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**ON THE POSSIBILITY OF THE METALLIC
TRANSITION OF MgO CRYSTAL AT THE
BOUNDARY OF THE EARTH'S CORE**

BY

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On the Possibility of the Metallic Transition of MgO Crystal at the Boundary of the Earth's Core

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(Communicated by Prof. K. Sassa)

Ramsey's hypothesis on the origin of the Earth's core is applied to the model that the D-layer and the core are composed of the molecular and the metallic phase of MgO, respectively. The approximation of tight-binding method is employed to investigate the electronic band structure of MgO crystal. It is resulted that the pressure-induced transition of MgO to metallic phase occurs at a pressure of about 1.2×10^6 bars.

1. Introduction

The suggestion that the large increase of density at the boundary of the Earth's core is due to a pressure-induced transition from a molecular to a metallic phase, was first proposed by Ramsey (1948). He abandons the iron-core hypothesis and assumes that the mantle and the core have the same chemical composition, for example, such as olivine. Olivine, however, may not seem to compose the D-layer, since the ϕ ($=K/d$, where K and d denote incompressibility and density, respectively) of olivine is not compatible with that of the D-layer deduced from seismic data.

Recently Марницкий (1953) and Shimazu (1959) suggested the process $\text{Mg}_2\text{SiO}_4 \rightleftharpoons 2\text{MgO} + \text{SiO}_2$ within the C-layer, which demands the D-layer composed mainly of MgO. In fact, it will be shown in the present paper that the elastic properties of MgO agree fairly well with those of the D-layer deduced from seismic data.

Originally, Ramsey put forward his hypothesis to account for the density of the terrestrial planets. On his hypothesis the pressure at the boundary of the core should be characteristic of the chemical composition — MgO in our model. Although it is important to determine whether the dimensions and masses of the terrestrial planets can or not show that this hypothesis is tenable, the possibility of the metallic transition of the constituent material at

the boundary of the Earth's core gives a determinable evidence to his hypothesis.

The critical pressure at which a metallic transition occurs depends upon the variation of the forbidden band (the energy gap between the conduction and the valence band) with pressure. It is desired that the electronic band structure of MgO crystal under a high pressure of about 10^6 bars is investigated. Since at present we can hardly expect to carry out it experimentally, although the recent development of shock-wave technique should be noted (Alder and Christian (1956)), the theoretical investigation is the only way to do so.

2. The electronic band structure of MgO crystal

MgO crystal consists of two kinds of ions, Mg^{2+} and O^{2-} , which have closed shell structures. We suppose that the uppermost valence bands of MgO crystal have $6N$ states, and they are completely filled with $6N$ electrons, since the crystal is an insulator. Then we may assume that the wave functions of these bands are approximately given by LCAO (linear combination of atomic orbitals) Bloch functions formed from suitable atomic orbitals which have the character of $2p$ -orbitals of O^{2-} ion.

The fundamental problem in the determination of the electronic band structure of a crystal in the ordinary Hartree-Fock approximation is to find the eigenvalues of the equation.

$$F_{0p}(\mathbf{x}, \mathbf{k}) = \epsilon_p(\mathbf{k}) \psi_p(\mathbf{x}, \mathbf{k}) \quad (1)$$

$\psi_p(\mathbf{x}, \mathbf{k})$ are the one-electron wave functions ($\mathbf{x}$ stands for both space and spin coordinates), $\mathbf{k}$ is a vector in the reciprocal lattice (body-centered cubic in the case of MgO) and the index p denotes the Brillouin zone number in $\mathbf{k}$ -space. F_{0p} is the effective one-electron Hamiltonian operator in Fock's approximation. To obtain an approximate solution of Eq. (1), we suppose that the $\psi_p(\mathbf{x}, \mathbf{k})$ may be expressed as LCAO. For the valence band of MgO crystal containing N molecules, the atomic orbitals selected are the 12 free ion spin-orbitals consisting of $6N$ $2p$ spin-orbitals on the O^{2-} ions and $6N$ $2p$ spin-orbitals on the Mg^{2+} ions. These orbitals will be denoted by $\phi_p(\mathbf{x}, \mathbf{a})$, where the vector $\mathbf{a}$ specifies the position of the ions, and the index p goes over all spin-orbitals associated with the ion at $\mathbf{a}$. The radial parts of the orbitals used in present calculation are given by

