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MELTING POINT IN THE EARTH'S MANTLE

BY

Isamu HIRANO

1. Introduction

The first attempt to estimate the melting point in the earth's mantle was made by Uffen (1952) with the help of Lindemann's law of fusion. Lindemann's law has been widely used because it agrees well with experimental data for monoatomic crystal substances. However, Lindemann's law does not necessarily hold good for more complicated substances such as ionic crystals. Kurosawa (1957) has suggested that the contribution of lattice defects is more important than that of lattice vibration for the melting of ionic crystals. According to him, melting phenomenon is a sort of phase transition caused by the coulombic interaction between defects, and this transition temperature is near the melting point. From this viewpoint, Kurosawa has established the relation between the melting point and the formation energy of a pair of defects.

The present paper is intended to put forward a new method of estimating the melting point in the mantle on the basis of Kurosawa's theory of fusion. It must be added to note that Zharkov (1959) has already used the theory of thermal defects for estimating the melting point in the earth. He considered that fusion occurs if the fractional density of defects reaches a certain critical limit. However, it is difficult to understand why the mere increase of the number of defects can cause a large and discontinuous change such as melting, if the interaction between defects is not taken into account, say, by Zharkov. This point will be discussed again in the next section.

2. Theory

If there is no interaction between defects, the concentration of defects in the state of equilibrium at temperature $T$ is given by

$$f = c \exp\left(-\frac{W_0}{2kT}\right),$$

(1)

where $f$ is the fractional density of defects, $W_0$ is the formation energy of a pair of defects at $0^\circ K$, and $c$ is a factor of the order of $10^{-100}$. Zharkov (1959) considered in his estimation of the melting point in the earth that the critical density of defects at which fusion may occur is expressed on the basis of eq. (1) as follows:
\[ f_m = c \exp \left( -W_0 / 2kT_m \right). \]  (2)

If we give the value \(3 eV\) for \(W_0\) of an ordinary silicate such as olivine, then we have the value of \(f_m\) at the melting point to be of the order of \(10^{-3} \sim 10^{-4}\). This value may be somewhat too small to cause a large and discontinuous change such as melting. Moreover, it is difficult to understand why the mere increase of the number of defects leads to the discontinuous change at the melting point. Therefore, it remains doubtful to evaluate the melting point on the basis of eq. (2).

According to Kurosawa, the lattice defects interact each other and this interaction causes an apparent decrease of the formation energy. He has shown that the fractional density of defects cannot exceed to a certain critical limit due to the interaction between defects. He has, furthermore, given some experimental supports to the fact that the temperature at which the fractional density of lattice defects converges to the critical limit is the melting point.

We now establish the relation between the melting point and the formation energy of a pair of defects following Kurosawa’s paper, and derive the basic formula which is applicable to an estimation of the melting point in the earth’s mantle.

If the effect of the interaction between defects is taken into account according to Debye-Hückel’s theory of strong electrolytic solution, the equilibrium condition without the interaction,

\[ W + 2kT \ln f = 0 \]  (3)

is replaced by

\[ W + 2kT \ln f - c \frac{e^2}{Ea} \left( \frac{e^2}{EaT} \right)^{1/2} = 0, \]  (4)

where \(W\) is the formation free energy per a pair of defects, \(E\) is dielectric constant, \(k\) is Boltzmann constant, \(e\) is electronic charge, \(c\) is a constant characteristic of substance, and \(a\) is lattice parameter. \(W\) is expressed as follows:

\[ W = W_0 - \beta T, \]  (5)

where

\[ \beta = \frac{(\partial \ln W / \partial \ln V)_o a W_o}. \]  (6)

In this equation, \(\alpha\) denotes the coefficient of thermal expansion and \((\partial \ln W / \partial \ln V)_o\) is \((\partial \ln W / \partial \ln V)\) at zero temperature. It is found that there is no solution of eq. (4) above the temperature \(T_c\), which is given by the following equation:

\[ W(T_c) = W_0 - \beta T_c, \]

\[ = 2kT_c \left( \ln c^r (e^2 / EaT_c)^3 + 2 \right), \]  (7)

where \(c^r\) is a numerical constant characteristic of crystal. This fact indicates that
the free energy for solid decreases with the increase of temperature in the region of temperature more than $T_c$. This suggests that a sort of phase transition occurs at temperature $T_c$. Kurosawa has shown that $T_c$ is almost equal to melting point $T_m$ with the help of the experimental data of ionic crystals. If $T_c$ is replaced by $T_m$ in eq. (7), then eq. (7) becomes

$$W(T_m) = W_0 - \beta T_m$$

$$= 2kT_m \ln (e^{\beta E_0 / E_0 T_m})^3 + 2).$$  \hfill (8)

This is used as the basic formula which expresses the dependence of the melting point on the formation energy of a pair of defects in the present paper.

