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28. *Geophysical Evidence of the Olivine-spinel Transition Hypothesis in the Earth's Mantle.*

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Summary

Assuming olivine-spinel transition of Mg_2SiO_4 at the depth of 400 *km* in the earth, the difference in free energy between substances composing the upper and lower mantle is estimated. The difference obtained here is approximately the same as that deduced by Ringwood from experimental results.

The influence of the transition on the electrical conductivity is also studied. The steep increase of the electrical conductivity at the depth as inferred from the studies of geomagnetic variations seems to be justified by the transition hypothesis.

1. Introduction

A discontinuity of seismic wave velocities, density and electrical conductivity has been suggested through geophysical investigations at a depth of about 400 *km* in the earth's mantle. One of the possible causes of such a discontinuity might be a polymorphic inversion in olivine as has been suggested by Bernal[1] and Jeffreys[2]. On the basis of the fact that Mg_2GeO_4, which is closely related to Mg_2SiO_4, has both olivine and spinel structures, Bernal suggested that olivine-spinel transition of Mg_2SiO_4 might occur at high pressures. In that case, an increase in the density would be necessarily expected.

No direct proof of Bernal's hypothesis has been given. It is also not possible to produce spinel-type Mg_2SiO_4 artificially. However, a method of calculating the pressure required to cause Mg_2SiO_4 invert from the olivine to the spinel structure has been recently advanced by Ringwood[3]. He studied experimentally Ni_2GeO_4—Mg_2SiO_4 spinel solid

1) J. D. BERNAL, *Observatory*, **59** (1936), 268.
2) H. JEFFREYS, *The Earth* 3rd ed., (1952), Cambridge Univ. Press.
3) A. E. RINGWOOD, *Geochimica et Cosmochimica*, **13** (1958), 303.

solutions. It was found that Ni_2GeO_4, which has a spinel structure, dissolves 9 per cent of Mg_2SiO_4. A thermodynamical theory of the relationship between the amount of solid solution between Mg_2SiO_4 and Ni_2GeO_4 and the free energy of transition between olivine and spinel Mg_2SiO_4 was also developed. Combining the experimental results with the theory, Ringwood found that the molar free energy of transition between olivine and spinel Mg_2SiO_4 amounts to $70{,}000 \pm 10{,}000$ *Joule/mole* at 1500° *C*. The lattice constant of spinel-type Mg_2SiO_4 was also estimated at 7.99 Å by extraporation.

It seems to the writer that Ringwood's study has an important bearing on various geophysical problems in the earth's mantle because the energy of the transition and the lattice constant of Mg_2SiO_4 spinel deduced by Ringwood may give some clue to check the physical quantities inferred from other geophysical methods. The purpose of this paper is to estimate the internal energies and electrical conductivities of the substances composing the upper and lower mantle. These quantities will be examined from the results obtained by Ringwood.

In Section 1, the difference in Gibbs free energy between the substances composing the upper and lower mantle is estimated with the aid of appropriate thermodynamical relations together with the density and pressure distributions. The difference in internal energy between both the substances at zero pressure and temperature is also obtained. These values will be criticized by Ringwood's result. On assuming the lattice constant for the spinel Mg_2SiO_4 which was obtained by Ringwood, the difference in the activation energy for electrical conduction between olivine and spinel Mg_2SiO_4 is estimated in Section 2 and is discussed in relation to the distribution of electrical conductivity which has been obtained by the writer from analyses of geomagnetic variations.

Wada[4] has published a paper in which it is concluded by comparing the lattice energies for both the structures that the transition between olivine and spinel Mg_2SiO_4 would not be possible. Since the difference in lattice energy is much smaller than the lattice energies themselves, small errors in the estimation of lattice energies would seriously affect the conculsion, though it has been successful to discuss the stability of certain structures in this way for a number of simple crystals such as AgCl, CuCl and so forth. Accurate estimate of lattice energies of complicated crystals such as Mg_2SiO_4 will be therefore of great difficulty, so that it might not be impossible to suppose that Wada's conclusion is

4) T. WADA, *Zisin*, **11** (1958), 55. (in Japanese)

a little modified. All through this paper, the olivine-spinel transition in the earth's mantle is taken for granted. The advantage of admitting the hypothesis is discussed from the two points mentioned in the last paragraph.