$$P_0 = 0.07800 r \exp(-0.714 r) + 8.51793 r \exp(-3.412 r) + 1.6649 r \exp(-1.38 r) \quad (2)$$

for the $2p$ orbitals of O^{2-} (Watson (1958)) and

$$P_{Mg} = 7.360 r \exp(-2.7226 r) + 22.795 r \exp(4.808 r) + 21.348 r \exp(-7.9907 r) \quad (3)$$

for the $2p$ orbitals of Mg^{2+} (Löwdin (1953)), respectively. For brevity, in what follows we condense our indices (p, a) and (p, k) into the single symbols a and k , and write

$$\phi = \varphi C' \quad (4)$$

where ϕ and φ are row matrices. C' is taken as a square $(6N \times 6N)$ matrix so that Eq. (2) defines a set of $6N$ crystal spin-orbitals. The row matrix φ is ordered such that the first $3N$ elements are the spin-orbitals on the O^{2-} ions, and the last $3N$ elements are those on the Mg ions. Let the indices μ, ν and λ denotes the orbitals on the O^{2-} ions, and l, m and n denotes the orbitals on the Mg^{2+} ions. The indices α, β, γ and δ will be used to denote any orbitals on the O^{2-} and the Mg^{2+} ions.

The set of orbitals φ are not all orthogonal at any finite lattice parameter. An orthonormal set Φ are introduced by Löwdin transformation (for example, Löwdin (1956), Callaway (1958)). Thus

$$\Phi = \varphi L \quad (5)$$

where

$$\left. \begin{aligned} L &= (\mathbf{1} + S)^{-1/2} \\ S_{\alpha\beta} &= \int \phi_{\alpha}^*(\mathbf{x}) \phi_{\beta}(\mathbf{x}) d\mathbf{x} - \delta_{\alpha\beta} \end{aligned} \right\} \quad (6)$$

Eq. (4) is expressed by the set Φ as

$$\left. \begin{aligned} \phi &= \Phi C \\ C^{\dagger} C &= C C^{\dagger} = \mathbf{1}. \end{aligned} \right\} \quad (7)$$

Using Eq. (7) in Eq. (1) our fundamental approximation is expressed as

$$C^{\dagger} F C = \epsilon \quad (8)$$

where ϵ is a diagonal matrix, and the matrix F has element $F_{\alpha\beta}$ defined by

$$F_{\alpha\beta} = H_{\alpha\beta} + \sum_{k\gamma\delta} C_{k\gamma}^{\dagger} G_{\alpha\beta}^{\gamma\delta} C_{\delta k}, \quad (9)$$

where

$$\left. \begin{aligned} H_{\alpha\beta} &= \int \phi_{\alpha}^*(\mathbf{x}) H \phi_{\beta}(\mathbf{x}) d\mathbf{x}, \\ G_{\alpha\beta}{}^{\gamma\delta} &= \int [\phi_{\alpha}^*(\mathbf{x}_1) \phi_{\gamma}^*(\mathbf{x}_2) G \phi_{\beta}(\mathbf{x}_1) \phi_{\delta}(\mathbf{x}_2) \\ &\quad - \phi_{\alpha}^*(\mathbf{x}_1) \phi_{\gamma}^*(\mathbf{x}_2) G \phi_{\delta}(\mathbf{x}_1) \phi_{\beta}(\mathbf{x}_2)] d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned} \right\} \quad (10)$$

where $\mathbf{H}$ is the Hamiltonian operator for an electron moving in the field of the ion-cores, and $\mathbf{G} = (1/2) \mathbf{r}_1 - \mathbf{r}_2$.

Let $\mathbf{B}$ be a unitary matrix which transform $\mathbf{F}$, the matrix representation of all $F_{\alpha\beta}$, to a new matrix ϵ' , where

$$\epsilon' = \mathbf{B}^\dagger \mathbf{F} \mathbf{B}, \quad (11)$$

and $\mathbf{B}$ is chosen such that the submatrices $\epsilon'(\mu, \mathbf{m})$ and $\epsilon'(\mathbf{m}, \mu)$ are null matrices. Then a set χ of orthonormal atomic spin-orbitals is introduced according to

