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Experiments on the Displacement of the Ultraviolet Absorption Edge of Olivine at High Pressures

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The effect of pressure on the fundamental excitation energy of valence electrons in the ferromagnesium orthosilicate, the mineral olivine, is of interest in the theory of the electrical conductivity of the earth's mantle. The experimental determination of this by observation of the displacement of the ultraviolet absorption threshold of olivine up to pressures of about 30 000 bars is described.

1. INTRODUCTION

EXPERIMENTAL techniques at high pressure, such as those developed largely by Bridgman,[1] have been used mainly to determine the mechanical properties of solids such as their breaking strength and changes of density. These methods, when applied to minerals, have been of considerable geophysical interest in the interpretation of the elastic properties and densities of the earth's mantle inferred from the data of seismology. The electrical, and related optical, properties of minerals at high pressures and temperatures are now of considerable interest in view of the renewed interest in the origin of the main geomagnetic field. Bridgman[2] had recently adapted his shearing apparatus for the measurement of the electrical conductivity of the elements up to 100 000 bars. In this technique the specimen is in the form of a very thin disk, which is compressed between Carbaloy pistons. This principle of obtaining high pressures is well adapted for optical absorption measurements, where the specimen must also be in the form of a thin plate.

Lahiri and Price,[3] from a study of the transient variations of the geomagnetic field, have shown that the electrical conductivity of the earth's mantle must rise rapidly at depths greater than about 700 km. This has been interpreted by Coster,[4] Runcorn,[5] and Hughes[6] by supposing that the earth's mantle acts as a semiconductor; the assumption being made that the temperature of the earth increases with depth. Coster[4] suggested that ionic conduction is likely to be the chief component of the electrical conductivity at depth within the mantle. Runcorn[5] suggested that intrinsic semiconduction would be likely to be the more important effect in view of the tendency of pressure to inhibit the motion of ions. If the effect of pressure is ignored, it is possible by making different assumptions about the temperature distributions in the mantle, about which little is directly known, for either process to be made to fit the conductivity data. Runcorn and Tozer[7] have estimated the effect of pressure on ionic conduction in olivine and conclude that in the mantle it is effectively suppressed. Hughes[8] had measured this effect by electrical conductivity

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measurements on olivine at temperatures of about 1000°C up to a pressure of 10 000 bars and finds a pressure coefficient about the same as the estimated one.

Runcorn[5] shows that if the most plausible temperature distribution in the deep mantle is assumed, the conductivity there is well explained by intrinsic semiconduction. However, little is known of the effect of pressure on the excitation energy of the intrinsic semiconduction process, and this paper describes the experimental determination of this for olivine up to 30 000 bars.

2. INTRINSIC SEMICONDUCTION

The conductivity σ of an intrinsic semiconductor is given by

$$\sigma=\sigma_0 \exp(-E/2kT), \quad (1)$$

where E is the excitation energy, i.e., the width of the forbidden energy zone between the highest level of the valence band just filled at 0°A, and the lowest level of the conduction band, unoccupied at absolute zero, k is Boltzman's constant, and T the absolute temperature. σ_0, the conductivity at infinite temperature, is proportional to the mean mobility of electrons (v) and the square root of the number (n) of valence electrons per unit volume. The effect of pressure on v is unknown but Bridgman in his work on the conductivity of metals finds it to be small. It seems likely that the change of E with pressure will be of most importance in the extrapolation of laboratory measurements to the conditions existing in the earth's mantle. The direct determination of the change of E with pressure requires measurements of electrical conductivity at high pressures and temperatures. An alternative method of determining E is to measure the threshold frequency (ν_0) of ultraviolet absorption in the olivine crystal. Very large absorption of the light occurs for frequencies greater than E/h, where h is Planck's constant; the valence electrons having then sufficient energy to enter the conduction band. Hughes[6] compares at ordinary pressures the value of E obtained by these two methods for olivine. Table I gives his results, which are in good agreement.

Thus an experimental determination of the change of the E for intrinsic semiconduction may be made by observing the shift in the ultraviolet absorption edge with pressure. This paper describes such experiments for olivine.

TABLE I.

