increasing pressure. Thus the decomposition temperature increases, reaches a maximum, and then decreases with increasing pressure. The ($2MgO + SiO_2$) model for the region D, however, does not seem to be reasonable, since the value of ϕ for SiO_2 is low.

Another decomposition process was suggested by MacDonald (1956). He pointed out that the molar volume change for reaction (3.9) is negative with coesite phase and thus the decomposition of Mg_2SiO_4 is realized at high pressure. Though the compressibility of coesite is unknown, one report (see, Coes, 1953) says that the hardness of coesite is of the same order as spinel or garnet. Thus the ($2MgO + SiO_2$ coesite) model for the region D will be unreasonable since the value ϕ would be too small.

Apart from the mixture model above described, Shimazu suggested the decomposition with squeezing of SiO_2, as expressed by

$$Mg_2SiO_4 \rightleftarrows 2MgO + SiO_2 \text{ (coesite)} \uparrow \qquad (3.10)$$

where SiO_2 (coesite) can migrate through the system. He considered the reaction system of which components are Mg_2SiO_4 (forsterite), $MgSiO_3$

(enstatite), MgO (periclase), and SiO_2 (coesite), as follows :

$$\left.\begin{aligned} &Mg_2SiO_4 \rightleftarrows 2MgO+SiO_2\ (\text{coesite})\uparrow \\ &2MgSiO_3 \rightleftarrows Mg_2SiO_4+SiO_2\ (\text{coesite})\uparrow \\ &MgSiO_3 \rightleftarrows MgO+SiO_2\ (\text{coesite})\uparrow \\ &Mg_2SiO_4 \rightleftarrows MgO+MgSiO_3 \end{aligned}\right\} \qquad (3.11)$$

And similar reactions can be expected for the system of Fe_2SiO_4 (fayarite), $FeSiO_3$, FeO (wüstite) and SiO_2 (coesite), as follows :

$$\left.\begin{aligned} &Fe_2SiO_4 \rightleftarrows 2FeO+SiO_2 \\ &2FeSiO_3 \rightleftarrows Fe_2SiO_4+SiO_2 \end{aligned}\right\} \qquad (3.12)$$

The curves of equilibrium temperature versus depth for the mantle condition is given in Fig. 7. One can see in Fig. 7 that $MgSiO_3$ decmposes into Mg_2SiO_4 at about 200 *km* depths and Mg_2SiO_4 into MgO at about 600 *km* depth both with squeezing SiO_2. The stable region for $MgSiO_3$ is restricted to the shallow part of the region B, and MgO is stable at the deeper mantle. And Fe_2SiO_4 decomposes at about 100 *km* depth and is not stable at the deeper mantle than 100 *km* depth.

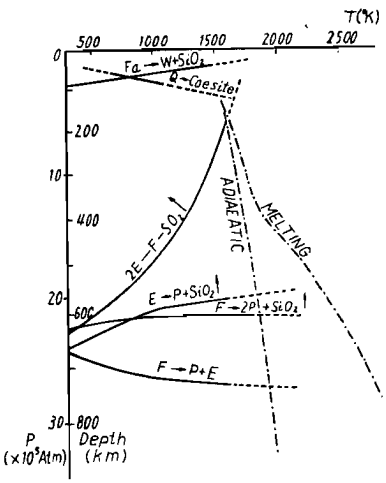

Fig. 7. Phase-diagram of ferromagnesium silicates. F=Mg_2SiO_4, Fa=Fe_2SiO_4, E=$MgSiO_3$, P=MgO, Q=quartz (after Shimazu).

In this decomposition process the region C is regarded as composed of MgO-SiO_2 (coesite) mixture, in which the mixing ratio is determined by the degree of squeesing at each depth. Let us attempt to know whether the decomposition process with squeezing gives the density d and ϕ compatible with those in the region C. As will be described later in section 4.1., we have an equation of state of MgO (normal ionic crystal), obtained by the writer or Трубицын (1958). Let us adopt the equation obtained by Трубицын since this equation will give better result than that obtained by the writer. Let now us express the degree of squeezing by a parameter α, as follows :

$$2MgO+(1-\alpha)SiO_2 \qquad (3.13)$$

The ϕ_0 of the mixture could be approximately given by

$$\phi_0=\frac{2K_m v_m+K_s v_s(1-\alpha)}{2m_m+m_s(1-\alpha)}=\frac{2\phi_m m_m+\phi_s m_s(1-\alpha)}{2m_m+m_s(1-\alpha)} \tag{3.14}$$

where the suffices 0, m, s signify the values of the mixture, MgO and SiO_2, and m, v, K denote molecular weight, volume per mole and incompressibility. If the mixture has the value of ϕ_0 compatible with that in the region C, the ϕ_0 should be equal to the observal value of ϕ_c. The ϕ_s of SiO_2 given from (3.14) as

$$\phi_s=\phi_0+(\phi_0-\phi_m)\frac{2m_m}{m_s(1-\alpha)} \tag{3.15}$$

Using the observal value in place of ϕ_0, the calculated value of ϕ_m and m_m, m_s in (3.15), the value of ϕ_s is given in the column (1) of Table 7. On the other hand, the volume v_s of SiO_2 can be written by

$$v_s=\left\{\frac{2m_m+m_s(1-\alpha)}{d_c}-2v_m\right\}\left(\frac{1}{1-\alpha}\right) \tag{8.16}$$

where d_c denotes the density at each depth of the region C. The mean value of ϕ_s, denoted by $\bar{\phi}_s$, in the region between the depth 1 and 2, is expressed by

$$\bar{\phi}_s=\bar{v}_s\frac{\Delta p}{\Delta v_s}\Big/(m_s/\bar{v}_s) \tag{3.15'}$$

where $\bar{v}_s$ denotes the mean density given by $(v_{s1}+v_{s2})/2$. The values of $\bar{\phi}_s$ are listed in column (2) of Table 7, in which the depths 600, 800 and 1,000 *km* are taken.

Table 7. Comparison of ϕ derived from (3.15) and (3.15′).

Depth	ϕ_c	ϕ_m	ϕ_s $(km/sec)^2$							
			$\alpha=0$		$\alpha=0.25$		$\alpha=0.5$		$\alpha=0.75$	
	$(km/sec)^2$	$(km/sec)^2$	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
600	67.5	71.0	51.1	20	48.3	10	40.1	5	16.7	2
800	71.5	76.5	64.8	65	62.6	50	58.1	30	44.7	15
1,000	77.3	81.6	71.5		69.6		65.8		54.3	

ϕ_s : derived from Bullen's values.

ϕ_m : derived from the equation of state obtained by Трубицин.

Column (2) denotes the average values of ϕ_s responsible for the average depths between 600 and 800, or 800 and 1,000 *km*.

Table 8. Structures of IV–VI compounds.

	O	S	Se	Te
Be	W	Z	Z	Z
Mg	NaCl			W
Ca	structure			
Sr				
Ba				

	O	S	Se	Te
Zn	W(Z)	WZ	Z	WZ
Cd	NaCl	WZ	WZ	Z
Hg		Z	Z	Z

(W indicates wurtzite, Z zinc blende, and NaCl rock-salt structure)

If the region C is composed of the mixture of MgO and SiO_2, the values of column (1) should be in accordance with those of column (2). From Table 7, however, the agreement between both values is found to be wrong, especially in the case of high degree of squeezing, and comparatively good in the case of $a=0$. But in the latter case the ϕ of SiO_2 must be very high value in comparison with that of normal SiO_2. This may be not favourable to the decomposition of Mg_2SiO_4 Then we recognize that the $2MgO$-SiO_2 mixture, even with squeezing of SiO_2, can not simultaneously give the ϕ and d reconsiled with the observed values in the region C. But this does not mean that the decomposition of Mg_2SiO_4 is impossible and would better be interpreted as indicating that at least one component of the mixture must be such as its changes of ϕ and d in the region C being *abnormal* corresponding to these found from seismic observation. Though the present result is made for $2MgO$-SiO_4 mixture, the same results may be obtained for the other mixture, for example, olivine-spinel mixture, if the ϕ and d of one component of each mixture do not vary *abnormally*.

3.3. Ionic-intermetallic transion

Even if olivine-spinel transition or decomposition of Mg_2SiO_4 occurs, we could hardly explain the abnormal increases of ϕ and d in the region C, if each component shows such a *normal* changes of elastic properties versus pressure as expected from an extrapolation of experimental value. Of course if multi-components system is considered, and many kinds of

systems are permitted, the *abnormal* character of the region C could be explained by mixture model. Such a complicated model, however, appears too artificial to be considered. Thus it seems reasonable that we expect that at least one component of the mixture considered should be suffered by the influence of pressure and temperature to possess the *abnormal* changes of ϕ and d, which are never seen under ordinary condition. On the other hand, the expectation that the region D may be composed of periclase (MgO) is accepted by several authors. Especially the high value of ϕ of MgO is compatible with that of the region D and the variation versus pressure appears to be reconciled with that of the region D, as will be shown later. Though the density of MgO is less by about 20% in the deeper part of the region D, some mixture containing MgO as one component or some high-pressure modification of MgO is expected to possess the ϕ and d reconciled with those of the region D, since the region D exhibits a *normal* elastic behaviour in contrast with the region C. Then the writer will set up the idea that the decomposition of Mg_2SiO_4 takes place and simultaneously MgO produced transforms from the original ionic state to the covalent state.

3.3.1. Intermetallic state

According to Pauling (1939), there is no evidence that the extreme ionic bond transforms directly to the extreme metallic bond, and in the system of substances looking as if it undergoes the direct transition, at first the transition from ionic bond to covalent bond takes place necessarily and then the transition from covalent bond to metallic bond follows. This fact is also interpreted as follows; the metallic bond is essentially equivalent to covalent bond, disregarding that free electrons move freely in metallic state. In the resonating bond theory of Pauling (1938, 1949), the metallic bond is interpreted in terms of bond hybrids, and this approach is better suited for considering the geometrical arrangement of the atoms. There are many phenomena suggesting that a simple picture of the physical situation may be obtained if we regard the metallic bond as related to the chemical bond. From this point of view, it is suggested that the metallic bond has more definite directional properties than is usually imagined For example, the operation of direc-

tion of directional forces is suggested by the fact that crystals of solid solution are formed. It is now genefally accepted that in a solid solution there is not an uniformly expanded or contracted lattice, but that local distortions occur so that atoms are displaced from their lattice points, and this displacement may be considerable. In spite of this, the lattice on the average keeps up its pattern, and this fact suggestes the existence of directional forces.

For covalent crystals such as the diamond, the existence of directional bonding and the actual structure taken up can be explained by assuming that well-known hybrid orbitals are responsible for the bonding, e.g. tetrahedral sp^3 bonding for the diamond. With metals, there are insufficient electrons to form covalent bonds, but we suggest that, if we regard the hybrids as being only partly occupied, we may still regard particular hybrids as determining the geometrical arrangement of the atoms in the metallic crystal.

