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QUARTERLY REPORT NO. 3

ON

INFRARED STUDIES OF CRYSTALS II

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TABLE OF CONTENTS

	<u>Page</u>
I. PURPOSE OF THE RESEARCH	1
II. ABSTRACT	1
III. PUBLICATIONS	1
IV. FACTUAL DATA	
A. Barium Titanate	1
B. Brucite	2
C. Micas	2
D. Gypsum	5
V. CONCLUSIONS	5
VI. FUTURE PROGRAM	6
VII. PERSONNEL	7

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I. PURPOSE OF THE RESEARCH

The general purpose of this research is to complete the investigations started in May, 1951 under Contract DA 36-039 sc-56736 on the infrared spectra and structure of barium titanate, brucite, mica and gypsum.

II. ABSTRACT

The effect of temperature on the spectrum of strontium titanate was studied in order to make a comparison with barium titanate. An effort was made to interpret the 3μ spectrum of biotite in terms of a unit cell having space group C_s^3 , as deduced from X-ray diffraction data. A comparative study was made of the far infrared spectra of several varieties of mica. The interpretation of the gypsum spectrum is proceeding.

III. PUBLICATIONS

The work done during the period covered by this report has not yet been prepared for publication.

IV. FACTUAL DATAA. Barium Titanate

Our previous work (Quarterly Report No. 2, December, 1954) showed that the spectrum of $BaTiO_3$ changes as the temperature is raised above the Curie point, although the association of this change with a sharp transition at $120^\circ C$ was not established. The principal change observed was a broadening on the long wavelength side of the band centered near 500 cm^{-1} as the temperature is raised.

In an attempt to see whether this effect might be correlated with the ferroelectric properties of $BaTiO_3$, the spectrum of non-ferroelectric $SrTiO_3$ (powder compressed in a KBr disc) was obtained at high and low temperatures. A smaller but similar temperature effect was also found for the $SrTiO_3$ band centered near 450 cm^{-1} .

The spectrum of a single crystal of $BaTiO_3$ was observed at room temperature and at $180^\circ C$, using polarized infrared radiation. The spectrum obtained with the incident electric vector parallel to the ferroelectric axis appears to be identical with

the spectrum obtained when the electric vector is perpendicular to the ferroelectric axis. As the temperature is raised from room temperature to 180° C, the absorption band near 10 μ gradually broadens toward shorter wavelengths, with the gradual disappearance of "plateaus" at 7 μ and 10.5 μ ; the small transmission peak at 8.5 μ tends to become flattened.

B. Brucite

No further work to report.

C. Micas

The sample of biotite which we investigated thoroughly in the 3 μ region has now been examined by X-ray diffraction (by Dr. A. A. Levinson at Ohio State University). He reported that on the basis of work by Hendricks and Jefferson¹, his X-ray photographs indicate that the structure of this sample of biotite is one-layer monoclinic and the space group is $C_2^3 - Cm$. The following discussion is based on this structure.

The space group $C_2^3 - Cm$ is isomorphic with the point group C_s . The symmetry properties of this space group are shown in Fig. 1. One reflection plane is parallel to the ac plane and is located at $y = b/2$ in the crystallographic unit cell. Two glide reflection planes σ^g with translation parameter $a/2$ are also parallel to the ac plane and pass through $y = b/4$ and $y = 3b/4$ respectively. The type of lattice for this structure is face-centered on one pair of opposite faces (the ab faces). The Bravais cell of the smallest size is half of the crystallographic unit cell. Therefore, only 2 OH groups are involved in one Bravais cell.

