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on

Infrared Studies of Crystals

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I. Purpose of the Research

See 1st Annual Report.

II. Account of Work Done and Future Program

(A) BARIUM TITANATE (Mr. R. T. Mara): Nothing new to report here except that work is under way to obtain the spectra of TeO_2, IrO_2, GeO_2, SnO_2, PbO_2, MnO_2, VO_2, and CrO_2, all of which have the same crystal structure as TiO_2.

(B) MICA (Mr. R. T. Mara): Work has been done on the dichroism of certain OH bands in muscovite and on the spectra of muscovite and phlogopete in the region between 10 and 33μ.

(a) Polarization Studies

Preliminary observations (see the First Annual Report) seemed to indicate that the dichroism of the 1.4μ band in muscovite was much greater than that of the 2.8μ band. This observation is inconsistent with the assignment of the 2.8μ band as due only to the OH stretching fundamental and the 1.4μ band as its overtone. In an effort to clarify this situation, further study was made of the polarization characteristics of these bands.

The early polarization work on the 1.4μ band was done with a muscovite sample 250μ thick. This resulted in only about 15% absorption at 1.4μ, which was not sufficient for accurate quantitative measurement. Polarized spectra of a thicker sample (about 902μ) of the same muscovite have been obtained covering the 1-2.5μ region. Spectra were

taken with twenty settings of the polarizer covering 180°. A plot of the percent transmission (I/I_o) vs the angle of polarization was made for the 1.4μ and 2.2μ bands. Using a thin sample (about 2μ thick), the same was done for the 2.8μ band.

The curves indicated that the 1.4μ, 2.35μ, 2.45μ, and 2.8μ bands are polarized in the same direction, with their maximum absorption along the b-axis of the crystal. The 2.2μ band exhibited its maximum absorption when the polarizer was oriented along the a-axis (perpendicular to the b-axis). The directions of the a and b axes (which are in the plane of the mica sheet) were determined by use of a polarizing microscope.

For the thick sample (about 902μ), the fractional transmission I/I_o for the 1.4μ band varied from 0.310 to 0.650 when plotted against the polarization angle. Defining

$$\delta_{\substack{min \\ max}} = \ln\left(\frac{I_o}{I}\right)_{\substack{max \\ min}}$$

and the dichroic ratio ρ as

$$\rho = \frac{\delta_{max}}{\delta_{min}}$$

a value $\rho_o = 2.72$ was obtained for the 1.4μ band.

When the thin sample (about 2μ) was used, I/I_o for the 2.8μ band varied from 0.250 to 0.585. This gave $\rho_F = 2.61$ for the 2.8μ band.

The values of ρ_o and ρ_F differ by about 4%, which is within the expected experimental error. This result confirms the assignment of the 1.4μ band as the overtone of the band at 2.8μ. It should be noted that these values are considerably higher than that obtained by Tsuboi for the 2.8μ band (viz. 1.37).

Assuming Beer's Law, $I = I_o e^{-kx}$, the absorption coefficient, k, at the peak of the 1.4μ band was calculated to be 1.05×10^{-3} per micron. This value was checked by predicting the percent transmission at 1.4μ for the various thicknesses. The variations from the observed percent transmissions were within experimental error.

The above work was done on the muscovite sample whose spectrum was given in Fig. III of the First Annual

Report, and whose extended spectrum is given in Fig. I (a) of this report. All polarization work reported here was performed on a Perkin-Elmer model 21 double beam instrument equipped with a rock salt prism.

(b) Long Wave Length Region

The long wave length region has been explored for three mica samples. The spectrum shown in Fig. I (a) is of a muscovite sample that shows only the free OH band at 2.8μ and its overtone at 1.4μ, and no other OH bands (see Fig. III, First Annual Report). The muscovite sample used for Fig. I (b) exhibits not only the free OH bands, but also hydrogen bonded bands at 3.1μ and 7.05μ (see Fig. IV, First Annual Report). Synthetic phlogopite containing no hydroxyl groups was used for Fig. I (c).

It was hoped that by comparing these three spectra an OH deformation frequency could be located in the longer wave length region.

It will be observed that the muscovites which exhibit stroup OH bands near 2.8μ also exhibit a band near 410 cm^{-1} which is absent from the spectrum of synthetic phlogopite which has no OH groups (and no band at 2.8μ). It is not certain yet whether this correlation is significant. It may be noted, however, that the spectra of two phlogopites which contained varying amounts of OH (Figs. II (a) and II (b) of the 4th Quarterly Report) show significantly more absorption in the region of 410 cm^{-1} than the phlogopite containing no OH.

The only other important differences between the three spectra of Fig. I are that (a) and (b) show a clearly resolved band at 930 cm^{-1} which only appears as a shoulder in (c) and that (a) and (b) show a band at 800 cm^{-1} which is absent in (c).

A Perkin-Elmer model 21 double beam instrument with a rock salt prism was used to obtain the spectra in the 1-10μ region, and a Perkin-Elmer model 112 double pass spectrometer with a CsBr prism was used for the 10-33μ region.

FUTURE PROGRAM: Work will continue on the identification of OH frequencies in the micas and on measurements of their polarization properties.

(C) DIAMOND (Mr. W. G. Simeral): The greater portion of the period has been devoted to calculations concerning the loca-

tions of the maxima in the frequency distribution of diamond. The results are incomplete and will not be presented at this time.

The following experimental results have been obtained:

(1) Neutron Bombardment: Four diamonds have been exposed to a total of 30 hours of irradiation in the Oak Ridge Pile. The infrared classification of the stones ranged from strong Type I to Type II (see First Annual Report). At the end of the 30 hours of irradiation all four diamonds showed a dark green color by transmitted light. The color of the individual stones appeared to be independent of their Type or their original color. No definite effects were found in the infrared spectra of the irradiated diamonds. If there was any increase in the intensity of the Type I bands, it was too small to be clearly separated from the experimental variations. Before returning the diamonds for additional bombardment, the absorption spectra in the near ultraviolet and visible will be examined.