Although semiconductors are characterized by well-known electrical properties which differentiate them from metallic or ionic conductors and molecular crystals, it has not been possible in general to recognize or predict intrinsic semiconductors as a class of substances from a consideration of other than electrical properties. An interest in understanding and classifying intrinsic semiconductors in terms of the valencies and bonds of the constituent atoms has led us to make use of the valence bond treatment first developed and applied to metals by Pauling. Most, if not all, semiconducting inorganic compounds so far discovered can be assigned an entirely ionic formula, in which the normal valence requirements of the constituent atoms appear satisfied. That most semiconductors can be represented as ionic and yet have appreciably covalent bonding is not inconsistent, since a complete range of bond types exists between covalent and ionic extremes, the degree of ionicity depending upon the difference in electronegativities of the bonded atoms. Recently, "a semiconducting bond" has been postulated by Mooser and Person (1956), resulting from the presence of essentially covalent bonds. This bond must be present in a compound for it to be a semiconductor. They can say which intermetallic compounds will be metallic conductors and which will be semiconductors, and we can generally predict which substances will be stoicheometric formulae of the compounds. If a diatomic compound is to be a semiconductor,

at least one atom of the two must acquire completely filled *s*- and *p*-shells. The presence of vacant metallic orbitals on some atoms in a compound does not destroy semiconductivity provided that these atoms are not bonded together. It may, however, gives rise to pivoting resonance (Pauling 1949) so that the coordination numbers of atoms can exceed their valencies. The bonds in a semiconductor must form a continuous one, two or three dimensional network running throughout the whole crystal. These properties define the semiconducting bond, necessary for the occurrence of intrinsic semiconductivity in a solid. As an atom can not gain a number of electrons greater than its valency through a process of electron sharing, it follows that filled *s*- and *p*-subshells can only occur in atoms lying in Group IV to VII of the Periodic Table (excluding the transition element in these Groups) and we have an explanation of the fact that all semiconductors contain elements lying in these Groups. Semiconductors therefore obey the rule

$$n_e/n_a+b=8 \qquad (3.17)$$

where n_e is the number of valence electrons per molecule in the semiconductor, n_a is the number of atoms in the molecule lying in Group IV to VII (excluding transition elements) and b is the average number of bonds formed by one of these atoms with other atoms of Group IV to VII. Metallic conductors do not obey this rule.

The relationship of the semiconducting bond to other bond types is of interest. In a semiconductor, where at least one of any two atoms bonded together has a filled subshell, it is necessary to promote an electron to a higher orbital for it to be free to move throughout the lattice as a conduction electron. In a metal, however, neighbouring atoms bonded together have only partially filled valence shells and the remaining empty metallic orbitals are available for the valence higher orbitals. In this, the advantage of the valence bond treatment over the band model is most apparent, for the valence treatment allows a clear distinction to be made between a semiconductor and a metal in terms of atomic properties only, while the band scheme does not follow directly from the properties of the component atoms. The predominantly covalent character of the bond in semiconductors is apparent from the electronegativity differences of the component atoms which are generally less than unity. This value corresponds to some 25% ionic character of the bonds. In oxide semiconductors the elec-

tronegativity difference is higher and reaches 2.6 for BaO.

However, the distinction between ionic and semiconducting compounds is not important to discuss the semiconducting bond, for we recognize the former as potential semiconductors with a large energy gap. Indeed, simple ionic conductors such as NaCl, obey the rule (3.17). While, therefore, we may conclude that substances showing intrinsic semiconductivity under thermal excitation have predominantly covalent bonds. The energy gap of BaO was evaluated to be 10.4 *ev.* assuming that BaO is in purely ionic state (namely valence electrons localized on the lattice ions), whereas the experimental value is 4.2 *ev.* This result is regarded as due to presence of somewhat covalent character of bond in BaO. Thus the intermetallic compounds are regarded as possessing the intermediate character of bonds between ionic and covalent (or metallic) character of bonds.

Ramsey's hypothesis, the metallic transition of silicate, may be considered in connection with the intermetallic state as follows: the silicate mineral having mainly ionic character of bonds must first transform to intermetallic state somewhere in the way to transform to metallic state, because the direct transition to metallic state from ionic state is not likely to be realized. In the following section, the process of the transition of the composition in the mantle from ionic to intermetallic state will be suggested to occur within the region C, and the origin of the region C will be discussed.

3.3.2. Ionic-intermetallic transition

Магницкий (1956) suggested first the possibility of existence of "covalent Mg_2SiO_4". He estimated the energy curves of ionic and covalent state of Mg_2SiO_4 assuming that the composition of the mantle is Mg_2SiO_4. The transition from ionic to covalent state takes place in Mg-O bond in Mg_2SiO_4, to change the bond length from 2.10 A to 1.95 A, corresponding to ionic bond and covalent bond lengths, respectively. The decrease of density amounts to 18%. Assuming the transition occurs at the depth of about 500 *km*, he estimated the energy curves of covalent Mg_2SiO_4 using the expression

$$U = -A_0 \exp(-B_0 v^{1/3}) + A \exp(-B v^{1/3})$$

and comparing the energy curve of ionic one, he obtained the increase of

ϕ of 1.9 $(km/sec)^2$. His results, however, appeared to succeed not sufficiently to explain the abnormal character of the region C, because of the insufficient increase of ϕ and especially the insufficient explanation for the gradual changes of K_T, d. Moreover the abnormal behaviour of electric conductivity in the region C is not touched.

The present writer will attempt to realize the transition from ionic to intermetallic state in detail, to explain the properties of the region C deduced from seismic and geomagenetic data.

The continuous character of the ionic-intermetallic transition is originated from the resonance of heteropolar (or ionic) and homopolar (or covalent) bonds. Coulson and Fischer (1949) showed that the resonance of these two bond changes according to the equilibrium interatomic distance, in the most simple case of hydrogen molecule. According to the principle of wave mechanics, the electron distribution in a compound containing mixed bonding should oscillate between the homopolar limit, described by a wave function ψ_{hom}, and the heteropolar limit, described by a wave function ψ_{het}. In homopolar bonds, the orbital-electrons responsible for bonding should be concentrated along the shortest line joining neighbouring atoms, as in the Heitler-London model of the hydrogen molecule. In heteropolar bonding, on the other hand, the electrons group themselves in such a way as to form rare gas structures. Thus homopolar hydrogen molecule is characterized by the fact that two hydrogen atoms are by a homopolar bridge, whereas in heteropolar hydrogen molecule, H^+ and H^- attract one another as a function of their electronstatic charges. The true wave function of the system is a linear combination of the two case as follows :

$$\psi = \psi_{hom} + \lambda \psi_{het}, \tag{3.18}$$

where the coefficient λ is defined in such a way that the total energy is a minimum. The coefficient λ is shown in Fig. 8, as a function of the equilibrium distance between two atoms, r.

In Fig. 8 one can see that the increase of homopolar bonding as the decreasing of r from the normal equilibrium distance r_0 is required to satisfy the stability of the total energy, disregarding a slight increase of hetropolar bonding in a short range of r near r_0. If the similar estimation is made by using the molecular orbitals, one could obtain the results

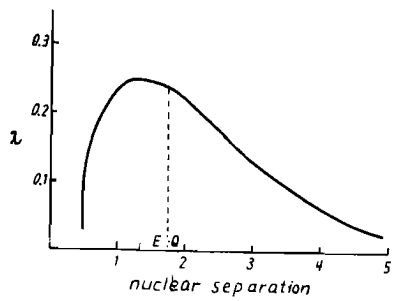

Fig. 8. Coefficient λ indicating resonance between ionic and covalent bonds as a function of nuclear separation in H_2 (after Coulson and Fishcer).

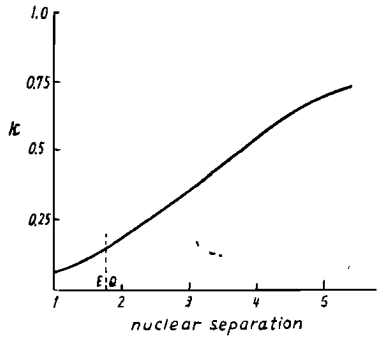

Fig. 9. Coefficient κ as a function of nuclear separation in H, and $\kappa=\{(1-S)/(1+S)\}k$, $\lambda=(1+k)(1-k)$, where S is overlap integral between ls-orbitals (after Coulson and Fischer).

shown in Fig. 9, in which the homopolar bonding is seen to increase gradually as the decreasing of r (Coulson and Fischer 1949). Since atomic orbital method gives a good approximation in the range of r that is near r_0 and larger than r_0, whereas molecular orbital method gives a good approximation in the range of r that is smaller than r_0, these two figures enable us to write a schematic figure, as shown in Fig. 10.

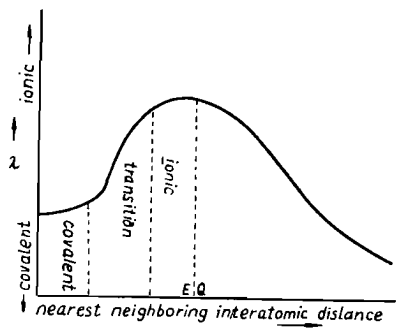

Fig. 10. Schematic diagram indicating resonance between ionic and covalent bonds in MgO crystal.

We can see in Fig. 10 that there are the three regions of λ corresponding to the rate of change of λ with the decreasing of r; near the normal equilibrium distance r_0 changes slightly, the following region of r corresponds to the sharp increasing of homopolarity, and near the hydrogen core the increasing of homopolarity is comparatively small. These regions are regarded as the comparatively ionic region, the transition region from ionic to covalent state, and the covalent region. Although this feature is obtained for hydrogen molecule, the increasing of homopolarity with the decreasing of interatomic distance may be expected generally in the other molecules or crystals. Recently Heywang and Seraphin (1956) gave these

conceptions a quantitative form. In place of (3.18) they employ the more general relation

$$\psi = x_0\psi_0 + x_1\psi_1 + x_2\psi_2 \tag{3.19}$$

in which ψ_0 corresponds to the Heitler-London function and to the purely covalent part of the bonding state. In other words,

$$\psi_0 = a(1)b(2) + a(2)b(1) \tag{3.20}$$

The functions a and b are the well-known hydrogen wave functions

$$\left.\begin{aligned} a &= \frac{(1+\varepsilon)^{3/2}}{\pi}\exp[1-(1+\varepsilon)r_a] \\ b &= \frac{(1-\varepsilon)^{3/2}}{\pi}\exp[1-(1-\varepsilon)r_b] \end{aligned}\right\} \tag{3.21}$$

The parameter ε provides a measure of the unequal charge of the nuclei. The case $\varepsilon=0$ corresponds to the normal hydrogen molecule. The functions ψ_1 and ψ_2 correspond to the ionic state in which the two electrons find themselves simultaneously on nuclei a or b:

$$\left.\begin{aligned} \psi_1 &= C_a(1)C_a(2) \\ \psi_2 &= C_b(1)C_b(2) \end{aligned}\right\} \tag{3.22}$$

The functions C_a and C_b are chosen to be the helium-like wave functions of Hylleraas. They differ from the hydrogen functions by a screening factor of 5/16.