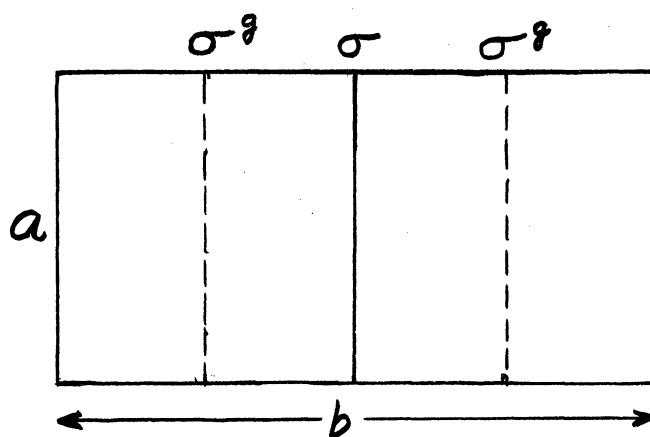


Fig. 1 Symmetry Elements of Space Group $C_2^3 - Cm$.

According to Hendricks and Jefferson's atomic coordinates for this type of biotite the oxygens of the OH group are

located on the (ac) reflection plane. If the hydrogens also obey the C_2^v space group, the OH bonds must be perpendicular to the b-axis to preserve the symmetry about the reflection plane. However, the hydrogen atoms can take any position within the ac plane without destroying the overall symmetry. Since the OH bonds in this model are normal to the b-axis, there will be no electric moment change along the b-axis associated with the OH stretching vibrations.

There will be two stretching modes of vibration involving the two OH bonds, one mode in which the H atoms move "in phase" and another in which their motions are "out of phase". Both will be infrared active and each will be expected to show infrared absorption along both the a-axis and the z-axis, unless the OH bonds have a special orientation in the ac plane. (Note: we define the z-axis as perpendicular to the a- and b-axes. The c-axis does not coincide with the z-axis, but is inclined to it by about 10° in this crystal. The ab plane is the natural cleavage plane for micas.)

Our infrared spectrum of biotite contains two absorption bands assigned to the OH stretching vibrations. It should be noted, however, that one of these bands (at 2.83μ) has a strong component along the b-axis (as well as along the a-axis), in complete disagreement with the spectrum predicted from the C_2^v model. The assignment of the 2.83μ band to an OH stretching vibration cannot seriously be questioned, as it is supported by a great deal of evidence from earlier infrared work. We are forced to the conclusion, then, that the OH bonds do not lie in the ac plane, and that the H atoms cannot fulfill the symmetry requirements of space-group C_2^v . In other words, infrared evidence indicates strongly that the unit cell of single-layer biotite does not have the symmetry which has been assigned to it on the basis of X-ray investigations.

The other stretching band (at 2.73μ) observed for single-layer biotite has an electric moment change which is nearly perpendicular to the ab plane. This indicates that the mode of vibration responsible for the 2.73μ band is one in which the dipole moment change associated with the stretching of the two OH bonds has nearly equal and opposite components in the ab plane, but whose components normal to this plane add to give a resultant infrared absorption.

Far Infrared Spectra of the Micas

The spectra in the far infrared region from 300 cm^{-1} to 100 cm^{-1} have been obtained for six varieties of mica (Fig. 2). One band (at approximately 150 cm^{-1}) appears to be common to biotite, zinnwaldite, and phlogopite, but several other bands were observed in muscovite and synthetic phlogopite. The lepidolite sample was so thick that only one discrete absorption maximum near 170 cm^{-1} has been observed (Fig. 2b). Two different samples of muscovite have been investigated in this region; the