(2) Ultimate Carbon Analysis: Samples from three diamonds were submitted to Clark Microanalytical Laboratory for a measurement of the total carbon content. Previous results on diamond dust (see First Annual Report) indicated that this procedure would be successful. However, it did not prove possible to oxidize the small fragments of diamond at a fast enough rate to make a successful analysis. Either the impurities in the dust catalyzed the previous oxidation, or the state of subdivision influences the rate of combustion. The latter observation seems more plausible.

(3) Vacuum Ultraviolet Absorption: Measurements have been made in the spectral region form 1300 to 5000A using a Cario-Schmidt-Ott spectrograph. The source of radiation was a hydrogen discharge lamp. The absorption spectra of several diamonds of varying Type all showed complete absorption in the spectral region from 1300A to 2250A. Construction of a new source for use in obtaining the infrared spectra of diamonds in the 20μ region is underway

FUTURE PROGRAM: Construction of the above mentioned source will be completed. It has been found that present equipment must be

modified before the small diamonds in the Grenville Wells collection (see Quarterly Report No. 4) can be examined in the infrared. The necessary modifications are underway. Samples of highest purity germanium should be available in the near future. These samples will be examined in the entire infrared spectral region available on our apparatus (1 to 150μ). The calculations dealing with the correlation of theory and experiment for the infrared spectra of silicon, germanium, and diamond will be continued.

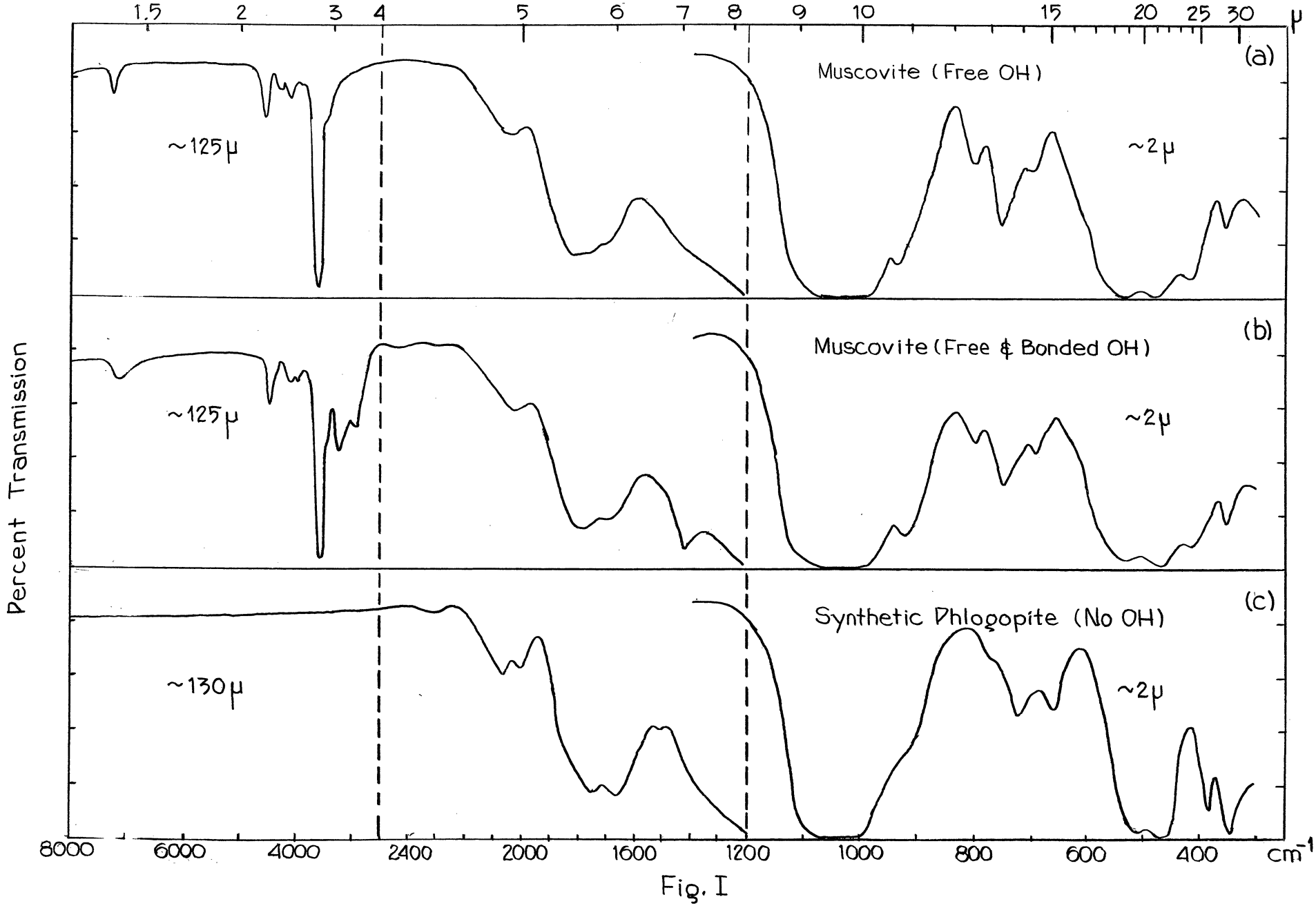

Fig. I

Spectra of three micas (a) a muscovite containing free OH groups, (b) a muscovite containing free and bonded OH groups, and (c.) a synthetic phlogopite containing no OH groups — for comparison in the long wave length region.