$$\lambda = \Phi \mathbf{B}. \quad (12)$$

ϕ is expressed in terms of the set χ as

$$\phi = \chi \mathbf{V}, \quad (13)$$

where $\mathbf{V}$ is a unitary matrix, which reduces ϵ' to diagonal form with the eigenvalues $\epsilon_p(\mathbf{k})$ of Eq. (1) on the diagonal. Thus

$$\epsilon = \mathbf{V}^\dagger \epsilon' \mathbf{V} \quad (14)$$

To find the eigenvalues we first construct the Bloch functions

$$\eta_p(\mathbf{r}, \mathbf{k}) = N^{1/2} \sum_{\mu} x_p(\mathbf{r}, \mu) \exp(2\pi i \mu \cdot \mathbf{k}) \quad (15)$$

Then

$$\phi_p(\mathbf{x}, \mathbf{k}) = N^{-1/2} \sum_q \eta_q(\mathbf{x}, \mathbf{k}) U_{qp}(\mathbf{k}) \quad (16)$$

where

$$U_{qp}(\mathbf{k}) = N^{1/2} \exp(-2\pi i \mathbf{k} \cdot \mu) V_{qp}(\mu, \mathbf{k}) \quad (17)$$

Using Eq. (17) in Eq. (14), we arrive the secular equation

$$\det |\epsilon_{pq}(\mathbf{k}) - \delta_{pq} \epsilon(\mathbf{k})| = 0 \quad (18)$$

for the eigenvalues $\epsilon_p(\mathbf{k})$. In Eq. (18)

$$\left. \begin{aligned} \epsilon_{pq}(\mathbf{k}) &= \int \eta_p^*(\mathbf{x}, \mathbf{k}) F_{0p} \eta_q(\mathbf{x}, \mathbf{k}) d\mathbf{x}, \\ &= \epsilon_{pq}'(\mu, \mu) + \sum_{\lambda} \epsilon_{pq}'(\mu, \mu + \lambda) \exp(2\pi i \lambda \cdot \mathbf{k}), \end{aligned} \right\} \quad (19)$$

where λ is a vectors which maps out the O^{2-} ion lattice from an arbitrary chosen O^{2-} ion at μ .

The ϵ' is obtained from Eq. (11) by treating all non-diagonal elements of $\mathbf{F}$ as first order small quantities and applying perturbation theory (Grimley (1958)). The results can be written in terms of the matrix elements defined in Eq. (10) and the matrix $\mathbf{R}$ with elements $R_{\alpha\beta}$ defined by

$$R_{\alpha\beta} = \sum_{\gamma} B_{\alpha\gamma} B_{\gamma\beta}^{\dagger} \quad (20)$$

For numerical calculation, it is more convenient to express Eq. (21) in terms of matrix elements formed with the given non-orthogonal spin-orbitals. A new matrix corresponding to $\bar{\mathbf{R}}$ is defined by

$$\bar{R}_{\alpha\beta} = \sum_{\gamma} \bar{B}_{\alpha\gamma} \bar{B}_{\gamma\beta}^{\dagger} \quad \bar{B}_{\alpha\beta} = \sum_{\gamma} L_{\alpha\gamma} B_{\gamma\beta}$$

We can separate from $\bar{\mathbf{R}}$ a new matrix $\bar{\mathbf{P}}$ representing the contribution from the O-Mg interaction, i.e. $\bar{P}_{\mu\nu} = T_{\mu\nu} - \bar{R}_{\mu\nu}$, where $T = (\mathbf{1} + S_1)^{-1}$, and S_1 is the submatrix of S consisting of all elements of the form $S_{\mu\nu}$. In terms of these quantities we obtain

$$\begin{aligned} \epsilon_{\mu\nu}' = & \bar{H}_{\mu\nu} - 2G_{\mu\nu}{}^{\nu\mu} \bar{P}_{\mu\nu} - 2\sum_m \bar{G}_{\mu\nu}{}^{m\mu} \bar{P}_{\mu m} - 2\sum_m \bar{G}_{\mu\nu}{}^{\nu m} \bar{P}_{m\nu} \\ & + \sum_m \bar{P}_{\mu m} \bar{P}_{m\nu} (H_{\mu\mu} - H_{mm}) + \bar{H}_{\mu\mu} \sum_{\lambda} \bar{S}_{\mu\lambda} S_{\lambda\mu} - \sum_{\lambda} S_{\mu\lambda} \bar{H}_{\mu\lambda} \end{aligned} \quad (22)$$

where $\bar{H}_{\alpha\beta}$ and $\bar{G}_{\alpha\beta}{}^{\tau\delta}$ stand matrix elements like $H_{\alpha\beta}$ and $G_{\alpha\beta}{}^{\tau\delta}$ in Eq. (10) but with the set φ replacing the set Φ .