$$\left.\begin{aligned} C_a &= \frac{(11/16+\varepsilon)^{3/2}}{\pi}\exp[-(11/16+\varepsilon)r_a] \\ C_b &= \frac{(11/16-\varepsilon)^{3/2}}{\pi}\exp[-(11/16+\varepsilon)r_0] \end{aligned}\right\} \tag{3.23}$$

Let H denote the Hamiltonian operator of the system. Then the total energy

$$E = \frac{x_0^2H_{00} + x_1^2H_{11} + x_2^2H_{22} + 2x_{01}H_{01} + 2x_{02}H_{02} + 2x_{12}H_{12}}{x_0^2S_{00} + x_1^2S_{11} + x_2^2S_{22} + 2x_{01}S_{01} + 2x_{02}S_{02} + 2x_{12}S_{12}} \tag{3.24}$$

Here,

$$\left.\begin{aligned} H_{ik} &= \iint \psi_i H \psi_k d\tau_1 d\tau_2 \\ S_{ik} &= \iint \psi_i \cdot \psi_k d\tau_1 d\tau_2 \end{aligned}\right\} \tag{3.25}$$

Fig. 11 shows the binding energy of the ground state and the first excited state as a function of the separation of the nuclei. The position

of the minimum varies with decreasing values of ε, to be shortened. Moreover, the spacing between the ground state and the first excited state increases with increasing heteropolar. This corresponds to the decrease of the energy gap of ionic crystal with the increase of homopolarity, as will be noted in the following section. Heywang and Seraphin's result corresponds to the estimation of energies with the change of ε arbitrary chosen, whereas Coulson and Fischer's result corresponds to the examination of stability of bond type by finding the energy minimum. Therefore, the latter shows that a decrease of lattice constant induces an increase of homopolarity, whereas the former suggests changes of some physical properties induced by an increase of homopolarity.

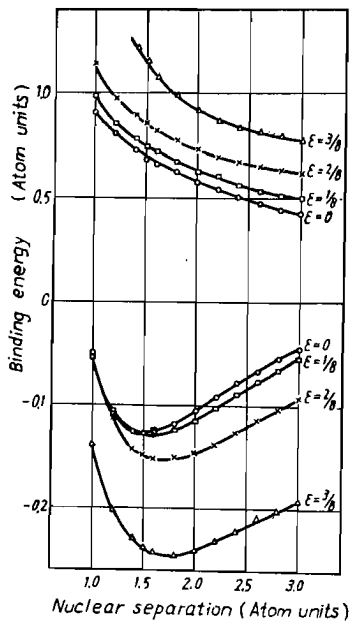

Fig. 11. Binding energy of a hydrogen molecule possessing a nuclear charge $1+\varepsilon$ and $1-\varepsilon$ as function of the nuclear radius (after Heywang and Seraphin).

Let us examine the bonding character of MgO crystal expected as the composition in the region C and D. The ionic bonds correspond to the configuration of electrons as follows:

$$Mg^{++} : (1s)^2\ (2s)^2\ (2p)^6$$
$$O^{--} : (1s)^2\ (2s)^2\ (2p)^6$$

On the other hand, there is the possibility of covalent bonds originated from the configuration of electrons as follows:

$$Mg : (1s)^2\ \boxed{(2s)^2\ (2p)^6}\ \boxed{(3s)^1\ (3p)^3}$$
$$O : (1s)^2\ \boxed{(2s)^1\ (2p)^3}$$

where we see the sp^3 hybrid orbitals formed. The sp^3 hybrid orbitals form the homopolar electron bridge to bond both kinds of atoms, Mg and O. Table 9 shows the crystal type of II-VI compounds. MgTe has a wurtzite structure, which corresponds to a tetrahedral covalent bonds existing in

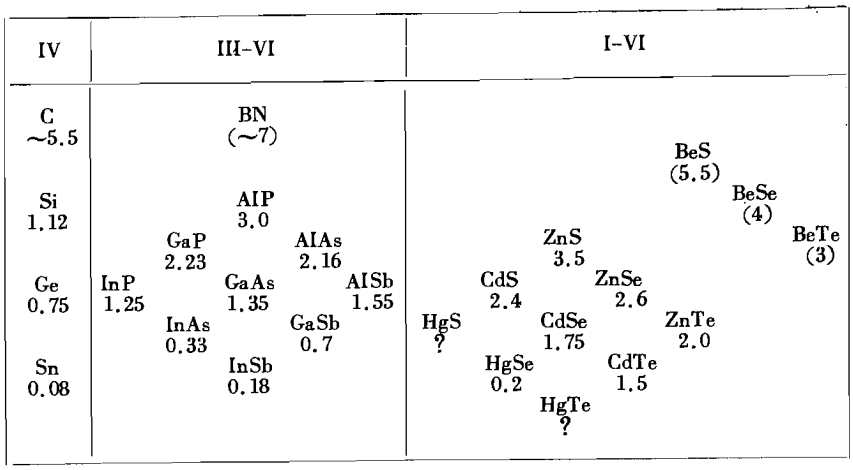

Fig. 12. The best-known diamond type compounds belonging to III-V and II-VI series with zinc blende structure in comparison with IV elements, where values beneath each materials indicates its energy gap (after Goodman).

itself. The best-known diamond-type compounds are the III-V and II-VI series with zinc blende structure. These, together with the related series of IV elements, are set out in Fig. 12 in such a way as to emphasize the periodic variation of energy gap with bond length and electronegativity difference and to show the effects of vertical and cross-substitution. Energy gap is indicated beneath each materials (Goodman, 1958). The II-VI zinc blende series are noteworthy for the lack of magnesium derivatives, which have wurtzite structure or rock-salt structure. According to Goodman's opinion, this is probably connected with the low electronegativity of magnesium which would tend to induce ionic bonding, for it would seem that there is a limit of ionicity beyond which the zinc blende lattice is not stable.

Considering the fact that the homopolar content in bonding increases with the decreasing of lattice parameter, we may expect that the homopolar content in the bonding of MgO increases with the pressure-increase, namely sp^3 hybrid orbitals are preferred under a high pressure. Regarding the crystallographic structure, the sp^3 hybrid orbitals have a directional character corresponding to tetrahedral bonding in zinc blende or wurtzite structure (in essence equivalent to diamond structure). Then the extreme form of MgO in the intermetallic state may be considered as the structure with four coordination numbers, e.g. zinc blende or wurtzite type. It, however,

appears not necessarily that we expect the sharp transition from rock-salt (ionic) to zinc blende type (covalent). As mentioned already, BaO has a rock-salt type lattice, but is bonded by an amount of covalent bonds, at least much more than in a normal MgO. HgS (cinnarbar) has a distorted rock-salt structure, and GeS, SnS, etc. in IV-VI compounds crystallize in distorted rock-salt type lattices. These distorted lattices are interpreted as intermediate structures between rock-salt and zinc blende structure. Thus we may expect, also, the gradual deformation of crystal structure of MgO while the ionic-intermetallic transition is progressing with a gradual increases of homopolarity. These situation is shown schematically in Fig. 13.

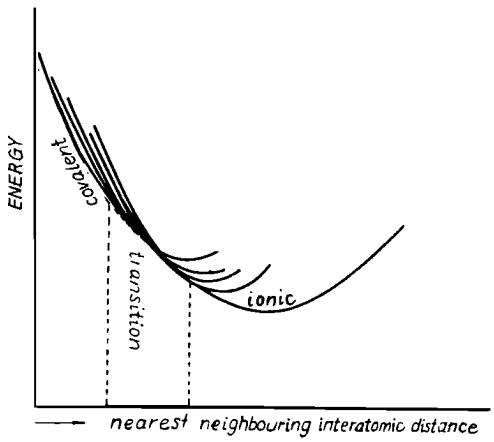

Fig. 13. Schematic figure expressing ionic-intermetallic transition with many small jumps in density.

The energy expression is considered as a function of the two parameters, volume v and ε denoting a measure of homopolarity in bonds. The energy is expressed by

$$U=U(v,\ \varepsilon) \tag{3.26}$$

$$dU=\frac{\partial U}{\partial v}\,dv+\frac{\partial v}{\partial \varepsilon}\,d\varepsilon \tag{3.27}$$

Introducing a parameter δ, if $\partial U/\partial \varepsilon=0$ for $d\varepsilon \leqq \delta$, then we could obtain the expressions

$$\left.\begin{aligned} p&=-\left(\frac{\partial U}{\partial v}\right)_{\varepsilon} \\ K_T&=-v\left(\frac{\partial p}{\partial v}\right)_{\varepsilon} \end{aligned}\right\} \tag{3.28}$$

This assumption means that a transition due to the contraction of lattice can not occur by a small dilatation such as seismic disturbance, so that incompressibility is determined by the energy curve denoted by a fixed ε until a certain amount of pressure induces a transition between some two states represented by two energy curves. On other words, the resonance

between the two kinds of bonds is not permitted to change continuously, but restricted to change with some discontinuity.

Regards as the possibility of the transition to zinc blende form, one question arises from the fact that the zinc blende form is less closely packed than rock-salt form, and then, if the interatomic distance remains unchanged, the density should decrease at the transition. Moreover, this kind of transition is not yet found. In several ionic compounds such as alkali halides, the transition with density-increase takes place, for example, from NaCl form to CsCl form. However, in these cases it seems true that the bonding character does not change and the ions are rearranged to be more compact. In fact, in this kind of transition, the bond length is rather streched, though the density increases. Therefore, the increase of homopolarity should not be realized. If the bond length of MgO in zinc blende form decreases somewhat in comparison with that of normal rock-salt form, we might expect the transition to zinc blende form. The covalent radii of Mg and O are found to be 1.40 and 0.65 A, respectively (see, for example, Wells, 1950). But these values must be examined because the procedure of estimating these values, based upon the additive rule, can not necessarily give good approximations to all cases. Noting the covalent radii of Mg being deduced from only one compound in wurtzite form, MgTe, we should regard the covalent radius of Mg as being in question. (It seems provable that MeTe has considerably ionic character

Table 9. The nearest neibouring interatomic distances of oxides, sulfides, selenides and tellurides of zinc, cadomium and mercury for their actual crystal structures (upper value) in comparison with the sum of the ionic radii of constituent ions (lower value). (unit . A)

	O	S	Se	Te
Zn	1.94 2.14	2.35 2.58	2.45 2.72	2.94 2.95
Cd	2.14* 2.35	2.52 2.81	2.62 2.95	2.79 3.18
Hg			2.63 3.08	2.80 3.31

* The actual crystal structure of CdO is rock-salt type. Therefore 2.14 A denotes the actual interatomic distance and 2.35 A the sum of the ionic radii of Cd and O.

with more covalent content than normal MgO, since the interatomic distance of MgTe, 2.75 A seems somewhat larger than the purely or predominantly covalent one.) The Table 9 shows the observed values of interatomic distances in oxides, sulfides, selenides and tellurides of Zn, Cd and Hg, as considered as the typical semiconducting intermetallic compounds belonging to II-VI compounds, in addition to the interionic distances of their hypothetical ionic compounds, obtained by adding the ionic radii of each pair of two kinds of ions. We can see in Table 9 that the covalent bond length decreases by some 10~20% than the ionic bond length. The compounds in the left hand side of Table 9 have more covalent character than in the right hand side and the lower side than the upper side. Then it is provably true that the contraction of bond length increases with the increase of covalent content. Assuming the contraction of the interatomic distance of MgO in zinc blende form about 10~20%, we obtain the value of volume change due to the transition from rock salt to zinc blende form, as follows:

bond contraction	volume change
10%	+10%
15	− 7
20	−27

Thus we may expect the possibility of the transition to zinc blende form. The existence of the intermediate forms of lattice structure between rock-salt and zinc blende forms may not permit a discontinuous contraction of bond length with an abrupt increase in the density, disregarding the small contraction observed in ZnSe, ZnTe, BaTe and HgS (see Birch et al, 1942), Some of them are regarded as the transitons from wurtzite to zinc blende form (see Edwards et al, 1959).

