ABSORPTION SPECTRA OF SOME SILICATES IN THE VISIBLE AND NEAR INFRARED*

SYDNEY P. CLARK, JR., *Dunbar Laboratory, Harvard University, Cambridge, Massachusetts.* †

ABSTRACT

Absorption coefficients of olivine, diopside, and three varieties of garnet have been measured in the spectral range between 0.3 and 4 microns. Olivine and diopside have absorption peaks at a wave number of about 10,000 cm^{-1}. Almandine has a strong peak at about 8000 cm.$^{-1}$ and numerous weaker peaks. A garnet between andradite and grossularite in composition showed no strong peaks. The ultraviolet absorption edge of the latter garnet lies at about 16,400 cm.$^{-1}$, and those of the other crystals lie between 27,000 and 29,000 cm.$^{-1}$. The positions of the absorption peaks can be explained by electronic transitions between a relatively small number of excitation levels.

At wave numbers between 2000 and 7000 cm.$^{-1}$ the absorption coefficient of olivine is less than 0.5 cm.$^{-1}$. and that of diopside is about 1 cm.$^{-1}$. These results support the hypothesis that radiative transfer is important in the earth's mantle.

INTRODUCTION

A recent development in geophysics is the recognition of the fact that radiative transfer may play an important role in the heat balance of the earth (Preston, 1956; Clark, 1956). In non-opaque media, the energy transferred by radiation is in addition to that carried by lattice vibrations, and the effect appears as an enhanced thermal conductivity. The term which represents the effect of radiative transfer in the expression for thermal conductivity contains one material constant, the optical absorption coefficient. The work described here was undertaken as a step towards estimating absorption coefficients in the earth.

The absorption coefficients of minerals give important information about some of their fundamental properties. The pioneer work of Coster (1948) and the careful study by Hughes (unpublished) have demonstrated that the electrical properties of silicates are similar to those of oxide semiconductors. Absorption maxima should occur at frequencies corresponding roughly to the excitation energies of the various conduction processes. Measurements of absorption spectra aid in the identification of the types of conduction mechanisms, and contribute basic data towards the understanding of the electronic structure of silicates.

MATERIALS STUDIED

Most of the results were obtained from single crystals of peridot (the gemstone variety of olivine), diopside and three varieties of garnet.

Physical properties of these materials are given in Table 1, and chemical analyses of two of the garnets are given in Table 2. Measurements were also made on a single crystal of orthoclase, var. adularia, from Madagascar, and on a polycrystalline specimen of jadeite from Burma.

Flawless plates were cut from the crystals of olivine, diopside, almandine, and adularia. The grossularite was unaltered, but the specimen used in the measurements was marred by small conchoidal fractures irregularly distributed through it. The pyrope was also fresh, but it contained scattered inclusions of an opaque mineral, possibly ilmenite, and elongate prisms of a colorless mineral with refractive index less than that of the pyrope. Runs were made on two samples of pyrope; they agreed closely over most of the range of frequencies. The jadeite was milky and transmitted poorly as a result.

Compositions of the unanalyzed specimens can be estimated from the data in Table 1. The olivine contains 7–8 mol per cent fayalite according to its refractive indices, 8 per cent fayalite according to specific gravity,

TABLE 1. PHYSICAL PROPERTIES OF THE MINERALS STUDIED

Mineral	Specific gravity	Optical properties	X-ray properties	Thickness of specimen (mm.)
Olivine, Burma	3.31 ± 0.01	$\alpha = 1.648 \pm 0.003$ $\beta = 1.665$ $\gamma = 1.686$ $(+)2V = 85°$	$d_{130} = 2.772 \pm 0.002$ Å	1.55 & 12.9
Diopside, Rotenkopf, Tyrol. Harvard Museum No. 88405	3.29 ± 0.01	$\alpha = 1.672 \pm 0.003$ $\beta = 1.680$ $\gamma = 1.702$ $(+)2V = 60°$ $Z \wedge C = 40°$		1.56
Pyrope, Benenitra, Madagascar. Harvard Museum No. 85426	3.72 ± 0.01	$n = 1.776 \pm 0.003$	$a_0 = 11.49 \pm 0.01$ Å	1.27_5 & 1.29_5
Almandine, India	4.16 ± 0.01	$n = 1.807 \pm 0.003$	$a_0 = 11.52 \pm 0.01$ Å	1.56_5
Grossularite, South Africa	3.71 ± 0.01	$n = 1.801 \pm 0.003$	$a_0 = 11.94 \pm 0.01$ Å	1.16