We can express all non-vanishing elements $\epsilon_{pq}'(\mu, \mu + \lambda)$ as follows:

$$\left. \begin{aligned} \epsilon'_{xx}(\mu, \mu) &= \epsilon'_{yy}(\mu, \mu) = \epsilon'_{zz}(\mu, \mu) = A_0 \\ \epsilon'_{xx}(\mu, \mu + \lambda) &= \epsilon'_{yy}(\mu, \mu + \lambda) = A_1 & \lambda = (r, r, 0) \\ \epsilon'_{zz}(\mu, \mu + \lambda) &= A_1' & \lambda = (r, r, 0) \\ \epsilon'_{xy}(\mu, \mu + \lambda) &= A_1'' & \lambda = (r, r, 0) \\ \epsilon'_{xz}(\mu, \mu + \lambda) &= A_2 & \lambda = (2r, 0, 0) \\ \dots\dots\dots & & \dots\dots\dots \end{aligned} \right\} \quad (23)$$

Here r is the cation-anion distance. The numerical calculation are carried out for three values of $r = 2.10, 2.00, 1.80$ Å. These are tabulated in Table 1.

Table 1 The values of ϵ'_{pq} in three cases of γ (see Eq. (23)).

ϵ'_{pq}	$\gamma = 2.10 \text{ \AA}$	$\gamma = 2.00 \text{ \AA}$	$\gamma = 1.80 \text{ \AA}$
A_0	0.205605	0.179944	0.100703
A_1	0.001162	0.009200	0.010147
A_1'	-0.009746	-0.013314	-0.025088
A_1''	0.017948	0.028438	0.041487
A_2	0.001628	0.005233	0.006604

Using Eq. (23) in Eq. (18) we now have

$$\left. \begin{aligned} \varepsilon_{xx}(k) &= A_0 + 4A_1(\cos 2\pi r R_x \cos 2\pi r R_y + \cos 2\pi r k_x \cos 2\pi r k_y) \\ &\quad + 4A_1 \cos 2\pi r k_y \cos 2\pi r k_z + 2A_2 \cos 4\pi r k_x \\ \varepsilon_{yy}(k) &= -4A_1'' \sin 2\pi r k_x \sin 2\pi r k_y \end{aligned} \right\} \quad (24)$$

and the other elements follow from (24) by interchanging x , y and z . The secular equation (18) is easily solved for several prominent directions in k -space, i. e., $(k, 0, 0)$, $(k, k, 0)$ and (k, k, k) . The final results are showed in Fig. 1.

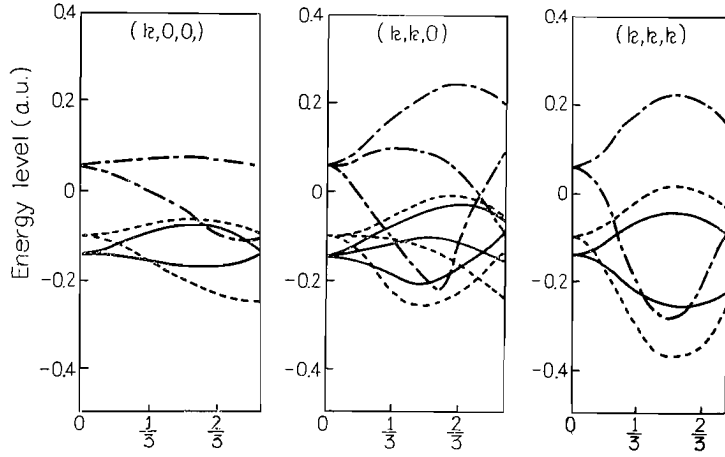


Fig. 1. Band structure of MgO in three cases of r along three directions in k -space. (.....; 2.10Å, —; 2.00Å, -.-.-; 1.80Å)

