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QUARTERLY REPORT NO. 2

ON

INFRARED STUDIES OF CRYSTALS II

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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 barium titanate has been studied. No new work has been done on brucite. The possibility of removing certain ambiguities in the location of the hydrogen atoms in muscovite and biotite has been investigated. A start has been made on the general interpretation of the absorption spectra of the micas in the range 2 to 100 μ . The interpretation of the spectra of gypsum is proceeding.

III. PUBLICATIONS

None of the work done during the period covered by this report has yet been published.

The following publications concerning work done on the preceding contract have now appeared:

"The Problem of the Two Types of Diamond".
G. B. B. M. Sutherland, D. E. Blackwell
& W. G. Simeral, Nature 174, 901 (1954).

"The Infrared Spectrum of Barium Titanate".
R. T. Mara, G.B.B.M. Sutherland & H. V.
Tyrell, Phys. Rev. 96, 801 (1954).

IV. FACTUAL DATA

A. Barium Titanate

The spectrum of a powdered sample of barium titanate has been obtained at a temperature above 150° C. (i.e. well over the Curie temperature of 120° C.) using the K Br disk technique. It

appears that there is an increase in the absorption intensity on the long wave side of the absorption band centered near 520 cm^{-1} . It has not yet been determined whether the change occurs at exactly 120° C . In the light of some recent work in Switzerland, it appears that the Curie temperature is much higher than 120° C . for very small crystals of barium titanate. The indications are that the surface layers of the crystal may have a much higher Curie temperature than the interior of the crystal. This means that there is no sharp transition point, the transition from the tetragonal form to the cubic form being smeared out over a temperature range which increases with decreasing particle size.

B. Brucite

Nothing new to report.

C. Micas

The orientation of the OH groups in muscovite and biotite is still occupying our attention. It was mentioned in our last report (Final Report, October 1954, p. 43) that the sign of the "a coordinate" of the hydrogen atom in the first layer must be positive. However, this conclusion depended on an arbitrary convention for the sign of the angle of refraction (r). If the sign of r is reversed, then "a" would have to be negative. We have therefore tried to see whether this ambiguity can be resolved by examining the environment of the hydrogen atom and using physical considerations.

In muscovite the two sheets of atoms adjacent to a sheet containing an OH group are composed of Si ions (about 1.6 \AA on one side of the OH sheet) and Al ions (about 1.2 \AA on the other side of the OH sheet) as shown in Fig. 1. We have already used physical considerations in concluding that the OH group in the first layer points towards the sheet of Si ions and away from the sheet of Al ions (i.e. the sign of z is positive, c.f. Final Report, October 1954, p. 43). The dichroic measurements have enabled us to find the angle the projection of the OH direction makes with the a and b axes, but since the signs of a and b are unknown the hydrogen atom may be in any one of the four quadrants, i.e. at A, B, C, or D in Fig. 1. If we assume that the equilibrium position of the hydrogen atom is determined by its electrostatic interaction with the surrounding ions, then the position A is to be preferred since the hydrogen is now placed much more symmetrically with respect to the Al ions than if it occupies position B, C or D. All four positions are virtually equivalent with respect to the Si ions. According to the conventions we have adopted, this means that the sign of "a" is positive so our previous conclusion is unchanged. Furthermore, this establishes the sign of "b" as negative.

In the case of biotite, the situation is much more complex. The exact locations of the Fe and Mg ions in the sheet

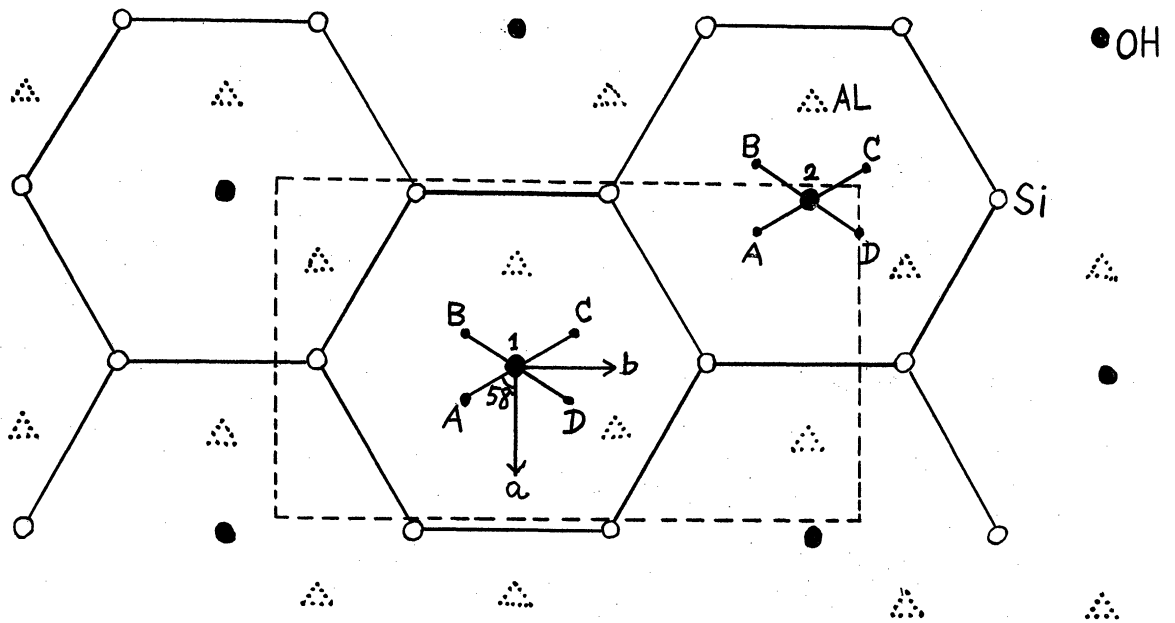


Fig. 1 The projection of OH Group (No. 1 and 2 in Fig. 5, p. 33, Final Report, October 1954) on cleavage plane in Muscovite.