TABLE 2. CHEMICAL ANALYSES OF ALMANDINE AND GROSSULARITE
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	Almandine*		Grossularite	
	Weight per cent	Mol. Prop.	Weight per cent	Mol. Prop.
SiO_2	37.69	628	36.92	615
TiO_2	0.07	1	0.12	2
Al_2O_3	20.62	202	12.47	122
Fe_2O_3	4.30	27	14.14	88
FeO	30.80	428	1.84	26
MnO	1.97	28	0.95	13
MgO	4.40	109	—	—
CaO	—	—	33.63	601
Na_2O	—	—	—	—
K_2O	—	—	—	—
H_2O--	0.36	—	0.57	—
H_2O+	—	—	—	—
	100.21		100.64	

* Only about 300 milligrams of material were available for this analysis.

and 9 per cent fayalite according to the interplanar spacing, d_{130} (Winchell, 1933; Yoder, 1954). The diopside contains 12 per cent hedenbergite by weight according to its optical properties and about 10 per cent hedenbergite according to specific gravity. The refractive index and unit cell size of the pyrope lead to an approximate composition pyrope$_{0.44}$ almandine$_{0.55}$andradite$_{0.01}$ (Sriramidas, 1957).

EXPERIMENTAL METHOD AND RESULTS

The reduction in intensity of a beam of light in passing through a crystal is caused by three processes: absorption within the sample, reflection at its surfaces, and scattering within the sample. In the absence of scattering, the relation between absorption, reflection, and transmission is (McMahon, 1950)

$$I = I_0 \frac{(1 - R)^2 e^{-\alpha x}}{1 - R^2 e^{-2\alpha x}} \tag{1}$$

where I_0 is the intensity of the incident beam, I the intensity of the transmitted beam, R the reflection coefficient, α the absorption coefficient and x the thickness of the specimen. If R is less than 0.1, the second term in the denominator can be neglected. The reflection coefficient at normal incidence is related to the refractive index, n, by the well-known Fresnel formula

$$R = \frac{(n-1)^2}{(n+1)^2} \tag{2}$$

Expressions (1) and (2) depend on the assumptions that the sample is a clear, flat plate with specularly reflecting surfaces which are parallel to each other and normal to the beam of light. Great care in sample preparation is necessary if accurate values of the absorption coefficient are to be obtained. If the surfaces of the sample are not flat and parallel, the specimen acts as a lens, which defocuses the spectrometer. If the surfaces of the sample are not highly polished, diffuse reflection, which may be far stronger than that predicted by (2), takes place. Scattering by flaws and inclusions in the sample increases the apparent absorption coefficient. The importance of careful sample preparation cannot be over-emphasized; the transmission of the grossularite sample was increased by a factor of three by repolishing after a preliminary series of measurements.

The samples used in the present work were carefully surfaced and polished, and the use of (1) and (2) in the reduction of the data is justified. Little can be done about scattering by flaws and inclusions; these were present in the grossularite and pyrope, and the absorption coefficients of these crystals are overestimated as a consequence. The error is probably not large, however, since the total cross-sectional area of flaws was only a small percentage of the areas of the crystals.

Measurements were made on a Perkin-Elmer model 12-C single-beam spectrometer, fitted with quartz optics. The transmissions of the specimens were determined by the "sample in, sample out" method, and repeat runs were made to check doubtful features of the spectra. The transmissions were reproducible to within about 2 per cent. All measurements were made at ambient temperature and covered the spectral range 0.3–4 microns.