	Excitation energy from conductivity measurements	Ultraviolet absorption edge	Excitation energy from absorption measurement
Peridot crystal	‖ to b-axis 3.36±0.16 ev	3700–3800 A	3.3 ev

3. EXPERIMENTAL METHOD

Bridgman's method in his electrical conductivity experiments was to apply the pressure to a disk of material by a simple hydraulic press. By using Carbaloy pistons to transmit the compressive stress, it was possible to achieve pressures of about 100 000 bars. Bridgman showed that this pressure would, if the specimen were very thin, approximate to a hydrostatic one. By replacing the Carbaloy pistons by transparent ones this method can be used for optical absorption experiments: the apparatus as designed for this purpose is shown in Fig. 1.

The piston was designed as a cone, which was driven by the pressure into a receiving conical hole in a supporting ring of steel D, such that the containing pressure on the curved surface of the cone was equal to the pressure on the flat making contact with the other piston. In this way an approximate equality of stress through the piston was obtained. The pistons were held in a precision die set C and the pressure was applied by a 30-ton hydraulic jack. The flat on the quartz cone was $\frac{3}{16}$ inch in diameter: thus the application to the piston of a force of two tons results in a pressure of 10 000 bars in the specimen. The force on the pistons was measured by a load cell F. The limiting pressure which can be obtained is set by the breaking compressive stress of the material used in the pistons. Initially quartz was used. Amorphous quartz was found to be more satisfactory than single crystals, for although the breaking compressive stress of the latter is given as 30 000 bars, very few specimens reach this value. It

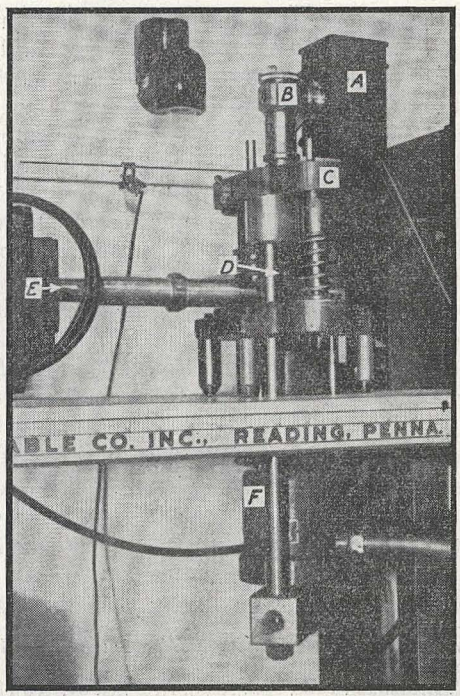

FIG. 1. High pressure apparatus.