To obtain the transition point, one may proceed in the following : start with MgO crystal in the ionic state and determine when the energy gap disappears. The maximum and the minimum energy values of the valence band are plotted against r in Fig. 2., which shows the broadening of the band with r . Since the evaluation of the conduction band of MgO crystal can hardly be made by the approximation of tight-binding, we assume that the conduction band broadens within the forbidden band as much as the valence band. At the ordinary lattice parameter $r=2.10 \text{ Å}$, it is found by using optical method that the energy gap is about 9 e. v.. With the assumption above cited, thus it is found that the energy gap disappears at $r=1.87 \text{ Å}$

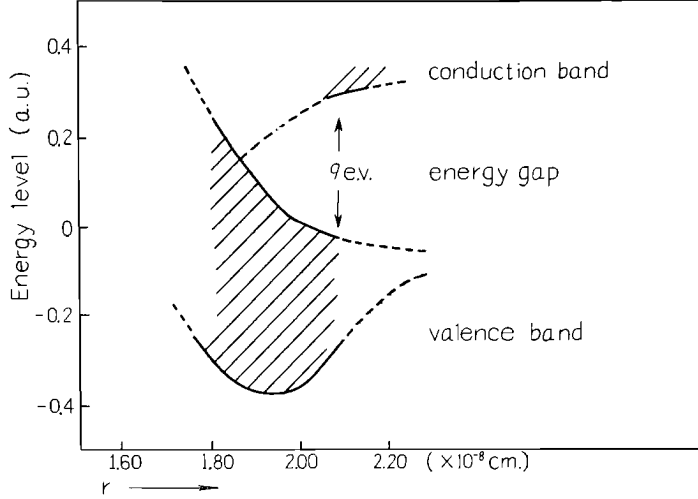


Fig. 2. The electronic band structure of MgO as a function of r . Conduction band and valence band are crossing at $\approx 1.87\text{\AA}$.

3. An equation of state of MgO crystal

To obtain the pressure of MgO crystal corresponding to the transition point, we must express the lattice energy of MgO crystal as a function of r . According to Born and Mayer's expression, the lattice energy E_r is shown by

$$E_r = -(\alpha_M z^2 e^2 / r) + b [MC_{12} e^{(r_1 + r_2 - r)/\rho} + M'/2] (C_{11} e^{2r_1/\rho} + C_{22} e^{2r_2/\rho}) e^{-a'r/\rho} \quad (25)$$

per molecule, where α_M is Madelung's constant (1.7476 for the NaCl type in MgO), M and M' are the numbers of unlike and like neighbours of each ion, respectively (6 and 12 for the NaCl type), a' is the ratio of the distance between like neighbours to that between unlike neighbours ($\sqrt{2}$ for the NaCl type), b is arbitrary constant chosen to have the value 10^{-12} erg, r_1 and r_2 are what shall be termed the radii of the ion 1 and 2, C_{ij} is a factor calculated by Pauling and is expressed as $C_{ij} = [1 + (z_i/n_i) + (z_j/n_i)]$ where z_i is the valence of i -ion, and n_i the numbers of valences electrons in the outer shell of i -ion.

According to Huggins and Mayer's method (1933), the unknown parameters r_1 , r_2 and ρ in Eq. (23) are determined by using some experimental values of MgO. The final results is expressed as

$$E_r = -76.76605/(r/r_0) + 1385,24705 \exp(-4.8837(r/r_0)) \\ + 3660.44466 \exp(-6.9066(r/r_0)) \quad (26)$$

By differentiating Eq. (26) once and twice we obtain pressure p , and incompressibility K_r as the functions of (r/r_0) . And the relation between

(r/r)	$p(.10 \text{ dynes/cm})$	$K_r (.10 \text{ dynes/cm})$	$d (\text{gr/cm})$
1.00	0.000	1.64	3.60
0.99	0.052	1.81	3.71
0.98	0.109	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	1.033	4.61	5.10
0.88	1.194	5.08	5.28
0.87	1.376	5.63	5.47

Table 2. Variation of density d , incompressibility K_r and pressure p of MgO versus change (r/r_0) .