The transmissions of the peridot, diopside, and garnets are shown in Figs. 1 and 2 as functions of wave number. (The wave number, $\tilde{\nu}$, equals the reciprocal of the wave length in centimeters.) The propagation direction of the light was parallel to the b-axis of the olivine and normal to one of the cleavage planes of the diopside. The adularia showed high transmission (60–80 per cent), which decreased smoothly towards higher frequency. No peaks were found, and the results are not shown graphically. The poor transmission of the sample of jadeite precluded quantitative measurements; rough results were obtained near the ultraviolet absorption edge, which was found to lie near 29,000 cm.$^{-1}$.

The refractive indices given in Table 1 were used to determine reflection coefficients. Mean values were used for the anisotropic substances, and the dependence of the refractive index on frequency was neglected.
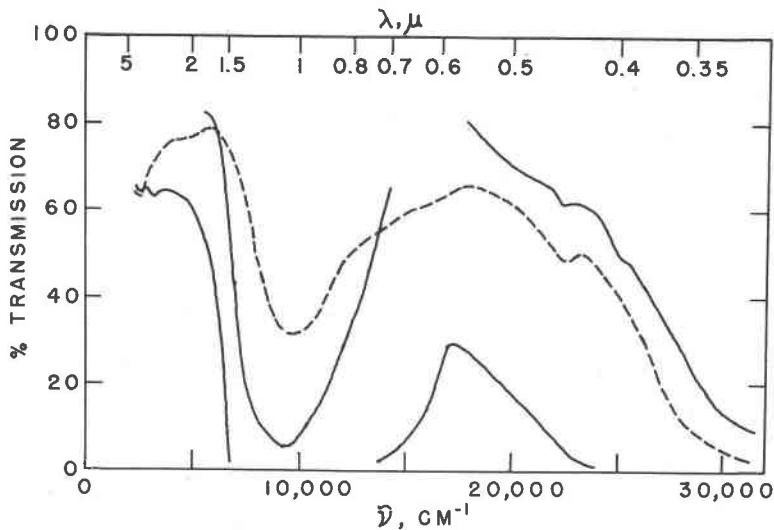
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Fig. 1. Transmission curves for olivine (solid curves) and diopside (dashed curve). Results are shown for two crystals of olivine of different thicknesses.
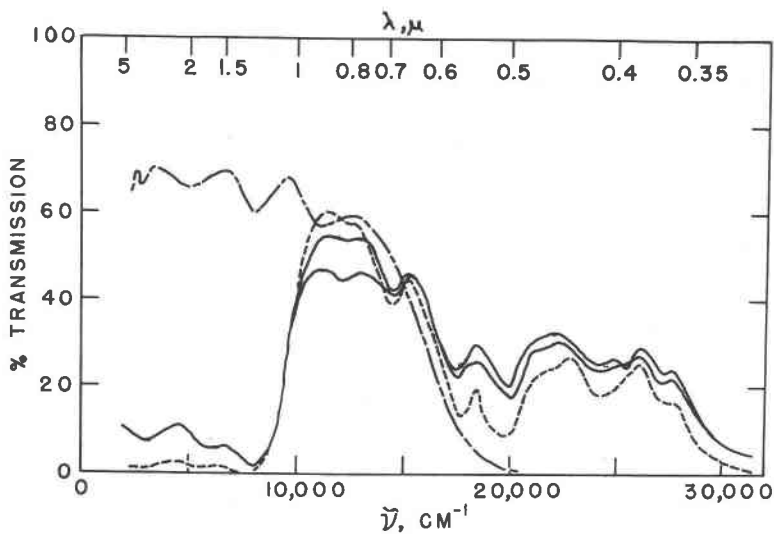

Fig. 2. Transmission curves for pyrope (solid curve), almandine (dashed curve), and grossularite (dot-dash curve).

Both of these approximations are justified, since the reflection coefficient is not a sensitive function of index for n less than 2.0. To sufficient accuracy, $R = 6$ per cent for olivine and diopside, and $R = 8$ per cent for the garnets.