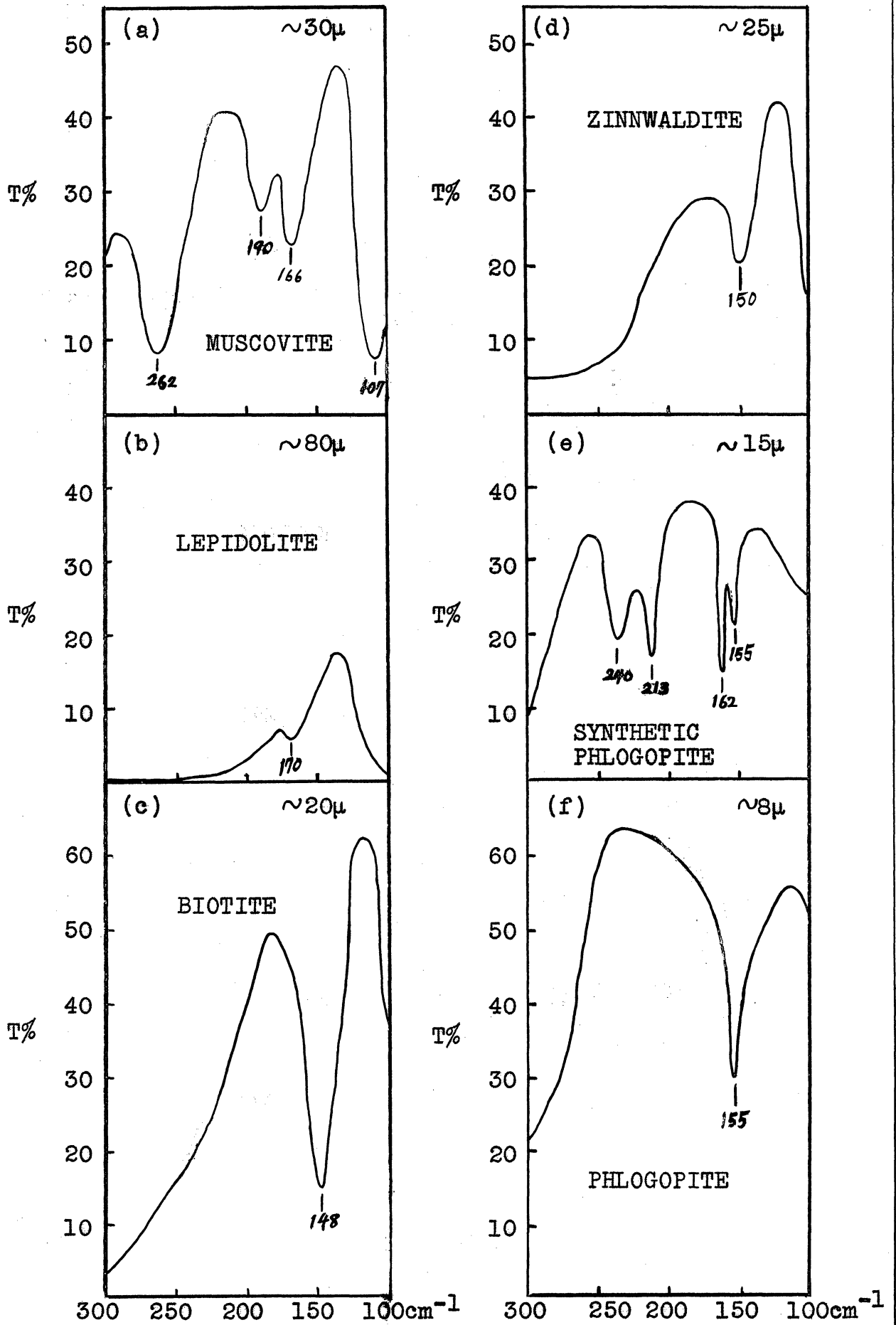


FIGURE: FAR INFRA-RED SPECTRA OF MICAS (GRATING DISPERSION)

difference between them is that the 3.1μ and 7.05μ bands are present in one of the samples but absent in the other. It is worth-while to mention that the far infrared spectra of the two samples are exactly the same.