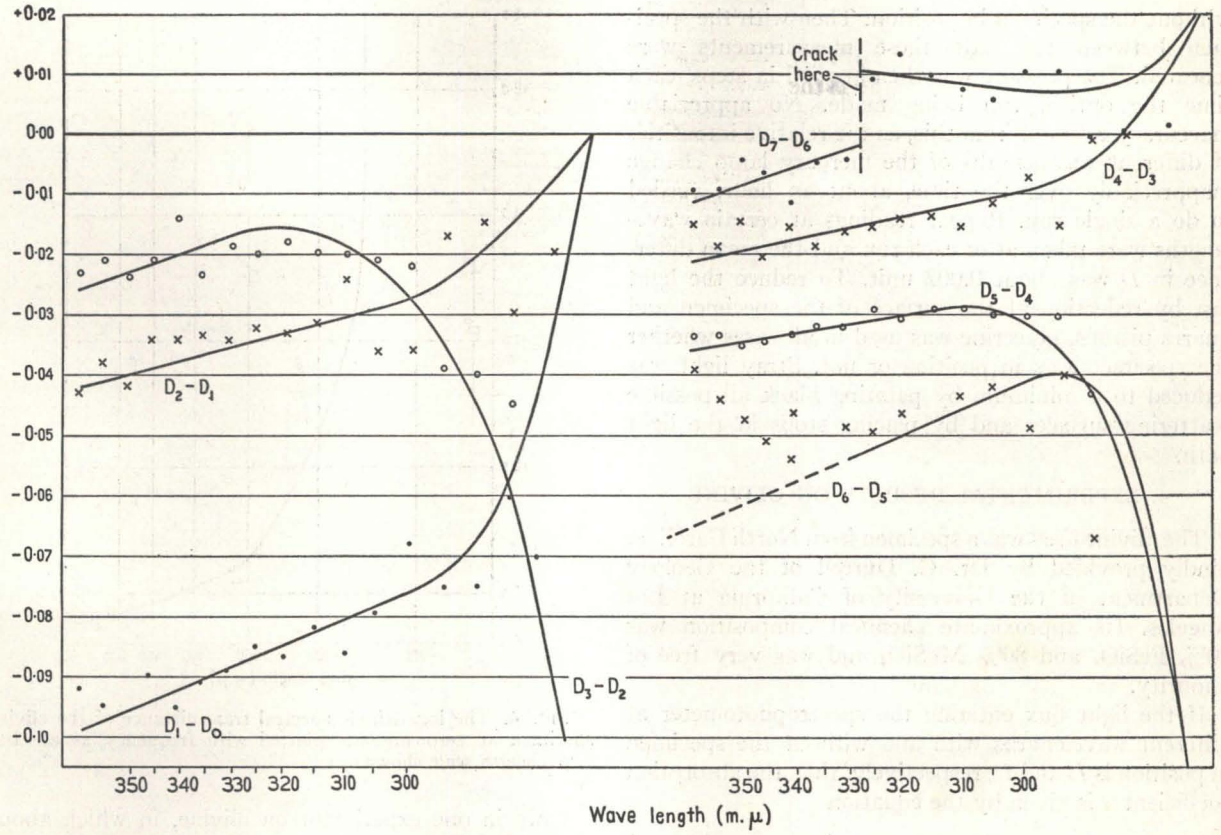

FIG. 2. The differences in the logarithmic spectral transmittances at successive pressures plotted against frequency (wavelength scale shown).

was found that pistons of amorphous quartz could be used up to its ultimate compressive stress, between 10 000 and 15 000 bars. It was, however, found that much higher pressures were obtained with sapphire pistons, and these were used in the final experiments.

The specimen of olivine is a slice of about 100μ thick; it was made in the usual way by grinding down a specimen of olivine cemented by Canada balsam to a glass slide, the cement being later dissolved away by xylol. Because of the lateral friction of the specimen in the quartz jaws under compression some approximation to hydrostatic pressure will obtain unless the elastic properties of quartz and olivine are the same.

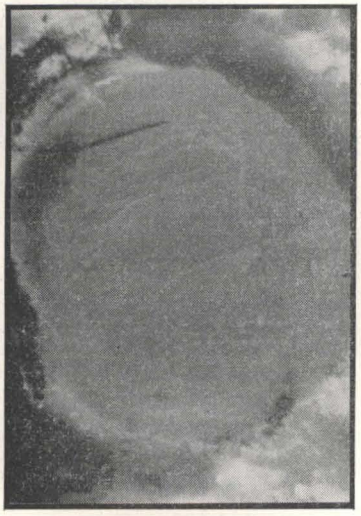

FIG. 3. Olivine slide after being subjected to 30 000 bars pressure.

The spectral transmittance, i.e., the ratio of transmitted to incident radiant flux, of the olivine at different wavelengths and pressures, was measured with a Beckman quartz spectrophotometer, with minor rearrangement of the light path entering the instrument (See Fig. 1). A quartz-mercury lamp A, of the type usually supplied with the spectrophotometer, was mounted above the high pressure apparatus and light from it was directed through the tube B and focused on the olivine specimen. The light transmitted by the specimen was brought to focus on the input slit E of the spectrophotometer by a long focus lens. The normal procedure followed in obtaining the absorption spectrum of a specimen is to measure the transmittance at each wavelength setting by alternatively extracting and replacing the specimen in the incident beam. In these experiments it was impracticable to remove the specimen between measurements at successive pressures. Thus the light intensity entering the spectrometer at the different wavelength settings was first measured

without the specimen in position. Then with the specimen between the flats these measurements were repeated. The pressure was then applied in steps, each time the optical run being made. No appreciable inaccuracy resulted from this, as the relative intensities of different wavelengths of the mercury lamp change inappreciably over the time, about an hour, needed to do a single run. Repeat readings at certain wavelengths were taken after each run and the mean difference in D was about 0.002 unit. To reduce the light lost by reflection at the surface of the specimen and quartz pistons, glycerine was used in all cases whether the specimen was in position or not. Stray light was reduced to a minimum by painting black all possible scattering surfaces and by placing stops in the light path.