It is noted that in Fig. 13 the increase of homopolar content in MgO induces the increase of the strength of the bonds, but the energy relative to the energy of the normal state decreases, since in normal MgO, (Mg^{++} O^{--})-state is more stable than the state corresponding to their sp^3 hybrid orbitals. The resonance integral may depress the total energy most effectively when a certain mixing ratio between hetropolar and homopolar states is reached. Accordingly the strength of the bond in mainly ionic compound such as normal MgO increases with the increase of homopolar

content, and on the other hand, that of mainly covalent compound increases with the increase of hetropolar content. The energy gap, however, decreases always in both the cases, because the decrease of energy gap depends directly on the potential difference of the two kinds of atoms situated at lattice points, as will be described in the following section.

3.3.4. Intrinsic conduction of intermetallic compound

Energy gap E between the conduction and valence bands decreases with the increase of homopolar character, as shown in Fig. 11 obtained by Heywang and Seraphin. In fact, the energy gap of typically ionic compound is about 10 *ev.*, and the energy required to create a lattice defects (e.g. Schottky defect) is some 2 to 3 *ev.* and is relatively independent of the bond type. Thus typically ionic crystal behaves as ionic conductors under thermal excitation, but electronic conductivity may be observed, specially, at a lower temperature under photoelectric excitation. Therefore we may conclude that substances showing intrinsic semiconductivity under thermal excitation have predominantly covalent bonds. In Table 10 are shown several II-VI compounds and their energy gaps, together with the other physical properties discussed later on.

If ZnO is purely ionic crystal, the energy gap would be some 10 *ev.*, that is about twice as much as the observed value shown in Table 10. This

Table 10. Energy gaps, melting points, and mobilities of electron and hole of II-VI compounds.

compound	energy gap (*ev.*)	melting point (°C)	mobility of electron (cm/volt·sec)	mobility of hole (*cm/volt·sec*)
MgO	9~12	2900		
BaO	4.2	1913	5	
ZnO	3.2	1975	200	
ZnS	3.7	1880		
ZnSe	2.6	1000	100	
ZnTe	2.2	1239	100	
CdS	2.6	1750	250	
CdSe	1.8	1350		
CdTe	1.45	1045	650	60
HgSe	1.0	690	10000	
HgTe	1.0	670	10000	

means that the electron wave function of ZnO should not be localized at the ions situated at the lattice points. The homopolar character prevents the valence electrons from being localized at their ions, so that the valence band broadens and the electrons in conduction bands can not take part in the bonds. Therefore the electrons in conduction bands are not so influenced as in valence bands by the periodic potential in crystal field and then the localization in conduction electron is less than in valence electron. Seraphin (1954) showed this situation clearly, using Kronig and Penny's one-dimensional model. In order to have the one-dimensional model describe the three-dimensional structure, we shall represent the layers of atoms of the same type by a potential trough. Each trough will represent the average to the potential relations which are valid for the atoms in the given crystallographic plane. In the one-dimensional model the different planes are represented by potential trough having unequal depth. Let P_0 be the depth of the potential trough for monoatomic lattice and let the difference in the depth of the potential troughs for the two unequal atoms in a compound be designated by $2\Delta P$. We shall assume, in a very rough approximation, that $\Delta P/P_0=2$ for the II-VI compounds. Actually, one should associate somewhat smaller values of the ratio $\Delta P/P_0$ for this II-VI compounds, corresponding to the fact that the valence electrons enter the deeper potential trough preferably and have a tendency to level it. The structure of the energy bands given by this model is shown in Fig. 14, as a function of two parameters, namely the ratio of the separations of neighbouring

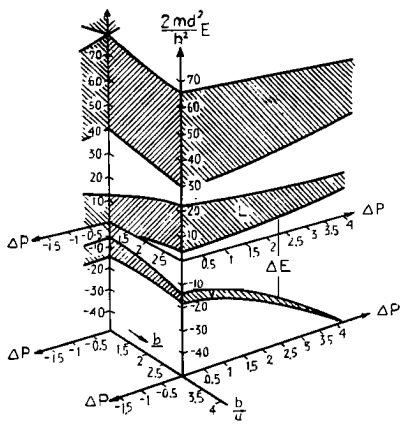

Fig. 14. Structure of energy bands as a function of hetropolar parameter P and the ratio of the separations of the potential troughs b/a. Constant h denotes Plank's constant divided by 2π (after Seraphin).

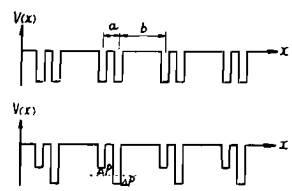

Fig. 14'. One-dimensional potential model used (after Seraphin).

planes, b/a, and the parameter ΔP governing the hetropolar character. An exact investigation shows that two lowest bands, designated by V and L, correspond to the valence and the conduction bands. The increase of the energy gap ΔE with increasing ΔP is understandable without further comment. Fig. 14' shows the one-dimensional model of potential troughs used here.

Thus the decrease of the energy gap of MgO is induced from the increase of homopolarity and the contraction of volume. Then the electronic (intrinsic) conduction exceeds the ionic conduction at a certain critical pressure. Tozer (1959) estimated the critical temperature such that the electronic and ionic conduction will be balanced within the mantle. This critical temperature T_c is given by

$$T_c = \frac{\Delta E_{ion} - \frac{\Delta E_{int}}{2}}{k \log \frac{\sigma_{ion}}{\sigma_{int}}}. \qquad (3.29)$$

To determine the value of T_c and the conductivities at a depth, the various quantities in the equations should be taken at constant volume. This modification increases the experimentally determined value (at constant pressure) of σ_{int} for the magnesium-rich olivine (90% Mg_2SiO_4) by a factor of two and decreases the value of σ_{ion} by a factor of five. His result is shown in Fig. 15 and listed in Table 11.

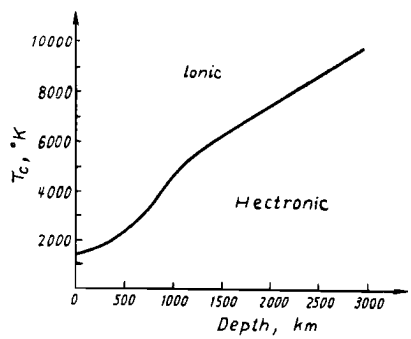

Fig. 15. The critical temperature at which the ionic conductivity for a mantle consisting mainly of olivine (after Tozer).

Comparison of the T_c with modern estimates of the temperature distribution in the mantle (for example, Verhoogen, 1956) shows that below a few hundred kilometers T_c is greater than the estimated temperatures. His conclusion is that below a few hundred kilometers the electronic conduction exceeds the ionic conduction. From his results we can see that the value of ΔE within the regions C and D should be expected to be less than 3 *ev*.. Examining the values of ΔE_{int} given in Table 10, we may conclude that the hypothetically covalent MgO

Table 11. Parameters governing intrinsic conduction and ionic conduction in a mantle composed of olivine (after Tozer).

Depth (*km*)	$[\sigma_1]_v$ ($\Omega^{-1}cm^{-1}$)	E_1 (*ev*)	$[\sigma_2]_v$ ($\Omega^{-1}cm^{-1}$)	E_2 (*ev*)	T_c (°K)
0	5	3·2	1·0.10^6	3·00	1450
200	7	3·14	0·9.10^6	3·24	1680
400	6	2·94	0·9.10^6	3·55	2100
600	7	2·85	0·8.10^6	3·87	2650
1000	8	2·43	0·7.10^6	5·55	4900
1400	11	2·34	0·7.10^6	6·15	6100
2200	16	2·18	0·7.10^6	7·08	8000
2900	15	2·08	0·7.10^6	8·0	9800

in zinc blende form satisfies this postulation.

Moreover another desirable fact is that the value of σ_{int} will increase rapidly with the increase of homopolar character. According to the evaluation on the effective masses of electron and positive hole made by Adawi (1957), who used the one-dimensional model as well as Seraphin, the effective masses of electron and hole, especially of hole, decrease with decreasing of heteroporar parameter ΔP. His result is shown in Fig. 16, in which the effective masses of electron and hole, m^*_n and m_p^*, were evaluated from the relation

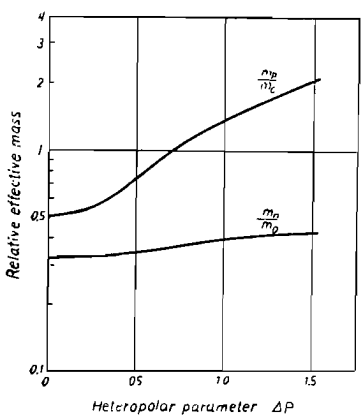

Fig. 16. Relative effective masses m_n/m_0 of the electrons and m_p/m_0 of the holes as a function of the heteropolar parameter P ; $P_0 = -3$ (after Adawi).

$$m^* = \hbar^2 \left(\frac{\partial^2 E}{\partial k^2} \right)^{-1} \tag{3.30}$$

and m^*_n/m_0, m_p^*/m_0 are shown for simplicity, where m_0 denotes the mass of electron. The decrease of effective mass means the increase of the mobility, so that we can expect the increase of σ_{int}. For example, the mobilities of II-VI compounds for electron and hole, listed in Table 10,

show that HgSe or HgTe has about a hundered times higher value than ZnS or ZnSe. HgSe or HgTe is considered to have more homopolar character than ZnO or ZnSe. Edward, Slykhouse and Drickamer (1959) measured the $d\Delta E/dp$ of several II-VI compounds, ZnO, ZnSe, ZnTe and CdS, by observing the absorption edges under pressure induced by shock-wave. Their measurements showed the initial blue shift corresponding to a positive values of $d\Delta E/dp$, and then the red shift corresponding to negative value of $d\Delta E/dp$, except for ZnO and CdS, both of which transform from wurtzite form to zinc blende form with some jumps of ΔE in negative sign, but general features of $d\Delta E/dp$ are positive. These results are interprated by them as follows: the band structures of ZnS, ZnSe and ZnTe shown in Fig. 17 have minimum energy gaps in the immediate vicinity of $k=0$, (k denotes a wave number vector in Brillouin zone) and on the other hand, Paul and Warschaure (1958) measured the absorption edges on Ge-Si alloys to show the behaviour of the band minima of these two elements under pressure, namely, the

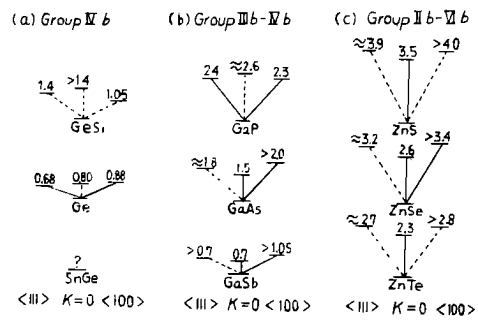

Fig. 17. Estimated conduction-band levels of semiconductors (above valence-band maximum 300°K) (after Edwards, et al).