2. Gibbs free energies in the upper and lower mantle

On the assumption that the olivine and spinel Mg_2SiO_4, which compose respectively the upper and lower mantle, are at equilibrium at the depth of 400 *km*, the difference in free energy will be estimated from the distributions of density and pressure and their extraporations.

Gibbs free energy at temperature (absolute) T and pressure P can be written as

$$\Psi(T, P)=\int_0^P V(T, P)dP+\Psi(T, 0)\ , \tag{1}$$

where V denotes the volume. V is given by

$$V(T, P)=V(0, P)(1+\alpha T)\ . \tag{2}$$

The volume expansion coefficient α is in general dependent on pressure amounting to some $10^{-5}/°C$. For an order-of-magnitude estimate, however, we may assume that the term αT can be ignored for the reason mentioned below. If we assume $\alpha=2.5\times10^{-5}/°C$ as has been given by Birch[5] for olivine and $T=1,800°\ K$ which has been suggested by many geophysicists for the part of mantle 400∼500 *km* deep, αT amounts to only 0.05 which may be ignored for the present estimate. Even if the possible ranges of α and T are taken into account, it does not seem likely that αT exceeds 0.1, so that the following estimate would be safely taken within a range of accuracy of 10 per cent.

For the part of the mantle above the 20° discontinuity, the density and pressure which have been obtained by Bullen[6] can be applied directly. In so far as we assume $V(T, P)=V(0, P)$ as stated above, the integral term of the righthand-side of (1) can be numerically calculated on the basis of Bullen's distribution. The upper limit of the integral is to be taken at the pressure just above the discontinuity.

For the substance composing the mantle deeper than the discontinuity, however, it is not possible to apply Bullen's distribution. In this case, in order to carry out the integration in (1), we have to

5) F. BIRCH, *Journ. Geophys. Res.*, **57** (1952), 227.
6) K. E. BULLEN, *An Introduction to the Theory of Seismology*, (1947).

know the hypothetical distributions of density and pressure which should have been observed in the upper part of the mantle if the transition did not occur. For the purpose of a crude estimate, we may extraporate the approximately linear distribution of the density as has been shown by Bullen below the depth of 800～900 *km*. In that case, the densities at depths of 0, 100, 200, 300 and 400 *km* are obtained to be 4.00, 4.08, 4.16, 4.24 and 4.32 gm/cm^3 respectively.

The density at zero pressure obtained by extraporation is almost 20 per cent larger than that of olivine Mg_2SiO_4. Ringwood[3)] has suggested that the increase in density caused by the olivine-spinel transition would be 11 ± 3 per cent. The difference might be caused by the simple extraporation. The influence of the difference will be discussed later.

It is not exactly known what the hypothetical distribution of pressure will be. For the sake of simplicity, the pressure distribution for this case is assumed to be the same as Bullen's one above the discontinuity. In any case, the upper limit of the integration is to be the same as that for the upper mantle. Since the distribution of pressure is almost linear, no large error will be introduced by the procedure.

Since the two phases are assumed to be at equilibrium at the level of the discontinuity, we have

$$\int_0^P V_1(T, P)dP + \Psi_1(T, 0) = \int_0^P V_2(T, P)dP + \Psi_2(T, 0) ,$$

which can be rewritten as

$$\Psi_2(T, 0) - \Psi_1(T, 0) = \int_0^P V_1(T, P)dP - \int_0^P V_2(T, P)dP , \qquad (3)$$

where subscripts 1 and 2 denote respectively the upper and lower mantle. Actual calculation based on the assumptions in the above gives

$$\Psi_2(T, 0) - \Psi_1(T, 0) = 0.65 \times 10^{10} \ erg/gm.$$

By taking into account the fact that the molecular weight of Mg_2SiO_4 amounts to 140.7, the difference in the Gibbs free energy becomes

$$\Psi_2(T, 0) - \Psi_1(T, 0) = 90{,}000 \ Joule/mole \qquad (4)$$

at zero pressure. The figure becomes a little smaller by taking into consideration the fact that the extraporated density is slightly higher than that supposed by experimental results.