4. EXPERIMENTAL RESULTS ON OLIVINE

The olivine used was a specimen from North Carolina, kindly provided by Dr. C. Durrell of the Geology Department of the University of California at Los Angeles. Its approximate chemical composition was 20% $FeSiO_4$ and 80% $MgSiO_4$ and was very free of impurity.

If the light flux entering the spectrophotometer at different wavelengths with and without the specimen in position is I_0 and I_i, respectively, then the absorption coefficient α is given by the equation

$$I_0 = I_i k^2 \exp -(\mu+\alpha)t, \tag{2}$$

when t is the thickness of the olivine, μ the scattering coefficient, and k is the transmission coefficient at the glycerine-olivine interface. It is assumed that μ depends on the presence of flaws and grain boundaries in the olivine of a size which will scatter light fairly equally over the range of wavelengths with which we are concerned. Thus Eq. (2) may be written

$$\log_{10} I_0 - \log_{10} I_i = 0.43\alpha t + \text{constant}. \tag{2a}$$

The logarithms may be read from the spectrophotometer scale directly. The difference on the left-hand side of Eq. (2a) will be called D_0 for experiments under zero pressures and $D_n (n=1,2\cdots)$ for experiments at successive pressures. Unfortunately, the constant in Eq. (2a) is not in general the same for different pressures —the contact between the different surfaces changes with pressure and affects the light lost by reflection, and inevitably more cracks appear in the olivine under high pressure. If

$$D_0 = f(\nu) \tag{3}$$

and if the frequency shift of the spectrum on applying unit pressure is h, the difference obtained in going from pressure p_{n-1} to pressure p_n is

$$D_n - D_{n-1} = h(p_n - p_{n-1}) f^-(\nu) + c, \tag{4}$$

where c represents the difference in light reflected and scattered on applying the increment of pressure.

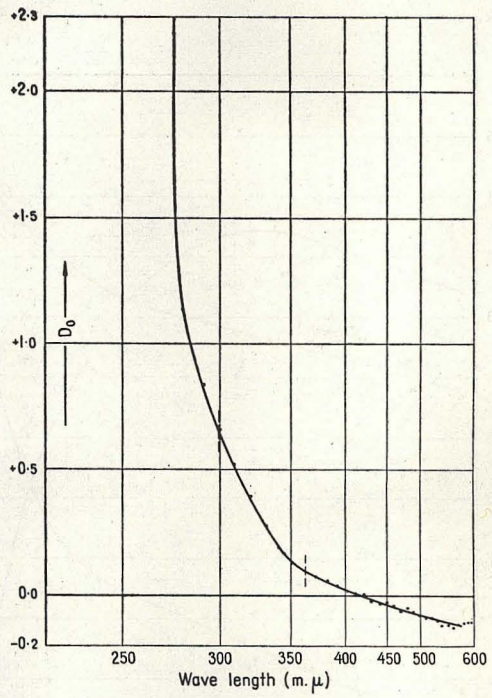

FIG. 4. The logarithmic spectral transmittance of the olivine specimen at zero pressure plotted with frequency as abscissa (wavelength scale shown).

Only in one experiment on olivine, in which about 30 000 bars pressure was reached, were satisfactory results obtained. These will now be discussed. Figure 2 shows a number of differences in logarithmic transmittances for successive steps in pressure. It is noticeable that at short wavelengths and high absorptions the divergence between D_{n-1} and D_n becomes large and irregular. At high absorptions the presence of cracks in a thin specimen are bound to cause large errors in the measured transmittance, which will change on applying pressure by producing new cracks or by closing up original ones. In the run at highest pressure a crack in the piston occurred in the course of the optical measurements altering the transmittance by a considerable amount, as shown in Fig. 2. After the specimen had been subjected to the highest pressure, the pistons were drawn apart and the specimen examined. Figure 3 is a photograph showing it lying

TABLE II.