In order to apply eq. (8) to the present calculation, we use the following equation which is given by a little modification of eq. (8):

$$W_{op} = 2kT_m(A + \ln \rho - 3\ln T_m),$$  \hfill (9)

where $W_{op} (= W_0$ in eq. (8)) is the formation free energy per a pair of defects at pressure $P$ and $0^\circ K$, and $\rho (\equiv a^{-3})$ is density, and $A$ is a function of dielectric constant expressed as follows:

$$A = \ln (c''/E^3),$$  \hfill (10)

where $c''$ is a constant characteristic of the substances. As the dependence of dielectric constant on pressure and temperature is the least well understood, it is assumed that dielectric constant does not vary through the mantle in the present paper. Hence, $A$ is regarded as a constant. The following relation is obtained from eq. (9) under this assumption:

$$\int_0^d \left( \frac{W_{op} - \beta T_m - 3\ln T_m - \ln \rho}{2kT_m} \right) \, d = 1,$$  \hfill (11)

where the suffix written outsides the parentheses denotes the depth to which the quantity enclosed by the parentheses refers. The density at various depths is well known from seismic data. Therefore, we can calculate the melting point at various depths by use of eq. (11) if the distributions of $W_{op}$ and $\beta$ are known.

$W_{op}$ depends on the volume which, in its own turn, depends on the pressure. The dependence of $W_{op}$ on the pressure is, therefore, expressed as follows:

$$W_{op} = W_{oo} \exp \left( -\int_0^P \frac{\partial \ln W_{op}}{\partial ln V} \frac{dP}{K_T} \right).$$  \hfill (12)

where $W_{oo}$ is the formation free energy at zero pressure and $0^\circ K$, $V$ is the volume and $K_T$ is the isothermal bulk modulus. The quantity $|\partial \ln W_{op}/\partial ln V|$ depends very
weakly on the pressure (Zharkov, 1958). Thus it can be assumed as constant, in the first approximation, which is ranged from 2 to 3 as shown by Zharkov. In this case, eq. (12) is approximated by

\[ W_{op} = W_{oo} \exp \left( \frac{\partial \ln W}{\partial \ln V} \rho d p K_T \right) \]  

(13)

This equation can be calculated numerically by use of seismic data. Thus we can obtain the value of \( W_{op} \) at various depths if the experimental value of \( W_{oo} \) is available. For most silicates that form rocks in the mantle, \( W \) at the normal pressure is about 3 eV according to the experimental results obtained by Coster (1948) and Hughes (1954). Coster's experiment shows that peridotite which is one of the most important rocks in the mantle has the value of 2.9 eV for its activation energy. We adopt 3.0 eV as the value for \( W_{oo} \) in the present calculation.

It has been made clear by the discussion in this section that we can calculate the melting point at various depths by using eqs. (6), (11) and (13).

3. Melting point

Numerical calculations were carried out in case of \( |\partial \ln W/\partial \ln V|_{oo} = 2, 2.5 \) and 3, respectively. The initial depth \( d_0 \) was taken to be 100 km, at which \( T_m \) was assumed to be 1800° K. Furthermore, it is assumed that \( \alpha \) in eq. (6) does not vary with depth. We set \( \alpha = 2.1 \times 10^{-5} \text{ deg}^{-1} \) as the value for the coefficient of thermal expansion with reference to the value of olivine. Seismic data used in the present calculation are those of Bullen's A-Model.

The values of \( T_m \) for various depths thus obtained are given in Table 1 and

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* Auxmed values, \( R = |\partial \ln W/\partial \ln V|_{oo} \)
Fig. 1. Table 1 contains the value of $W_{op}$ for various depths. This value was calculated by use of eq. (13). For comparison the melting-point curve calculated from Uffen's mean temperature gradient is also given in Fig. 1.

We now estimate the most probable value for $\frac{\partial \ln W}{\partial \ln V}^{\prime}$ at normal depth. The differentiation of eq. (13) with respect to $p$ leads to the following equation:

$$\frac{\partial \ln W}{\partial \ln V}^{\prime} = \frac{K_T}{T_m} \frac{dT_m}{dp} + 2kT_m \left(1 - 3K_T \frac{1}{T_m} \frac{dT_m}{dp}\right).$$

(14)

It is clear from eq. (14) that we can evaluate the value of $\frac{\partial \ln W}{\partial \ln V}^{\prime}$ with the help of the experimental values of $K_T$, $T_m$ and $dT_m/\partial p$ at the normal pressure.

It is widely accepted that the mantle is composed largely of olivine. Accepting this identification, we use the following values: $K_T = 1.27 \times 10^{12}$ dynes/cm$^2$, $T_m = 1890$ C and $dT_m/\partial p = 4.7$ C/1000 bars, then we obtain the value of about 1.9 for $\frac{\partial \ln W}{\partial \ln V}^{\prime}$. Thus, the melting point curve in case of $\frac{\partial \ln W}{\partial \ln V}^{\prime} = 2$ (shown in Fig. 1 by use of a solid line) seems the most probable for the olivine-rich mantle. The gradient of this curve is close to that of Uffen's curve except in the C-layer. The present method is not so much pronounced by the inhomogeneity in the C-layer as Uffen's method, because the anomalous abrupt of bulk modulus is considerably smoothened out by the integration.

As shown by a comparison of the curves in Fig. 1, the melting point given by Uffen is somewhat higher than the melting points obtained from the present method. In this paper, we assumed that $\frac{\partial \ln W}{\partial \ln V}$ does not vary with pressure. This quantity slightly decreases with the increase of pressure (Zharkov, 1958). Therefore, the differences between Uffen's curve and the present curves become larger especially in the deeper part of the mantle, if we take into account the effect of pressure on this quantity.

In this paper, we did not take into account the effects of pressure and temperature on dielectric constant as well as on coefficient of thermal expansion. A better result will be given in a separate paper in which these effects are taken into account.
References