A check on the above values of R and on the overall precision of the measurements is afforded by the results for the plates of olivine of different thicknesses. The absorption coefficients agreed to within 0.4 cm.$^{-1}$; at most frequencies the discrepancy between the two sets of data was half this. The absorption coefficients of all substances are estimated to be uncertain by no more than a few tenths cm.$^{-1}$. Results are given in Fig. 3; the absorption coefficient of adularia increased roughly linearly from about 2 cm.$^{-1}$ at a wave number of 2500 cm.$^{-1}$ to about 4 cm.$^{-1}$ at 30,000 cm.$^{-1}$.

THE RADIATIVE CONDUCTIVITY

The radiative conductivity, which relates the flux of radiant energy to the thermal gradient, was computed from the absorption coefficients shown in Fig. 3 (Table 3). Calculations were made by the methods developed previously (Clark, in press), under the assumption that the absorption is independent of temperature. For comparison with the values in Table 3, the ordinary conductivity of most silicates at room temperature is less than 0.01 cal./cm. sec.° C. With the exception of almandine and pyrope, the radiative conductivity exceeds this value at 1000° K. and increases markedly with temperature. The effect is particularly large in the cases of olivine and diopside.

It is unlikely, however, that such large values of the radiative conductivity exist in the earth. Crystals in the mantle are likely to be imperfect, and the attendant scattering may be more important than absorption in a material such as olivine. Furthermore, the absorption will increase with temperature. Both of these effects will reduce the radiative conduc-

TABLE 3. THE RADIATIVE CONDUCTIVITY

Values are given in cal./cm. sec.° C.

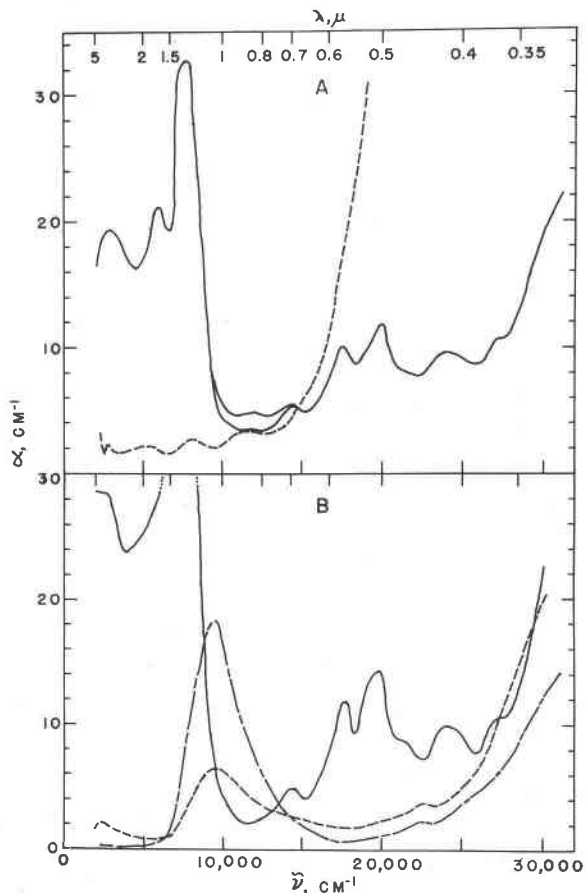| Mineral	Temperature (° K.)			
	1000	1500	2000	2500
Olivine	0.071	0.206	0.346	0.483
Diopside	0.016	0.057	0.106	0.173
Pyrope	0.001	0.005	0.018	0.044
Almandine	0.001	0.004	0.010	0.051
Grossularite	0.011	0.046	0.109	0.097

Fɪɢ. 3. (A) Absorption coefficients (α) of pyrope (solid curve) and grossularite (dashed curve). Results for the two crystals of pyrope differed appreciably between 10,000 and 15,000 cm.$^{-1}$, and are shown separately in this range of wave numbers. (B) Absorption coefficients of almandine (solid curve), diopside (dashed curve), and olivine (dot-dash curve).

tivity, since it is inversely proportional to the sum of the absorption and scattering coefficients.