In an effort to determine what type of vibration in the mica crystal is responsible for the 150 cm^{-1} band, our attention was directed to quartz. The crystal structure of quartz is composed of linked SiO_4 groups (the silicon atoms are arranged in a spiral form in the unit cell); linked SiO_4 groups are also an important part of the structure of all the natural and synthetic micas. Saksena^{2,3} has published a rather detailed study of α -quartz. Based on his normal coordinate calculations and the observed behavior of the lines in infrared and Raman spectra, he concluded that the low frequencies ($\sim 100\text{ cm}^{-1}$ to 200 cm^{-1}) occurring in quartz are due to the motion of the silicon atoms. It seems reasonable to assume, then, that the band near 150 cm^{-1} observed in biotite, zinnwaldite, phlogopite and synthetic phlogopite is associated with the oscillation of the silicon atoms in the linked SiO_4 groups. The origin of the other bands in synthetic phlogopite and muscovite remains to be investigated.

D. Gypsum

The computational work involved in transforming the reflection spectra to give absorption coefficients for the intense bands of gypsum has been completed. The interpretation of the spectrum is proceeding satisfactorily. Since this is a very complex problem and impossible to summarize, this work will eventually form the subject of a separate technical report.

V. CONCLUSIONS

A. Barium Titanate

A broadening of the band near 450 cm^{-1} with increasing temperature, qualitatively similar to that found for BaTiO_3 , has been observed for SrTiO_3 . On the basis of this result it is unlikely that there is any connection between the temperature effects observed in the BaTiO_3 spectrum and the change in ferroelectric properties of BaTiO_3 at the Curie point.

Furthermore, it now seems improbable that surface effects due to the small grain size of the BaTiO_3 powder used will affect our results. According to our most recent information⁴, surface effects appear to be pronounced only when the size of the particles is about 0.1μ . The powder we used was passed through a 75μ mesh and presumably has an average particle size greatly in excess of 0.1μ .

B. Brucite

No further work to report.

C. Micas

Our sample of biotite was examined by X-ray diffraction by Dr. A. A. Levinson, who reported that it has a single-layer monoclinic structure, with the space group $C_2^3 - Cm$, based on earlier studies by Hendricks and Jefferson. If the H atoms obey the symmetry requirements of this space group, the OH bonds must be perpendicular to the b-axis in this type of biotite. The 2.83μ OH stretching band which we have observed for this sample, however, has a strong component of infrared absorption parallel to the b-axis, indicating that the H atoms do not fulfill the symmetry requirements of space group C_2^3 . The infrared data, therefore, lead to a serious conflict with the X-ray results when an attempt is made to interpret them in terms of a biotite model. The exact positions of the H atoms in single-layer biotite are still uncertain.

From a comparison of the far infrared spectra of micas in the region of $30-100\mu$, it is possible to pick out a band at 150 cm^{-1} which is common to several varieties of mica. This band appears to be associated with a characteristic vibration of the linked SiO_4 tetrahedra.

D. Gypsum

It is still too early to report any definite conclusions.

VI. FUTURE PROGRAMA. Barium Titanate

Only a very limited amount of work will be carried out on this problem. It will be directed towards checking and confirmation of previous observations.

B. Brucite

No new work is contemplated by us, but it is hoped that arrangements can be made with Dr. Pepinsky to have neutron diffraction studies made on brucite.

C. Micas

Work will be continued in an effort to resolve the conflict between X-ray and infrared results on the structure of biotite, and to determine the hydrogen atom positions. This will involve correlation of infra-red and X-ray results on samples of various micas of known chemical composition. It may be necessary to investigate by infrared methods a molecule in which the H atoms have been unequivocally located by X-ray methods.

D. Gypsum

Interpretation of the spectrum, especially location of the H₂O molecules.

VII. PERSONNEL

The following have been engaged on the work reported here:

Professor G.B.B.M. Sutherland, Director (part time)
Mrs. C. Y. Pan Liang (half time)
Mr. M. Hass (part time)
Mr. D. E. DeGraaf (half time since 2/9/55)
Mr. A. Dockrill (technician, part time)
Mr. H. Diamond (part time, unpaid).

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- 4 Private communication from Professor W. Künzig.