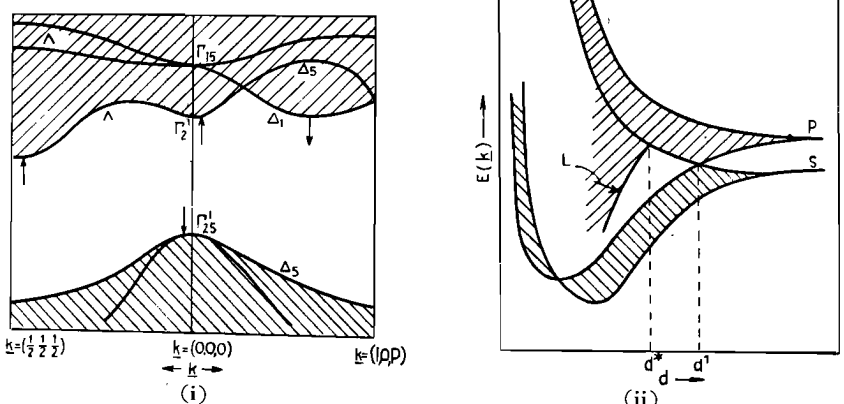

Fig. 18. (i). $E(k)$ versus k diagram for germanium (after Herman). Arrows incicate probable direction of shift with increasing pressure. (ii) General $E(k)$ versus k diagram for the diamond lattice (after Slykhouse, et al.).

rise of the k(111) minimum in the conduction band and the lowering of the k(100) minimum, relative to the maximum of the valence band. Thus it is explained that the initial blue shift takes place until the k(100) minimum becomes sufficiently low to cancel the energy difference between itself and the minimum in vicinity of $k=0$. This picture is consistent with Herman's result (1955), which is obtained theoretically, shown in Fig. 18.

We discussed mainly the changes of density, incompressibility and the energy gap, which play the most important roll for the investigation on the region C, arised from the ionic-intermetallic transition. Some of the other physical properties, induced from the transition, are pointed out. These are listed in brevity in Table 12.

Regarding (6) we can expect that the condition $\varepsilon \leq \delta$ in (3.27) indicates a sub-stable state, since if the constituent material is strained out the restriction, the $\partial U/\partial \varepsilon$ becomes effective and a small jump of volume change occurs. This might be related to an unstable state suggested by the existence of deep-focus earthquake within the region at the depth of about 600 *km*. Regarding (7) we know that the thermal conductivity κ of semiconductor contains the two parts, namely, the phonon term κ_{ph} and Wiedeman-Franz term κ_{el} due to free chages :

Table 12. The changes of some physical properties induced from ionic-intermetallic transition.

(1) bonding character :	ionic (heteropolar) → intermetallic (homopolar)
(2) crystal structure :	rock-salt → distorted rock-salt → zinc blende or wurtzite (equivalent to diamond)
(3) energy gap (the breadth of forbidden band) :	≈10 *ev* → ≈2~3 *ev*
(4) mobilities of electron and positive hole :	remarkably increase
(5) incompressibility :	increase with a rapid gradient
density :	increase with a rapid gradient and many small jumps
(6) mechanical stability :	stable→substable→stable
(7) thermal conductivity:	increase at high temperature
(8) melting point :	decrease somewhat

$$\kappa = \kappa_{ph} + \kappa_{el} \tag{3.31}$$

If we regard the two terms as functions of temperature alone, disregarding their dependence on the other factors, in the first approximation, the phonon term κ_{ph} is in proportion to $1/T$, and the Wiedemann-Franz term κ_{el} increases rapidly due to the increasing of number of charge carriers with temperature. Then the thermal conductivity decreases first and then increases abruptly with temperature, possessing a minimum point at a certain temperature. The Fig. 19 shows the thermal conductivity of InSb versus temperature, measured by Busch and Schneider (1954). Therefore we may expect that the thermal conductivity in the deeper part of the mantle will be considerably higher than suggested hitherto (Verhoogen, 1956). Regarding (8) the fact that the melting point of intermetallic compound depends on heteropolar character in bonds is generally accepted. We can see in Table 10 that the melting point is in proportion to the value of energy gap, though it is not complete, which depends on bond character. Then the covalent MgO could have the lower melting point than the ionic MgO, since the former is bonded in less heteropolar bonds than the latter.

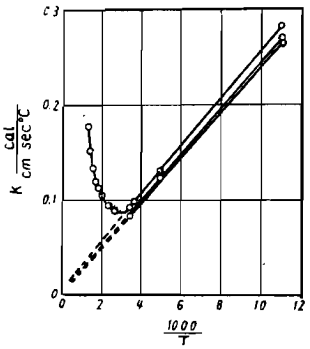

Fig. 19. Thermal conductivity of InSb as a function of $1/T$ (after Busch and Schneider).

4. The region D

The region D extends from 1,000 *km* to a depth of nearly 2,900 *km* where the P-velocity changes from 13.6 to 8.1 *km/sec* and the S-velocity drops effectively to zero. The regions A, B, C and D together constitute the earth's mantle. The latest estimation of the depth of the base of the mantle, made by Jeffreys (1939 c), is 2,898±3 *km*. Inside the region D, the velocity gradients are steady and moderate from zero in the lowest 150 to 200 *km* of the mantle: the subdivisions D′ and D″ refer to these two parts of D. Earlier work of Dahm (1936) had suggested discontinuous velocity-changes at a depth near 2,700 *km*, but the work of both Jeffreys and Gutenberg implies that the changes are continuous.

4.1. Equation of state of MgO

Birch (1952) showed that the velocity gradients in the region D are compatible with a uniform composition in that region using finite strain theory. The present writer attempted to compare the calculated values of K_T and d deduced from an equation of state of MgO in normal ionic crystal, with Bullen's values. According to (2.1), the equation of state of MgO is estimated as follows:

$$U=-76.76605/(r/r_0)+1385.24706\exp\{-4.8837(r/r_0)\} +3660.44466\exp\{-6.9066(r/r_0)\}\ (\cdot 10^{-12}), \quad (4.1)$$

where the energy U is expressed in *erg/molecule*. In the analogous way to (2.3) and (2.4), the pressure p and the incompressibility K_T are obtained as functions of (r/r_0). The third term expresses the double repulsion term of nearest neighbouring 0-0 interaction. The obtained values are listed in Table 13 and shown in Fig. 20, in comparison with Bullens values. The calculated value of ϕ is less by about 20% than Bullen's value. This discrepancy is considered as due to the poor approximation

Table 13. Variation of density, incompressibility and pressure of MgO versus change (v/v_0), computed from (4.1).

(v/v_0)	pressure ($\cdot 10$ *dynes/cm²*)	incompressibility ($\cdot 10$ *dynes/cm²*)	density (g/cm^3)
1.00	0.000	1.64	3.60
0.99	0.052	1.81	3.71
0.98	0.009	1.98	3.82
0.97	0.174	2.19	3.94
0.96	0.245	2.42	4.08
0.95	0.324	2.66	4.20
0.94	0.413	2.92	4.33
0.93	0.511	3.21	4.48
0.92	0.623	3.52	4.62
0.91	0.741	3.85	4.78
0.90	0.887	4.24	4.94
0.89	0.033	4.61	5.10
0.88	1.194	5.08	5.28
0.87	1.376	5.63	5.47

of the equation of state under a high pressure. Especially the repulsive terms are influenced by the deformation of $2p$ valence electron wave function of O^-, of which the long tail must be deformed with the contraction of crystal lattice. Considering the higher terms in the repulsive potential, as expressed in the form of exponential function, one can find the effect on the value of ϕ being about 20% under a pressure of about 1,000 *kbars*. (Wada 1959). Another equation of state of MgO was given by Трубицин (1958), who treated MgO quantum mechanically, especially statistically under very high pressure. His result is also approximated in the Born and Mayer's formula as follows:

$$U = -76.298857/(r/r_0) + 8105.0126\exp\{-6.57(r/r_0)\} + 50.7755. \quad (\cdot 10^{-12}), \qquad (4.2)$$

where the U is expressed in *erg/molecule*. He pointed out that the deformation in the $2p$-electron wave function of O^- induces an error on the value of ϕ by about 20%, as well as the writer. The K_T, d and p deduced from (4.2) are listed in Table 13′ and shown in Fig. 20.

Table 13′. Variation of density, incompressibility and pressure of MgO versus change (v/v_0) computed from (4.2).

(v/v_0)	pressure ($\cdot 10$ *dynes/cm²*)	incompressibility ($\cdot 10$ *dynes/cm²*)	density (g/cm^3)
1.00	0.030	2.03	3.60
0.99	0.034	2.242	3.71
0.98	0.106	2.50	3.82
0.97	0.188	2.79	3.94
0.96	0.279	3.09	4.08
0.95	0.381	3.43	4.20
0.94	0.496	3.81	4.33
0.93	0.625	4.20	4.48
0.92	0.769	4.64	4.62
0.91	0.926	5.12	4.78
0.90	1.107	5.66	4.94
0.89	1.306	6.22	5.10
0.88	1.525	6.84	5.28
0.87	1.773	7.53	5.47

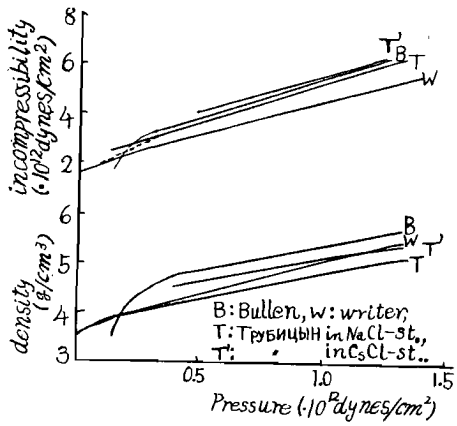

Fig. 20. Distributions of density and incompressibility within the region D, corresponding to several models.

It must be noted that the result deduced from Трубицын's equation (4.2) gives the rather poor approximation under a low pressure due to the adjustment of the equation for a higher pressure under the restriction of a single repulsive parameter used in the exponential form. Therefore the true equation should be expressed by the smooth curve drawn such as binding both the writer's and Трубицын's curves, especially in the intermediate pressure region of about 300–500 *kbars*.