This value should be compared to the one which has been estimated by Ringwood on the basis of experimental results. He gave $70,000 \pm 10,000$ *Joule/mole* for olivine-spinel transition of Mg_2SiO_4 at $1,500°C$. Although the estimate attempted here is very crude, it is interesting that the present and Ringwood's values are about the same. It might be therefore said that the olivine-spinel transition hypothesis is supported by thermodynamical theory based on the distributions of density and pressure deduced from seismology.

In the next place, the difference in internal energy between spinel and olivine Mg_2SiO_4 at zero pressure and temperature can be estimated from the above result. At zero pressure, Helmholtz free energy is defined by

$$F=\int_0^T C_v dT - T\int_0^T \frac{C_v}{T} dT + U_0 \, , \qquad (5)$$

where C_v and U_0 denote respectively specific heat at constant volume and internal energy at zero temperature. With subscripts 1 and 2, by which we designate olivine and spinel, the equilibrium condition leads to

$$U_{0,2}-U_{0,1}=F_2-F_1-\int_0^T (C_{v,2}-C_{v,1})dT + T\int_0^T \frac{C_{v,2}-C_{v,1}}{T} dT \, . \qquad (6)$$

As has been pointed out by Birch[5], C_v approaches 0.3 *cal/deg gm* for most of the rock-forming silicates at temperatures of the order of $1,000°C$. Although it is not possible to know exact values of C_v for both the olivine and spinel Mg_2SiO_4, it seems hardly likely that $C_{v,2}-C_{v,1}$ exceeds 0.03 *cal/deg gm* for a temperature range between several hundred degrees in centigrade and $1,500°C$. Below the Debye temperature, which is a few hundred degrees in centigrade, $C_{v,2}-C_{v,1}$ takes much smaller values. For an order-of-magnitude estimate, we may assume $C_{v,2}-C_{v,1}=0.03$ *cal/deg gm* between $0° \sim 1,800°K$. In that case, by assuming that the equilibrium is attained at $1,800°K$, the integral terms of (6) can be calculated as 6,000 *Joule/mole*.

Since F_2-F_1 has been estimated by Ringwood at 70,000 *Joule/mole* and 90,000 *Joule/mole* by the present writer, the influence of the integral terms is less than 10 per cent. For a crude estimation of the difference in internal energy at zero pressure and temperature, therefore, we may take $U_{0,2}-U_{0,1}=70,000$ *Joule/mole*.

3. Activation energies for electric conduction in the upper and lower mantle

It has been shown by Chapman[7], Price[7),8)], Lahiri[8] and Rikitake[9] that the electrical conductivity increases enormously at a depth of several hundred kilometers within the earth. According to Rikitake, the electrical conductivity increases discontinuously at the depth of 400 *km* from 10^{-15} *e.m.u.* to 10^{-12} *e.m.u.*

Applying the theory of ionic crystals to the electric conduction in the mantle, the conductivity σ is described by

$$\sigma=\sigma_0 e^{-\epsilon/kT} \tag{7}$$

where ϵ, k and T denote respectively the activation energy, Boltzmann's constant and absolute temperature. With suitable considerations concerning the effect of pressure, the distribution of temperature can be approximately obtained from the distribution of the electrical conductivity. Rikitake[10] has made this sort of estimate of temperature distribution in the earth down to a depth of 1,500 *km*. In that study, it is required that the activation energy of the substance composing the layer between the top of the mantle and a depth of 400 *km* is different from that below this level, otherwise a discontinuity must occur in the temperature distribution. The activation energy for the upper part amounts to 2.3 *eV* at zero pressure and temperature, while that below the depth of 400 *km* amounts to 1.8 *eV*.