Curve	Pressure increment (bars)	Slope of curve (sec)	Slope per bar
D_1-D_0	5.0×10^3	7.7×10^{-17}	15.4×10^{-21}
D_2-D_1	5.55×10^3	4.9×10^{-17}	8.83×10^{-21}
D_3-D_2	4.95×10^3	0.51 or 6.5×10^{-17}	13.2×10^{-21}
D_4-D_3	4.5×10^3	4.3×10^{-17}	9.56×10^{-21}
D_5-D_4	3.0×10^3	2.9×10^{-17}	9.67×10^{-21}
D_6-D_5	2.5×10^3	6.0×10^{-17}	24.0×10^{-21}
D_7-D_6	3.0×10^3	4.7×10^{-17}	15.7×10^{-21}
		Mean	13.8×10^{-21}

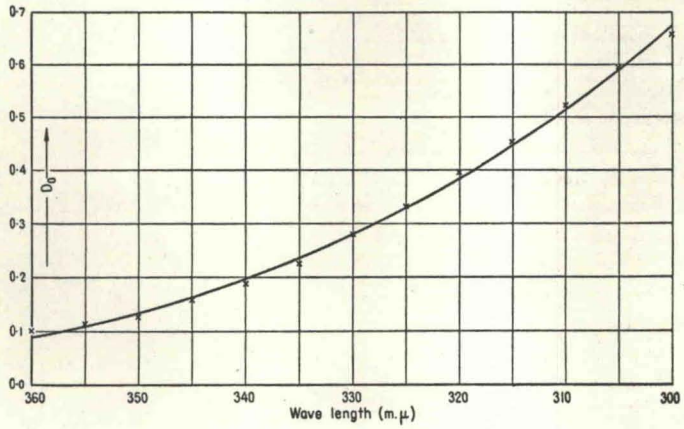

FIG. 5. Part of the curve of Fig. 4 fitted by a parabolic curve.

on the flat of one piston. It will be seen that though cracks have developed, the specimen had not been reduced to a powder. Apart from these two effects the differences can be reasonably well fitted by straight lines by the method of least squares as shown in Fig. 2. The gradients of the straight-line portion and the corresponding increments of pressure are shown in Table II.

It is easily shown that if the value of E is related to the threshold frequency ν_0, of wavelength λ_0, then

$$dE/E = -d\lambda_0/\lambda_0 = d\nu_0/\nu_0. \quad (5)$$

Figure 4 shows the transmittance D of the olivine plotted against frequency ν and Fig. 5 shows how this is well fitted by the curve

$$D_0 = 6.16 - 4890/\lambda + 9.9\times10^5/\lambda^2, \quad (6)$$

where λ is measured in mμ. Thus from Eq. (4) the value of h is

$$6.2\times10^8 \text{ sec}^{-1}.$$

Therefore $dE/E = 6.2\times10^{-7}$ bar^{-1}.

Extrapolating this value to a depth of 700 km in the mantle where the pressure is 300 000 bars,[9] we find a change of $E \gtrsim 0.3$ ev which should not be sufficient to alter the assumption made by Runcorn[5] and Hughes[6] that the electrical conductivity of the mantle is in the main determined by the rise of temperature.

5. THEORETICAL DISCUSSION

The change of E with pressure, i.e., with the lattice parameter on a simple lattice model, has been considered recently by Billig.[10] He shows that the width of the forbidden energy zone with pressure may increase or decrease, according to whether the main result of a decrease in lattice parameter is the decrease in the width of the potential troughs or the potential barriers. Apparently in this case the latter is of more importance.

A quantitative estimate of the change in E with pressure for a complex structure like olivine is difficult. However, an order-of-magnitude estimate is possible on the assumption that the fractional change of the lattice dimensions (da/a) through a rise of pressure will be of the same order as the consequent fractional change of the excitation energy (dE/E). Thus

$$dE/E = k da/a,$$

where k is a constant of the order of unity depending on the substance.

For a pressure increment of 1 bar the lattice parameter of olivine decreases by a factor 2.6×10^{-7} (the mean compressibility of dunite between 2000 and 12 000 bars is given by Birch[11] as 7.9×10^{-7} reciprocal bars). As the measured value of dE/E for olivine is 6.2×10^{-7} reciprocal bars, $k = 2.4$. Höhler[12] in similar experiments on cadmium sulphide crystals but at comparatively low pressures (100 and 330 bars) found a displacement towards the blue end of the spectrum of 0.002 mμ/bar. As the compressibility of this substance is about 17×10^{-7} reciprocal bars, k works out to be 8.8.

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The experimental apparatus for attaining high pressures was designed and constructed in the workshops of the Institute by Mr. Fred Banning.

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