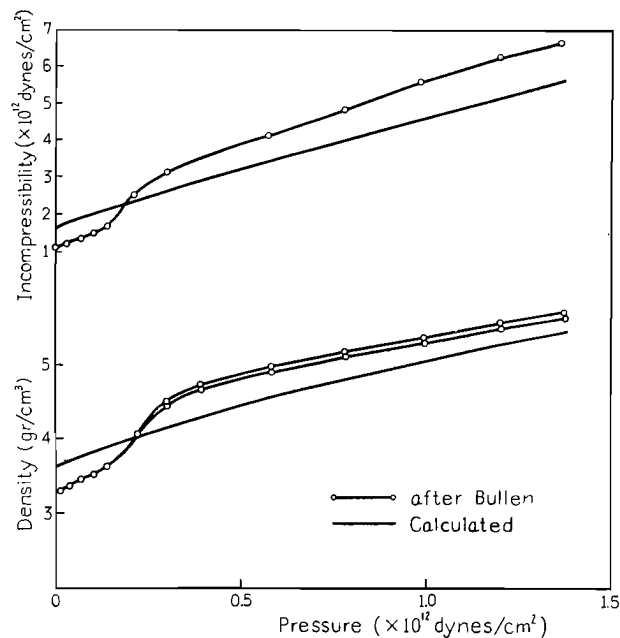


Fig. 3. Distribution of density (lower curve) and incompressibility (upper curve) within the Mantle.

density d and (r/r_0) is obtained by using the atomic weights of Mg and O. These values are given in Table 2. To examine the model that the D-layer is composed of MgO, these calculated values and Bullen's values (1953) are shown in Fig. 3, where we find that the maximum discrepancy between both values $\phi (=K_T/d)$ is about 20%. We must note that the accuracy of Eq. (26) decreases as the pressure increases (Wada (1959)) and the calculated values show the isothermal and, on the other hand, Bullen's values the adiabatic. At any rate, we may conclude that Eq. (26) will be enough good approximation to estimate the transition point, since the process in evaluating the electronic band structure is not so accurate that the discrepancy above cited plays a heavy roll.

4. Pressure-induced transition of MgO crystal to metallic phase

From sec. 2 and sec. 3 we find that the pressure corresponding to the transition point ($r=1.87 \text{ \AA}$) is about 1.2×10^6 bars, which is the pressure of the depth of about 2600 km in the interior of the Earth, as shown in Bullen's table. The result obtained, in the other word, shows that the energy gap between the conduction band and the valence band of MgO crystal disappears at $r=1.87 \text{ \AA}$. In this situation the valence electrons in ordinary ionic state are made free, and the electronic band structure becomes metallic. We must note that this transition point is not such as suggested by Ramsey. In the former no density-jump occurs, while in the latter density increases discontinuously. To estimate the latter type of transition, we must obtain the lattice energy curve of the metallic phase. Of course we may expect that the minimum point of the energy curve of the metallic phase could be near the transition point given in the present calculation. It is, however, not necessary that both transition occur at same pressure. This case that the transition with density-jump at a high pressure than the transition without density-jump, is very interesting. In this case the electronic conductivity increases abruptly at an certain depth in the deeper part of the D-layer and the density increases discontinuously at the boundary of the Earth's core. The suggestion that the electric conductivity will increase abruptly in the case of the transition to metallic phase, is made by Mott (1956). Mott's opinion is as follows : if an electron is removed from valence band to

conduction band, a mobile positive hole is formed. The minimum energy necessary to form a free electron and positive hole will decrease as the lattice parameter comes closer, but cannot tend to zero. since an electron and a positive hole attract each other with a force of which the potential energy for large r is of Coulomb's type. Thus small number of free carriers of positive sign is impossible in the ground state, since the free carriers of positive and negative sign are bounded to form pairs. On the other hand, when there is a large number of free carriers any pair of charged particles may be expected to attract each other with a force derivative from a screened potential, which does not necessarily lead to a bound state. Thus the transition to a state showing metallic conductivity will be sharp.

5. Conclusion

It is found that the valence band of MgO crystal broadens rapidly as lattice parameter decreases, and the energy gap will disappear at $r = 1.87 \text{ \AA}$ corresponding to pressure of about 1.2×10^6 bars which is deduced from an equation of state of MgO. We may expect that the pressure-induced transition of MgO crystal to metallic phase could occur at the boundary of the Earth's core. A new model that the electric conductivity increases abruptly in the deeper part of the D-layer and the transition from molecular (or ionic) phase to metallic one occurs at the boundary of the Earth's core with a large density-jump, is also suggested.

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