Although the value of ϕ deduced from (4.2) is compatible with Bullen's value, the density d deduced from (4.2) is not compatible with that of Bullen. Therefore let us consider the possibility of polymorphic transition to cesium chloride form, a denser form than rock-salt form. Utilizing the equation of state given by Трубицын, (4.2), we obtain the equation of state of MgO in cesium chloride form, which is expressed by

$$U = -76.958114/(r/r_0) + 1080.66835\exp\{-6.57(r/r_0)\} + 50.7755 \quad (\cdot 10^{-12}), \tag{4.3}$$

where U is expressed in *erg/molecule*.

The transition pressure is obtained by comparing (4.2) with (4.3), namely, the value of the pressure above 1,000 *kbars* is resulted. This treatment for finding the transition pressure does not give a good approximation. In the transitions of some alkali halides, the calculated pressure is much higher than the observed pressure. If the transition occurs at the pressure of a few hundreds *kbars*, the distributions of K_T and d are compatible with those of Bullen, as shown in Fig. 20. Accordingly the model that the region D is composed of MgO in cesium chloride form, should be worthy to be examined. Regarding the electric conductivity, the energy gap of MgO in cesium chloride form is expected to be lower than that in rock-salt form, since the energy gaps of some alkali halides decrease

discontinuously at the transition from rock-salt to cesium chloride form (see, Eppler and Drickamer, 1958; Zahner and Drickamer, 1959). However this model is not likely to give the K_T and d compatible with the abnormal values in the region C, since any mixture with SiO_2 could not give the K_T and the d compatible with those in the region C, as described already, and the transitions from rock-salt to cesium chloride form, in the cases of some alkali halides, take place with discontinuous jumps of the density, namely this kind of transition is regarded as a simple transition to more denser packing form with the increase of coordination numbers from 6 to 8, but without any change of the bonding character. Then it seems impossible that this kind of transition takes place gradually without density-jump.

On the other hand, the equation of state of MgO in covalent state is not obtained in a convenient form. One reports that the equation could be obtained by adjusting the electrostatic potential to the real charges of the two kinds of ions and taking the repulsive potential as the form of $\exp(-ar)$, so that we have a similar form to the equation of state of ionic crystal (Asano and Tomishima, 1956). Магницкий (1959) gave an equation of state of the region D such that the calculated values of K_T and d are in accordance with those of Bullen in region D. He used the formula given by Born and Mayer. The equation obtained by him is

$$U=-97.046/(r/r_0)+7834.527\exp\{-7.122(r/r_0)\} \quad (\cdot 10^{-12}), \tag{4.4}$$

where the U is expressed in *erg/molecule*. The transition pressure between both the phases expressed by (4.2) and (4.4) is resulted in about 6,000 *kbars* by using (3.4). The pressure is too high to be realized in the region C. Магницкий (1959) gave another equation expressing the energy of covalent MgO in the form of $U=(A/(r/r_0)-C)\exp\{-B(r/r_0)\}$, where A, B and C are constants. However the equation gives a much higher transition pressure than the former, if A, B and C are determined such as compatible with the region D.

5. The core, the region E, F and G.

The existence of a "central core" was established by Oldham (1906) and this term has been applied to the whole region of the earth below a

depth of 2,900 *km*. In the outer part, namely, the region E, extending down to a depth of about 4,980 *km*, the P-velocity gradient is fairly steady and is comparable with that in D′. It is well established that the region E is in essentially fluid state. This conclusion is confirmed by the total absence of reliable evidence of the occurrence of S-wave in the region E.

In determining his velocity distribution, Jeffreys (1939 b) found that he could not fit the arrival-time data unless the P-velocity decreases sharply over a range of depth just below the region E. This region F is not shown in Gutenberg's velocity distribution.

Between a depth of about 5,120 *km* and the center of the earth is "inner core", the region G. Its existence was postulated by Lehmann (1936).

The origin of the core has been discussed by many authors. For a long time it has been assumed that the central core is composed of iron or iron-nickel alloy. This view was developed by Wiechert near the beginning of the century in order to explain the relatively high density in the core. In the following section, the iron-core hypothesis will be discussed.

5.1 Iron-core hypothesis

The hypothesis that the core consists of iron or iron-nickel alloy is current widely. The main reasons in supports of this hypothesis are

(1) the mean density of the earth is considerably larger than would be expected from the materials found on or near the surface, thus the core must be composed of a heavy material and iron is the only aboundant heavy element,

(2) a ferromagnetic core may account for terrestrial magnetism, and

(3) the existence of iron meteorite.

Regrarding (1) Elsasser (1951) had attempted to estimate the densities of elements and compounds by the method based upon quantum mechanical theory. These theoretical estimations are based upon Thomas-Fermi-Dirac (T-F-D) model of the electronic density in a closest packed cubic monoatomic lattice and are obtained chiefly from the results of the computations of Feynman, Metropolis and Teller (1949). His results are shown in Fig. 21.

On the basis of these courses, Elsasser suggested that interpolation

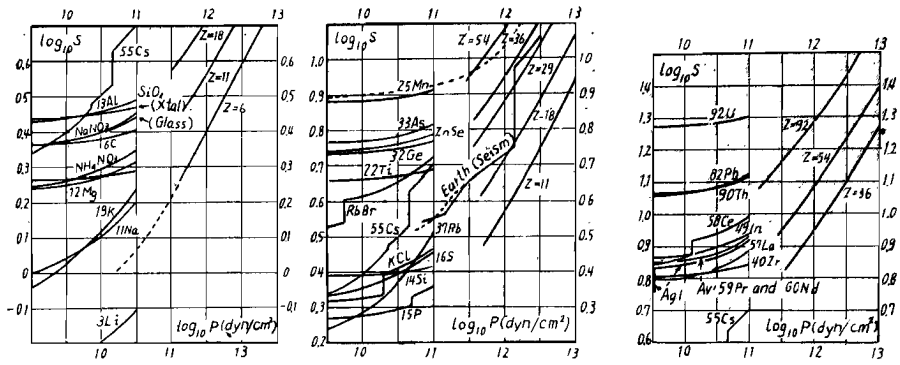

Fig. 21. Pressure-density relationships. Curves on left hand side: experimental reuslts. Curves on right hand side: results of T-F-D theory. Dashed curve (in (ii)) : experimental result of iron (Z=26) to a pressure of $4 \cdot 10^{12}$ *dynes/cm²* obtained by Al'tsuler, et al. (after Elsasser, excepting the experimental value of Fe)

between the measured value of low pressure and the computed value at very high pressure should allow density in the intermediate range to be estimated, with an uncertainty which he suggested should hardly exceed 15-20% anywhere. However, as Bullen (1952) has emphasized particularly, such a suggestion seems unduly optimistic. If we take the care Z=92 (Z denotes atomic number) first, then the T-F-D method is found to give a density of 11.9 *g/cm³*, at a pressure of $2.0 \cdot 10^{12}$ *dynes/cm²*. This is much lower than the known densities of uranium at pressure from zero to $0.1 \cdot 10^{12}$ *dynes/cm²*. Using the data observed under higher pressure than in Bridgemann's experiment (1945, 1948), we can see that Elsasser's estimation is not applicable to a pressure below $1 \cdot 10^{12}$ *dynes/cm²*. Al'Tshuler, Krupnikov, Ledenev, Zhuchikhin and Brazhnik (1958) obtained the compression curve of iron to a pressure of $4 \cdot 10^{12}$ *dynes/cm²*, using shock-wave technique. The observed density of Fe (Z=26) is much higher than the values obtained by T-F-D method, even in comparison with Z=29, as shown in Fig. 21. The density of Fe observed at the pressure of about $1.4 \cdot 10^{12}$ *dynes/cm²* is 11.7 *g/cm³*, whereas the density at the core-boundary, obtained from seimic data, is 9.7 or 9.1 *g/cm³*, according to Bullen's table, corresponding to his model A and B. Thus it is not reasonable that the density of the core is compatible with the density of iron. Also the T-F-D method can not be applied to a pressure below 10^{13} *dynes/cm²* without

much descrepancy. Indeed, as already mentioned by Ramsey (1950), it should be made here that it is to be expected that the density of all but the lightest elements will show a series of discontinuous jumps as the pressure increases, corresponding to the breaking down of inner shells. This will continue untill every atom is completely broken down, the electron then forming an imperfect degenerate Fermi gas. Thus, in this sense the T-F-D results even at extremely high pressure, can at best only be giving an average account of what would seem to be a complicated discountinuous relation between density d and pressure p for heavier elements. Of course, when the atom have been entirely broken down the T-F-D results should be completely realistic. An extremely crude estimate by Ramsey suggested that the critical pressure p_0 for this

$$p_c \simeq Z^{5/2} \cdot 10^{13} \ dynes/cm^2.$$

For the heavest elements the pressure thus obtained is 10^{12} *atm*. The maximum pressure obtained in the planets is $3 \cdot 10^7$ *atm* and this would seem to breake down only the lightest elements. It may be that the T-F-D curves are not physically meaningfull until pressures a great deal higher than 10^7 *atm* are reached.

Bullen (1952) has analyzed the data of Bridgemann (1945, 1948) and Feynman et al. and disagree with some of Elsasser findings. His calculation implies that atomic number to be associated with the material of the outer core, namely, the region E should be at least 6 units less than the value derived using simple extrapolations from T-F-D method. An extension of Thomas-Fermi (T-F) method to deal with compounds is made by Knopoff and Uffen (1954), who concluded that the outer core has the same density as a mixture of 90% iron and 10% olivine. Their result seems reasonable since the density of iron obtained experimentally is about 11-12 g/cm^3 at $1.4 \cdot 10^{12}$ $dynes/cm^2$. However, the calculated value of K_T derived from the compression curve of iron, measured by Al'Tshuler et al., is about $4.5 \cdot 10^{12}$ $dynes/cm^2$ at $1.4 \cdot 10^{12}$ $dynes/cm^2$, which is not compatible with the value of K at the core-boundary, $6.2 \cdot 10^{12}$ $dynes/cm^2$. Even if the mixture with 10% olivine is allowed, the result would be unchanged. Regarding (1) we can conclude that iron-core hypothesis, or the modified hypothesis is not supported.

Regarding (2), if the temperature within the core is beyond the Curie

point of iron, this support becomes meaningless. Slater (1940) reported that the increase of the Curie point with pressure is only several ten degree at 10^{12} *dynes/cm*^{2}. On the other hand, since the recent investation points out that the origin of the earth's magnetism is arised from the convection motion of conductive fluid within the core, (2) is not necessary to be examined.

Regarding (3) we can not yet know whether the parent body of meteorite is composed of the same material as of the earth. If it could be shown that the iron meteorite derived from the fragmentation of a planet, it would greatly strengthen the probability that the earth also contains iron. In fact, the origin of the iron meteorite is not certainly known, and they may have no relation to the core of a planet (Левин, 1957).