- Silicon on the Upper Sheet
- OH Group on the Middle Sheet
- △ Aluminum on the Lower Sheet

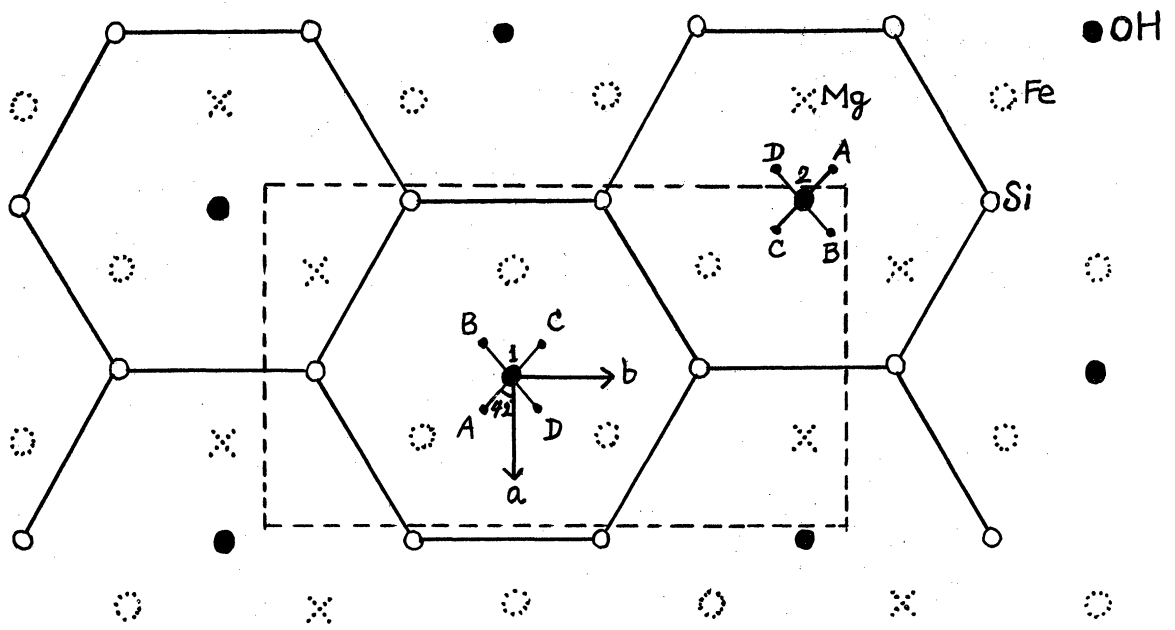


Fig. 2 The projection of OH Group on cleavage plane in Biotite.

- Silicon on the Upper Sheet
- OH Group on the Middle Sheet
- ⊙ Fe, × Mg on the Lower Sheet

adjacent to the OH sheet have not been determined. The infrared results indicate that the hydrogen positions in biotite should conform to the C_{2h}^4 space group. Taking the Fe/Mg ratio as exactly 2/1, it is possible to place these ions in the sheet so that the unit cell conforms either to the C_{2h}^6 or to the C_{2h}^4 space group. Since the hydrogens belong to the C_{2h}^4 space group, it seems more reasonable to make the Fe and Mg ions conform to the same space group. This leads to the positions of the Fe and Mg ions shown in Fig. 2. Again we have four possible positions for the OH direction corresponding to the hydrogen atom being at A, B, C or D. So far we have found no satisfactory way of deciding between these four possibilities.

Hitherto we have concentrated our attention almost exclusively on the interpretation of one band in the spectra of micas, viz. that due to the OH stretching frequency near 2.8μ . We have recently started to consider the overall interpretation of the mica spectra. This has been done using two approaches. The first was to compare carefully the spectra of all the micas examined over as wide a spectral range as possible. This involved some more experimental work to fill in gaps which became apparent and to check some of the earlier observational work. It is found that the spectra of the various micas have certain features in common, e.g. 5 strong bands in the range between 4μ and 35μ . The structural feature common to all micas is the existence of linked SiO_4 tetrahedra, and these 5 bands probably all originate from vibrations of these silicate groups. The second approach has therefore been to survey previous infrared work on silicates and see to what extent previous work on the silicates can be used in interpreting the common features of the spectra of the micas. This work is now in progress but it would be premature to report on it at this stage.

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 summarise, this work will eventually form the subject of a separate technical report.

V. CONCLUSIONS

A. Barium Titanate

It appears that there are small but real changes in the spectrum of barium titanate as it passes through the Curie temperature. The investigation of these changes will be difficult because in the powder form there may be complicating factors due to surface layer effects.

B. Brucite

Nothing new to report.

C. Micas

Although it has been possible to establish the positions of the hydrogen atoms in muscovite, it may not be possible to do so for biotite with the same degree of certainty.

D. Gypsum

Still too early to draw any important conclusions.

VI. FUTURE PROGRAM

A. Barium Titanate

Work on the temperature effect will be extended to include single crystals and comparison with SrTiO_3 .

B. Brucite

No new work contemplated.

C. Micas

The main effort will be on the general interpretation of the spectra of the micas. Some time will also be devoted to the preparation of earlier work for publication.

D. Gypsum

Interpretation of the spectrum, especially location of the H_2O 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. A. Dockrill (technician - part time)
Mr. H. Diamond (part time - unpaid).