Runcorn and Tozer[11] have also concluded that a considerable decrease in the activation energy would be necessary in some region of the mantle on the basis of their study on the electrical conductivity of olivine at high temperatures and pressures.

The purpose of this section is to estimate to what extent the activation energy will be affected by the olivine-spinel transition by applying the theory of lattice defect of ionic crystals.

Let us consider a Schottky-type lattice defect due to vacancies of Mg^{++} and O^{--}. The activation energy is then given by

$$\epsilon=\tfrac{1}{2}W+U \tag{8}$$

where W and U are respectively the energy required to make a lattice

7) S. CHAPMAN and A. T. PRICE, *Phil. Trans. Roy. Soc. London A*, **229** (1930), 427.
8) B. N. LAHIRI and A. T. PRICE, *Phil. Trans. Roy. Soc. London A*, **237** (1939), 509.
9) T. RIKITAKE, *Bull. Earthq. Res. Inst.*, **28** (1950), 45, 219, 263; **29** (1951), 61.
10) T. RIKITAKE, *Bull. Earthq. Res. Inst.*, **30** (1952), 13.
11) S. K. RUNCORN and D. C. TOZER, *Ann. Géophys.*, **11** (1955), 98.

defect and the potential energy which must be exceeded by thermal energy of ions in motion. The energy required to make a lattice defect in ionic crystals is given by

$$W=U^{+}+U^{-}-E \tag{9}$$

in which U^{+}, U^{-} and E denote respectively the energies required to take off a positive ion, to take off a negative one and to make a pair of ions.

By taking into account the polarization energy due to the electric field in ion vacancies, U^{+} and U^{-} are approximately given as

$$U^{+}=E-\frac{Z_{Mg}e^2}{q^{+}r}(1-1/\kappa)\ , \tag{10}$$

$$U^{-}=E-\frac{Z_{O}e^2}{q^{-}r}(1-1/\kappa)\ , \tag{11}$$

in which Z_{Mg}, Z_{O}, e and κ denote respectively number of electric charge of Mg^{++}, that of O^{--}, charge of electron and dielectric constant, while $q^{+}r$ and $q^{-}r$ denote the effective radii of vacancies of positive and negative ions. If r denotes the interionic distance, it is known that $q^{+}\sim 0.6$ and $q^{-}\sim 0.9$.

It is not possible to estimate U in (8) exactly. Since positive ions seem likely to contribute in the main to the conductivity of rocks as experimentally shown by Coster[12], however, we may assume $U=U^{+}$ for a crude approximation. In that case, putting $Z_{Mg}=Z_{O}=2$, the activation energies for olivine and spinel may be written as

$$\text{olivine:}\quad \epsilon_1=\tfrac{3}{2}E_1-\left(\frac{3}{q^{+}}+\frac{1}{q^{-}}\right)\frac{e^2}{2r_1}(1-1/\kappa_1)\ , \tag{12}$$

$$\text{spinel:}\quad \epsilon_2=\tfrac{3}{2}E_2-\left(\frac{3}{q^{+}}+\frac{1}{q^{-}}\right)\frac{e^2}{2r_2}(1-1/\kappa_2)\ . \tag{13}$$

We further assume $\kappa_1=\kappa_2=5$, $q^{+}=0.6$ and $q^{-}=0.9$. As to the distance between Mg and O atoms, it has been known that $r_1=2.078$ Å for olivine Mg_2SiO_4, while, for spinel Mg_2SiO_4 which is cubic, the lattice constant obtained by Ringwood, 7.99 Å say, leads to $r_2=1.998$ Å. Using these values, the difference in the activation energy becomes

$$\epsilon_2-\epsilon_1=1.5(E_2-E_1)-0.7 \tag{14}$$

in units of eV.

In the next place, we have to calculate E_2-E_1. According to

12) H. P. Coster, *Mon. Not. R. Astron. Soc. Geophys. Suppl.*, **5** (1949), 193.