5.2. Ramsey's hypothesis

Ramsey (1949) rejected the iron-core hypothesis that was current as if only the hypothesis would be reliable. His opinion is in essence in accordance with the opinion written in the section 5.1. Moreover Ramsey pointed out that the sharp discontinuities of K_T and d at the core-boundary, found by seismological observation, do not seem to be explained by iron-core hypothesis. He put forward the suggestion that the large increase of density at the core-boundary is due to a pressure-induced transition from the molecular to a metallic phases, rather than due to the appearance of a new material such as an iron-nickel alloy. He thus assumed that the earth is of uniform chemical composition which he identifies as olivine.

Originally Ramsey put forward his hypothesis to account for the densities of the terrestrial planets. This hypothesis requires that the pressure at the core-boundary will be characteristic of a chemical composition of the material which he assumes is the same for all the terrestrial planets. The relation between the dimension and density of each terrestrial planet seems favourable to Ramsey's hypothesis, disregarding Mercury possessing an abnormally high density.

Urey (1952) and Kuiper (1952) pointed out that this hypothesis is untenable. Their main objection is that Mercury rules out Ramsey's hypothesis and the mean densities, deduced to zero pressure, of the terrestrial

planets, are not necessarily favourable to the hypothesis. However the chemical composition of Mercury, the nearest planet to the Sun, might be different to that of the earth. Левин (1949) said that Mercury consists of heavier materials than the other planets, since lighter elements could not but be vaporized by the effect of high temperature due to the shortest distance between the Sun and Mercury in comparison with the other planets. The estimated values of average mean densities at zero pressure seem not necessarily reliable, since the procedure of estimation is not completely established.

5.2.1. Pressure-induced metallic transition

The transition to metallic phase are pointed ont by several experimental facts and suggested by some theoretical computations applied to comparatively simple crystals.

As Ramsey noted, tin (Sn), phosphous (P), and arsenic (As) transform to their metallic phases with much heavier densities than original phases. The recent development of high-pressure technique, especially shock-wave technique, enabled us to find that some of the other com-

Table 14. metallic transition of several compounds found experimentally and their critical pressure

compound	critical pressure (10^{12} *dynes/cm*^{2})	reference
I	0.13	Alder and Christian
CsI	0.20	〃
KI	0.20	〃
RbI	0.20	〃
$LiAlH_4$	0.05	〃
CBr	1.67	Suchan and Drickamer
SnBr	0.366	〃
HgCl	0.284	〃
CHI	0.283	〃
HgBr	0.195	〃
HgI	0.144	〃
CI	0.167	〃
S	0.4～0.5	Slykhouse and Drickamer
	0.23	David and Hamann

pounds transform to their metallic phases. Alder and Christian (1956 a, b) reported the metallic transitions of iodine (I), cesium iodide (CsI), potassium iodide (KI), rubidium iodide (RbI) and $LiAlH_4$. It is noted that Griggs, McMillan, Michael, and Nash (1958) gave some objections to Alder and Christian's results. David and Hamann (1958) reported that sulfur (S) undergoes a metallic transition. Slykhouse and Drickamer (1958) suggested the metallic transition of S. Moreover Suchan and Drickamer (1959) suggested the metallic transitions of certain molecular compounds. These results are listed in Table 14.

On the other hand, the theoretical computation was first applied to solid hydrogen (H) by Wigner and Huntington (1936), who examined the possibility of metallic form of hydrogen. Kronig, de Boer and Korringa (1949) estimated the transition pressure of hydrogen to the metallic phase, and they found the transition pressure of $0.7 \cdot 10^{12}$ *dynes/cm*^{2} and the density jump from 0.4 to 0.8 *g/cm*^{3}. Давыдов (1955) reported that these values must be altered to be $1.8 \cdot 10^{12}$ *dynes/cm*^{2} and from 0.7 to 0.96 *g/cm*^{3}. The metallic phase of hydrogen was investgated by Baltensperger (1953) and Stern and Talley (1955) in connection with the problem of the impurity band.

Ten Seldam (1957) estimated the interatomic distance at which a model of solid helium would become a metal. Assuming solid helium with a face-centered cubic structure, a pressure of $80.9 \cdot 10^{12}$ *dynes/cm*^{2} would be required to cause the energy of the top of valence band to be lower than the energy of the bottom of conduction band and so produce metallic behaviours.

Behringer (1959) investigated the dependence on lattice parameter, or pressure, of the energy gap between the last filled and first empty energy band in lithium hydride (LiH). As LiH is an insulating crystal with a relatively small energy gap (about 6.5 *ev.*) at atmospheric pressure, it was thought that it might undergo metallic transition at a relatively low pressure. However, his estimation of the transition pressure gave the value of $35 \cdot 10^{12}$ *dynes/cm*^{2}. In his estimation, he started with the metallic state and determined when the energy gap appears. Accordingly the calculation is not expected to be applicable for the nonmetallic phase, as in this limit the approximation of a uniform electron density is not valid. The transition pressure estimated in He or LiH

seems too high to be realistic. The computation applied to LiH or He is made based on the assumption that the top of valence band and the bottom of conduction band hold their wave number vectors unchanged with the decrease of lattice parameter (or the increase of pressure). In fact, however, there is no evidence that these vectors must be held unchanged. Howland (1958) computed the electronic structure of potassium chloride (KCl). His result showed that the wave number vector possessed of the top of valence band changes with the lattice parameter. The band structures of II-VI intermetallic compounds are found to change their wave number vectors corresponding to the minimum energy gaps with the decreases of lattice parameters, as mentioned in section 3.3.4.. This fact may arise an overestimation of the transition pressure. Another reason arising an overestimation is that some polymorphic transition might occur at a lower pressure than the metallic transition pressure expected when any polymorphic transition does not occur. A interesting calculation was made by Cassella (1958), who evaluated the band structure of carbon in a face-centered cubic structure, in spite of diamond in the normal case. The lattice constant was chosen so that the hypothetical crystal would have the same average electron density as diamond, and consequently is smaller than for diamond by a factor of $2^{1/3}$. He concluded that the face-centered cubic crystal of carbon becomes a metal.

The present writer (1959, 1960 a, b) computed the electronic structure of MgO using tight-binding method. The results are showed in Fig. 22.

The writer estimated the transition pressure, at which the energy gap disappears. Assuming that the depression of the bottom of conduction band is, in the rate of change, as same as the rise of the top of valence band, and adopting the equation of state obtained by Трубицын, the critical pressure was found to be $0.7 \sim 1.5 \cdot 10^{12}$ *dynes/cm*²*. Here the energy gap at zero pressure is 9~12 *ev*, experimentally measured. However, his result seems optimistic. In his treatment, Mg-O interaction is likely to be underestimated, since though O-O interaction is fully included, Mg-O interaction is included as a perturbed term for simplicity (see, Grimley, 1958). In fact, Mg-O interaction is too large to be regarded as a perturbed term. The valence band of Mg-O in the case when Mg

* The result shown in the writer's previous papers (1959, 1960a) must be revised, since the evaluation of the valence band contains some error.

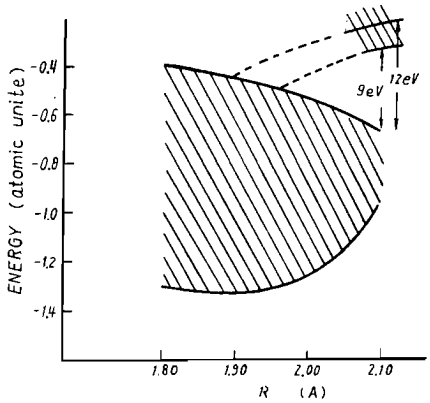

Fig. 22. Electronic structure of valence band of MgO as a function of the interionic distance R.

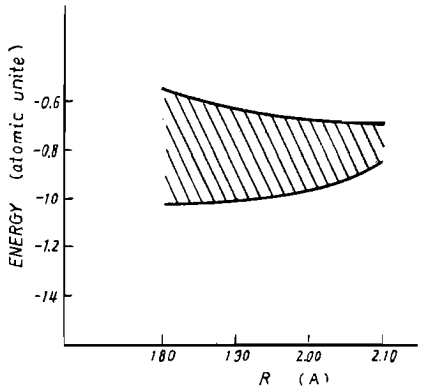

Fig. 23. Electronic structure of valence band of MgO, when Mg^{2+} ions are regarded as point-charges.

ion situated at each lattice point is regarded as a point charge and O-O interaction alone is conidered, as shown in Fig. 23.

The assumption concerning the depression of the bottom of conduction band seems optimistic, too. If we examine the result for LiH obtained by Behringer, the depression of the bottom might probably be not so much as expected. Thus whether MgO can transform ionic state of itself immediately to metallic state at a pressure reached at the core-boundary is open to question. In order to examine this problem, we should know that the deformation of electron configuration of MgO, due to which MgO could not be treated as a purely ionic crystal under a certain pressure range, should be induced. On other words, even if Mg-O interation is included sufficiently in computation, the result might not yet be realistic, since the overlap integral or exchange integral between the nearest Mg-O is found to change abnormally, due to the large and gradual tail of $2p$-electron wave function of O^{--}. A relatively large portion of electron cloud of $2p$ (O^{--}) invades into the negative parts of electron cloud of $2p$ (Mg^{++}), even in the normal condition, and then the overlap or exchange integral between $2p$ (O^{--}) and $2p$ (Mg^{++}) cancels partly itself, namely, it changes abnormally with the increase of pressure. Although the $2p$ (O^{--}) used in the computation, calculated by Watson (1959), is solved in a crystalline state (see Yamashita and Kojima, 1052), the $2p$-orbitals do not seem realistic in MgO crystal. The shorter the lattice

parameter becomes with the increase of pressure, the less the reality would be. A similar problem was investigated in the case of LiH or LiF (Benson and Wyllie, 1951 ; Yamashita, 1952 ; see also, Löwdin, 1956, 1957). It was resulted that in order to obtain a good approximation, homopolar bonds must be included together with hetropolar bonds. The density distribution of electrons in NaCl and LiF, observed experimentally, also showed that LiF must be regarded as having partly homopolar bonds and near the middle point between Li^+ and F^- there is much more density distribution of electrons than expected in purely ionic electron configuration, whereas in the case of NaCl the ionic configuration of electrons gives a good approximation. Thus we may conclude that also in the case of MgO homopolar bonds must be considered in treating the electronic structure, especially under a high pressure. On other words, it seems probable that the intermetallic state in MgO is the more realistic, the higher the pressure within the mantle. Thus it is reasonable that the ionic-intermetallic transition is indispensable for the metallic transition of MgO to occur under a relatively low pressure prevailing the core-boundary in comparison with the theoretical results on the transition of ionic crystal.