Nevertheless, the measurements strongly support the hypothesis that radiative transfer is important in the earth. Any attempt to estimate the radiative conductivity in the mantle would clearly be premature, but it seems reasonably certain that an appreciable effect exists.

Discussion

The positions of absorption peaks in the visible and ultraviolet are a measure of the difference in energy between the highest filled electronic

band in the crystal (the valence band) and the several excited states which may exist. The following tentative interpretation in terms of electronic energy levels is analogous to the familiar method of interpreting atomic spectra. The energies of the absorption maxima cannot strictly be combined in the simple additive manner characteristic of atomic spectra, however. The energy levels are broadened into bands by atomic interactions, and the optical selection rules in crystals require that the propagation vector of the electron be unchanged by a direct optical transition (Peierls, 1955, p. 188). Both the energy within a band and the transition

TABLE 4. POSITIONS AND ENERGIES OF ABSORPTION PEAKS

Principal peaks are marked with an asterisk; those marked (w) are very weak

Olivine		Diopside		Almandine		Pyrope		Grossularite	
Position $cm.^{-1}$	Energy eV	Position $cm.^{-1}$	Energy eV	Position $cm.^{-1}$	Energy eV	Position $cm.^{-1}$	Energy eV	Position $cm.^{-1}$	Energy eV
2500	0.31	2500	0.31	2900	0.36	2900	0.36	2800	0.35
3200	0.40			6000	0.74	6000	0.74	5000	0.62
9600*	1.19	9600*	1.19	7900*	0.98	7900*	0.98	8000	0.99
				12,100	1.50	12,100	1.50	11,300	1.40
				14,400	1.79	14,300	1.77		
				17,600	2.18	17,600	2.18		
				20,000	2.48	20,000	2.48		
				21,500(w)	2.67				
22,600	2.80	22,600	2.80	23,900	2.96	23,900	2.96		
25,200(w)	3.12			27,200	3.37	27,200	3.37		
Ultraviolet Absorption Edges									
29,100	3.6	27,200	3.3	27,600	3.4	27,600	3.4	16,400	2.0

Ultraviolet absorption edge of jadeite at roughly 29,000 $cm.^{-1}$ or 3.6 eV.

probability depend on the propagation vector, and therefore the energy of that electron in a given band which is most likely to be excited depends in part on its final state.

The most intense absorption is produced by electronic transitions from the valence band to the conduction band of the crystal. These transitions give rise to absorption in the visible and ultraviolet in silicates; they lead to intrinsic semiconduction when thermally excited. Several weak peaks were found at energies less than those of the ultraviolet absorption edges; these correspond in energy to exciton absorption *i.e.* to transitions involving levels between the valence and conduction bands. They are too weak and at too high frequencies to be interpreted as due to lattice vibrations.

Positions and energies of the various peaks and of the ultraviolet absorption edges are given in Table 4. The positions of the peaks could be

located within about 0.03 eV. The ultraviolet absorption edge is more difficult to locate because it is not a sharp feature. Its position was taken to be that at which the absorption coefficient reached 10 cm.$^{-1}$ This definition is arbitrary, and little importance can be attached to the exact numerical values of these particular data.

The spectra of olivine and diopside show striking similarities. The peak at about 10,000 cm.$^{-1}$ is interpreted as due to the Fe^{++} ion. It is more intense in olivine because of the higher concentration of iron atoms. This interpretation is supported by the presence of a peak at the same position in iron-bearing glasses (Weyl, 1951). Its energy corresponds to the excitation energy of "impurity" semiconduction in these minerals (Hughes, unpublished).