Wada's calculation[4] of lattice energy of spinel Mg_2SiO_4, the total lattice energy amounts to 168 *eV* at zero pressure and zero temperature. Meanwhile, it is also shown that the energy required to make a pair of Mg^{++} and O^{--} ions amounts approximately to 35.8 *eV*. We therefore see that the energy required to make an ion pair amounts to 21 per cent of the total lattice energy. For an order-of-magnitude estimate, the same proportion may be applied to olivine Mg_2SiO_4. The difference in internal energy between Mg_2SiO_4 of both the types has been thoroughly discussed in the last section. The difference in energy required to make an ion pair may be obtained by taking 21 per cent of 70,000 *Joule/mole*. This consideration leads to

$$E_2 - E_1 = 0.15 \ eV \, , \tag{15}$$

whence, from (14), we see

$$\epsilon_2 - \epsilon_1 = -0.5 \ eV \, . \tag{16}$$

Although the above estimate is based on various approximations, it is of interest that the activation energy would decrease by the transition from olivine to spinel. The amount of decrease estimated is in good agreement with the value supposed by the present writer previously. It may be said, then, that the steep increase in electrical conductivity below the depth of 400 *km* as inferred from studies of geomagnetic variations is in harmony with the hypothetical olivine-spinel transition in the mantle.

4. Discussion and concluding remarks

It has been shown in Section 2 that, so long as we admit the olivine-spinel transition of Mg_2SiO_4 in the earth's mantle, the difference in free energy between the two phases can be estimated from physical quantities such as density and pressure, though some extraporations are required to make actual calculation. Since the extraporations are not very reliable, the difference in free energy obtained here is not accurate. However, it is of interest that the energy difference thus deduced is about the same as that obtained by Ringwood on an experimental basis.

In the real earth, the chemical composition is likely to change gradually with depth. Especially, it is widely believed that such a change is highly likely at the depths between 400 and 900 *km*. The effect of Fe_2SiO_4 would be specially important in that part of the mantle, though no account has been taken of such an effect in this paper.

This point should be improved in the future.

It is highly important to see whether or not the olivine-spinel transition hypothesis accounts for the increase in the electrical conductivity at the depth of 400 *km*. The calculation of the conductivity, based on the theory of ionic crystals, has proved that the hypothesis approximately harmonizes with the electrical state. Although the calculation seems not very accurate, it is of interest and importance that the mechanical and electrical properties of the earth's mantle can be interpreted from a unified view-point provided the olivine-spinel transition of Mg_2SiO_4 is assumed at the depth of 400 *km*.

In conclusion the writer thanks Dr. S. Akimoto for his kind help in the estimation of interionic distance.

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28. 20° 不連続と電気的性質

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最近 Ringwood は，Ni_2GeO_4—Mg_2SiO_4 固溶体を調べ，地球中間層内に於て Mg_2SiO_4 がオリビンスピネル転移を起すことが可能であることを推論した．彼の研究によれば，転移に伴なう自由エネルギーの変化は 1,500°*C* に於て 70,000 ± 10,000 *Joule/mole*，密度変化は約 11%，スピネル Mg_2SiO_4 の格子常数は 7.99 Å となる．

本論文に於ては，深さ 400 *km* に於ける不連続面が，多方転移によつてできたものとして，その上部および下部を構成する物質の自由エネルギーの差を地震波速度分布による知識をもとにして，近似的に求め，90,000 *Joule/mole* という値を得た．計算の精度を考慮するならば，この値は Ringwood の値とよく一致しているといえよう．

つぎに，オリビンスピネル転移が電気的性質にどのような寄与をするかを，イオン結晶理論により，近似的に調べた。その結果電気伝導度に対する活性化エネルギーは 0.5 *eV* の減少をきたし，地磁気変化観測結果より推定されるように，電気伝導度がスピネル構造の発生に伴なつて，いちじるしく増大することがわかつた．したがつてオリビンスピネル転移仮説によつて，地下 400 *km* に於ける力学的および電気的不連続を統一的に解釈することができることになる．