As mentioned in section 3.3.4., the ionic-intermetallic transition makes the energy gap of ionic crystal drop from about 10 *ev.* to about 3 *ev.* in the intermetallic state. Edwards, Slykhouse and Drickamer (1959) observed

Table 15. Effect of pressure on band structure of several II–VI compounds.

compound	ΔE (*ev.*) (1 *atm*)	$d\Delta E/dp$ (10 *ev./dynes/cm²*)	pressure (10^{12} *dynes/cm²*)	Max. blue shift (*ev.*)
ZnS	3.54	+5.7	0.00−0.18	0.50
ZnSe	2.57	+6.0	0.00−0.13	0.50
		−2.0	0.13−0.21	
ZnTe	2.26	+6.0	0.00−0.045	0.22
ZnO	3.14 (wtz)	0.6−1.9	0.00−0.13	0.15
	(Znbl)	1.9	0.13−220	0.20
Cds	2.50 (wtz)	+3.3	0.00−0.0275	0.08
	1.7 (Znbl)	0.0	0.0275−0.05	0.00
		0.0	0.05−0.1	0.00

the changes of energy gaps with the increase of pressure in several II-VI compounds, Their results are listed in Table 15. In ZnSe, for example, the energy gap increases to 3.07 *ev.* untill the pressure reachs at $0.13 \cdot 10^{12}$ *dynes/cm*^{2} and then decreases with the rate of $-2.0 \cdot 10^9$ *ev/dyne/cm*^{2}. Adopting a linear extrapolation of this rate to a pressure of the core-boundary, we find the energy gap of ZnSe disappear at about $1.5 \cdot 10^{12}$ *dynes/cm*^{2}, which is compatible with the pressure of the core-boundary, $1.4 \cdot 10^{12}$ *dynes/cm*^{2}. Also in ZnS or ZnO, the decreasing of energy gap may be expected to start at about $0.2 \sim 0.3 \cdot 10^{12}$ *dynes/cm*^{2} with the same rate as that of ZnSe. MgO in intermetallic state may be expected to undergo the analogous change of the energy gap.

5.2.2. Density-jump induced from intermetallic-metallic transition

If MgO in intermetallic state possesses zinc blende structure under a pressure prevailing the region D, the nearest neighbour distance between Mg and O could be 1.55 *A* for MgO to have the density at the base of the region D, namely, 5.7 *g/cm*^{3}. The inner electrons of Mg and O form Ne- and He-cores, respectively. They are expected to have the radii of about 0.65 and 0.09 *A*, respectively, corresponding to the radii of Mg^{++} and 0^{6+}. On the other hand, the covalent radii (tetrahedral) of them are estimated as 1.40 and 0.66 *A*, respectively. Consequently we may regard the bonding parts of them as having the radii of $(1.40-0.65=)0.75$ and $(0.66-0.09=)$ 0.55 *A*, respectively. If these bonding parts overlap mutually by compression, then the nearest neighbour distance between the two kinds of atoms would be $(0.09+0.65+0.75=)$ 1.49 *A* in the extreme compression. A more contraction than 1.49 *A* may break down the inner shells, so that a very high energy must be reqiured. The value of 1.49 *A* is near the value of 1.55 *A*. Then it is confirmed that the intermetallic MgO in zinc blende form is compressed to be near a certain limit of the lattice structure and then the metallic state becomes preferable.

When the energy gap tends to zero, the electrons in the valence bands are exicited to the conduction bands, in which they can move freely through the lattice. Then the metallic state of MgO possesses a higher coordination numbers than 4, since the restriction that the valence bonds must

take predominantly 4-coordinations is lost. For example, 6-coordinations which means a rock-salt or a simple cubic form, if Mg is equivalent to O in a metallic state, may be expected. It is noted that the simple cubic form is possessed of Po, which is a metal but regarded as bonded by covalent bonds and, as an interesting fact, belongs to VI Group composed of O,S,Se and Te. The transition of MgO from zinc blende to rock-salt form causes the increase of density by 54% of that of the first form, if the bond length is left unchanged, Probably the volume contraction may be somewhat larger than 54%, since this transition takes place with some contraction of bond length. The density increase of 71~59% at the core-boundary estimated by Bullen is compatible with the above value.

5.2.3. Metallic MgO in fluid state.

The absence of reliable evidence of the occurance of S-wave in the region E is interpreted that the region E is in an essential fluid state.

In the iron-core hypothesis, it is generally accepted that the melting point of iron under a pressure prevailing the outer core would be somewhat lower than the actual temperature. Simon (1953) has computed the melting point of iron at a high pressure. His calculation is based upon experimental data for the change in melting point under pressure of substances (for example helium) with very low melting point which can be investigated over a wide range of pressure. These substance are found to obey the law

$$p/a=(T/T_0)^c-1 \qquad (5.1)$$

where c is a constant and a is simply related to the initial pressure $-(\partial U/\partial v)_T$, U being the internal energy. Simon determined the melting point of iron at the pressure corresponding to the bottom of the mantle, this is, about 3,000°K. Recently Strong (1959) determined experimentally the melting curve of iron to $0.096\cdot10^{12}$ *dynes/cm*^{2} and determined the melting point at the pressure corresponding to the bottom of the mantle, this is, about 2,610±200°C, based upon the Simon's formula (5.1).

On the other hand, regarding Ramsey's hypothesis, the fluid state of the core has not been explained untill now. A simultaneous occurrence of pressure-induced metallic transition and melting phenomenon at the core-boundary appears too accidental to be realized. The writer (1960 c), however, pointed out that a simultaneous occurrence of both the phenomena

should not be a necessary restriction. If the metallic phase induced by pressure has somewhat lower melting point than the intermetallic phase, we could expect the fluid state of the core on Ramsey's hypothesis, when the actual temperature is between their melting points of both phases as shown in Fig. 24. A similar suggestion was made by Jacobs (1954), who attempted to explain the origin of the inner core based upon iron-core hypothesis.

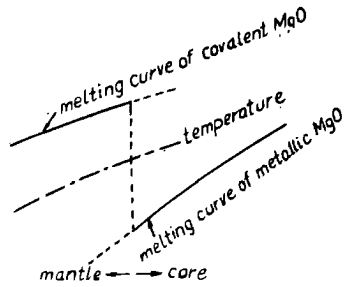

Fig. 24. Schematic diagram of melting curves of intermetallic (or covalent) and metallic MgO at the depth of the mantle-core boundary, in comparison with actual temperature.

The important problem is whether the melting point in metallic phase becomes lower than that in intermetallic phase. Although metallic bond corresponds to a low melting point, as generally accepted, the direct comparison with intermetallic bond on a compound composed of definite kinds of atoms has not been made. However, the fact that many intermetallic compounds are fused into liquid state, in which they show metallic behaviours, may be interpreted as a lower melting point possessed of metallic phase than that possessed of intermetallic phase, since the liquid state of intermetallic phase, if it exists, may be unstable, corresponding to higher melting point, and on the other hand, that of metallic phase more stable.

More interesting interpretation concerning the fluid state of the core is possible based upon intermetallic-metallic transition hypothesis. Wentorf (1957) reported that molten boron nitride (BN) conducts electrically about as well as graphite (C), whereas solid born nitride is a good insulator. Busch and Vogt (1953) reported that molten indium antimonide (InSr) has about four times higher conductivity than solid InSb. The experimental evidences that molten phases exhibit higher conductivity than the solid phases are reported also regarding germanium (Ge), bismnth (Bi), and tellurium (Te) (Hall, 1958, for Ge ; Bundy 1959, for Bi ; Epstein, Fritzsche and Lark-Horovitz, 1957, for Te). Such metals as Bi, Sb, Te, Ge, Si Sn, P, etc., are named "semi-metals" by Kubaschewski (see, Frost, 1954) These semi-metals are characterized by the volume contraction, the increase of coordination numbers and the increase of electric conductivity when they are molten. According to Bundy's experiment, Bi transforms at $0.025 \cdot 10^{12}$

dynes/cm^2 from the phase I in semi-metallic state to the phase II in metallic state with a certain volume contraction. The melting curve concerning the phase I decreases with the increase of pressure, whereas that concerning the phase II increases. The metallic phase of MgO induced by the pressure corresponding to the core-boundary, as suggested by the writer, should be classified into semi-metal group, since this has 6-coordination number whereas the coordination number of "true metal" is higher than 6, namely, from 8 to 12. Then we can expect the phase diagram of MgO near the core-boundary as shown in Fig. 25, from an analogy to the phase diagram of Bi.

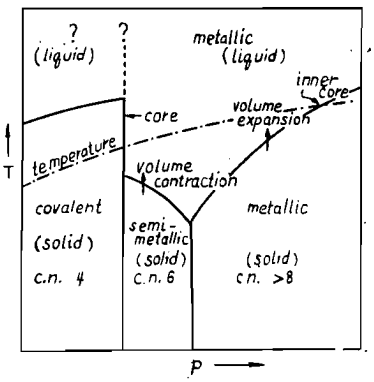

Fig. 25. Schematic diagram of melting curves of intermetallic, semi-metallic and metallic phases of MgO.

The molten phase of MgO in semi-metallic state should be somewhat denser than the solid phase (for example, in the case of Bi the increase of density is about 3.35%). It should be noted that the metallic state in the upper part of the region E is attained in the molten phase alone.

Moreover we may expect that the melting curve starts to go upward at a certain pressure, corresponding to the transition point between the phase I and II of Bi, and may exceed the actual temperature somewhere in the core. This means the existence of solid phase within the deeper part of the core, corresponding to the inner core.

6- Conclusion

Based upon modern solid state physics, the internal state of the earth is discussed. The seismic and geomagnetic evidences in the deeper part of the mantle are explained by the model that this region consists of the intermetallic phase of MgO. The region C is regarded as the transition region from ionic to intermetallic state of MgO. This transition is characterized by the gradual changes of the compressibillty and density, corresponding to the gradual increase of homopolar character in the bonding state of MgO, originally ionic crystal. The transition occurs due

to pressure-increase, and its possibility is examined based upon quantum mechanical theory of cohesive properties of solids. Moreover the gradual increase of homopolar character in bonds induces the decrease of energy gap of MgO, so that the region C exhibits the increse of electric conductivity compatible with the geomagnetic data.

Introducing this intermetallic transition at the region C, we can refines Ramsey's hypothesis on the origin of the core, since metallic transition seems possible only through intermetallic transition. Namely, investigating intermetallic state we can strengthen the possibility of the existence of metallic state in the core, and moreover realize the state of the core more essentially than made hitherto.

No existence of S-wave in the core is explained by molten phase of metallic state, due to the decrease of melting point in metallic state in comparison with that in intermetallic state.

Regarding the composition within the earth, the region B is composed mainly of olivine possessing mainly ionic bonds, the region C undergoes the decomposition of olivine to MgO and SiO with squeesing of the latter and simultaneously MgO transforms into intermetallic state. The region D is compossed of intermetallic MgO, and the core is composed of metallic MgO. The model applied to the earth's interior is shown in Table 16.

The present work must be made np by many quantitative computa-

Table 16. Earth's interior suggested by ionic-intermetallic-metallic transition hypothesis.

Region	Compositon	Bonding character	electrical conductivity	other
B	mainly olivine	ionic	ionic	
C	olivine decomposes into periclase and coesite	ionic-intermetallic transition	ionic→intrinsic	covalent (homopolar) character increases gradually
D	mainly periclase (zinc blende structure)	covalent (or intermetallic)	intrinsic	
E F G	mainly periclase (solid state : 6-coordination, liquid state : 8∼12-coordination)	semi-metallic but metallic in liquid phase.	metallic	melting point decreases with pressure within the upper core.

tions, some of which are progressing at the writer.

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