This peak may be the result either of an exciton level 1.19 eV above the valence band, which acts as an acceptor level, or of a donor level 1.19 eV below the conduction band. The two processes cannot be distinguished by absorption measurements alone, and ambiguity of this sort is present in all of the interpretations which follow. If the above level is 1.19 eV above the valence band, the peak at 22,600 cm.$^{-1}$ is interpreted as arising from the excitation of an electron from this level to the conduction band. Conversely, the peak at 22,600 cm.$^{-1}$ would represent a transition from the valence band to the exciton level if the latter lies 1.19 eV below the conduction band. The sum of the energies of the two peaks exceeds that of the ultraviolet absorption edge by about 0.4 eV, but the selection rules may forbid transitions from the exciton level to the bottom of the conduction band.

The peaks at 2500 cm.$^{-1}$ correspond roughly to similar peaks in the garnets. They suggest the existence of an exciton level of unknown origin about 0.3 eV above the valence band or below the conduction band. A similar peak was not found in adularia. The remaining peaks in the olivine spectrum are left unaccounted for. They did not appear in the diopside spectrum, and they may not appear in all crystals of olivine.

The results for almandine and pyrope closely resemble each other; both spectra are very complex. The positions of the peaks can be explained by exciton levels 0.36, 0.74, 0.98, and 2.48 eV above the valence band or below the conduction band. The peaks arise from transitions among these levels and between them, the valence band, and the conduction band. This scheme, however, may not account for the relative intensities of the peaks as well. With the exception of transitions to the conduction or valence band, it accounts for their positions accurately, the greatest discrepancy being 0.06 eV.

The spectrum of grossularite differs markedly from those of the other garnets; it may be explained by exciton levels at 0.35 and 0.99 eV. The

peak at 11,300 cm.$^{-1}$ would then represent a transition between the valence or conduction band and the level at 0.99 eV. The discrepancy between the position of this peak and the ultraviolet absorption edge is 0.2 eV.

The peaks in the garnets at about 8000 cm.$^{-1}$ are interpreted as due to the Fe^{++} ion. The difference between the positions of this peak in garnet and olivine is attributed to the difference in coordination of the iron (six-fold in olivine and eight-fold in garnet). A similar dependence on coordination number has previously been inferred in glasses (Weyl, 1951). The peak near 20,000 cm.$^{-1}$ in almandine and pyrope is presumably due to the Fe^{+++} ion. It corresponds to the ultraviolet absorption edge in grossularite, suggesting that the narrow exciton band in almandine and pyrope is broadened by the addition of ferric iron and assumes the role of either the valence or the conduction band as the amount of ferric iron increases. The behavior of Fe^{+++} in these garnets is analogous to the behavior of Ni^{++} in glasses and in NiO (Weyl, 1951; Johnston and Cronemeyer, 1954).

The interpretations given above must be regarded as tentative. They have the advantage of simplicity, but most of them depend on the possibility of an exciton level acting simultaneously as a donor and acceptor. This is possible if the average lifetime of excited states is sufficiently long. The specimen was exposed to white light, which continually excites the electrons, during the measurements.

Uncertainties in the causes of the exciton levels can be reduced by studies of synthetic crystals ranging in composition throughout solid-solution series. The behavior of the spectra as functions of composition will yield much information about the electronic structure of silicates.

Conclusions

Perhaps the most important result of this work is the discovery that certain silicates are highly transparent to radiation in the near infrared. The fact that olivine shows this property is almost certain to influence estimates of temperatures in the earth.

Spectra of iron-bearing silicates may show considerable complexity in the visible and near infrared. An absorption peak in the spectra of olivine and diopside corresponds in energy to the excitation energy of "impurity" semiconduction in these minerals; it is tentatively ascribed to fayalite or hedenbergite in solid solution in the crystals. In such a situation, the term "impurity" should be discouraged; the term "exciton" has been substituted in this paper. Elements present in quantities amounting to a few per cent can hardly be considered impurities in the same sense as traces of other elements in silicon or germanium.

It is expected that certain exciton levels will widen as the iron content of the crystal increases. They will assume the role of either the valence or the conduction band at compositions near the iron end member. An example of this type of behavior is provided by almandine and andradite-bearing grossularite.

ACKNOWLEDGMENTS

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