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QUARTERLY REPORT NO. 4

ON

INFRARED STUDIES OF CRYSTALS II

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INFRARED STUDIES OF CRYSTALS II

I. PURPOSE OF THE RESEARCH

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

II. ABSTRACT

The disagreement between the infrared and X-ray results on the space group of biotite has been studied. It appears that the X-ray work is not sufficiently refined, and gives only a first approximation to the space group. The conflict between the X-ray and infrared results having been removed, there remains the problem of explaining why the hydrogen atoms do not lie on the plane of symmetry which bisects the unit cell in the C_s^3 space group. This may arise from an unsymmetric distribution of Al^{+++} and Si^{++++} ions in the tetrahedral layer. High resolution studies on mica have been started to see whether still more structure exists in the infra-red absorption bands.

The effect of convergence in the incident beam on measurements of infrared dichroism in single crystals is being studied.

III. PUBLICATIONS

The work during the period covered by this report has not yet been prepared for publication. A conference was held at the University of Michigan on March 14, 1955 between Dr. H. Kedesdy and Mr. A. Schwartz of the Squier Laboratories, and Professor Sutherland and Mr. DeGraaf. The progress of the work on this contract was reviewed and the future program was discussed.

IV. FACTUAL DATAA. Barium Titanate

No further work to report.

B. Brucite

No further work to report.

C. Micas

In our previous report (Quarterly Report No. 3, March 1955)

we stated that the results of our infrared observations of the OH stretching vibrations in biotite were in direct disagreement with the assignment of space group C_3^2 , which was based on the results of X-ray diffraction. Continued study of this problem has indicated the way in which this conflict between the results of X-ray and infrared analysis may be resolved.

A review of the paper by Hendricks and Jefferson¹ on which the C_3^2 assignment was based, reveals that these authors did not carry out a complete X-ray structure determination based on the missing orders of reflection in the diffraction pattern. Instead, they apparently determined the lattice dimensions of their biotite sample from the X-ray pattern, concluded that the sample had a single-layer structure, and then deduced the unit cell orientation, atomic coordinates, and the space group on the basis of geometrical considerations. Thus, for single-layer biotite, the space group C_3^2 is possible, but the atomic coordinates given by Hendricks and Jefferson have not been definitely established by experimental measurements. It should be noted also that since X-ray scattering from H atoms is very weak, the observed X-ray patterns of micas do not give any indication of the hydrogen positions, and hence conclusions about the symmetry of mica crystals based on X-ray work pertain only to the non-hydrogen atoms of the crystal. Thus it is quite possible that the hydrogen atom positions in micas do not conform to the symmetry operations of the space group as deduced from X-ray diffraction.

It has further become apparent that we must take account of the mineralogists' concept of "isomorphous replacement" in interpreting X-ray results on crystals. The idea of isomorphous replacement is that the mineralogist considers, for example, that the Al^{+++} and Si^{++++} ions in the tetrahedral layers of micas are completely interchangeable; any site in the tetrahedral layer may be occupied by Si^{++++} or Al^{+++} , without doing violence to the symmetry properties of the space group. Isomorphism is also assumed for the divalent Mg^{++} or Fe^{++} ions in the octahedral sheets of micas.

Thus the space group C_3^2 ascribed to our single-layer specimen of biotite may be correct as an idealized description, but this space group may be an incorrect description of the crystal symmetry when the unit cell is considered in detail, and predictions of the infrared spectrum based on this space group are not likely to be correct. We must also be prepared for differences in the detailed structures of adjacent unit cells, in accordance with the various possibilities for isomorphous replacement, and in view of the fact that X-ray results in this case have nothing to say about hydrogen atom positions. In the light of this discussion, it is seen that our previously reported observation of the 2.83μ band in biotite as having a component along the b-axis is not really in contradiction to the X-ray results.

Assuming for the moment that the atomic site coordinates (with the exception of hydrogen) for the unit cell of single-layer biotite are given with fair accuracy by Hendricks and Jefferson, there remains the problem of specifying the hydrogen atom positions. Our previous results indicated that at least some of the hydrogens do not lie on the plane of symmetry which bisects the unit cell in space group C_3^2 . This suggests that these hydrogens are in an unsymmetric force field. It seems likely that the asymmetry in the force field which determines the equilibrium position of a given hydrogen atom may result from an asymmetric placement of the Al^{+++} and Si^{++++} ions in their sites in the tetrahedral layer. We have begun to investigate the consequences of this hypothesis as they relate to the predicted infrared spectrum. It is as yet too early to report any definite conclusions.

During this quarter a powerful new spectrometer has become available to us, which will permit more detailed observations of the OH-stretching frequencies in micas. This instrument is a high-resolution vacuum grating spectrometer, which has been under construction during the past two years in this laboratory. Preliminary studies using this instrument on muscovite and biotite have revealed the existence of additional infrared bands in the OH stretching region. It appears that there may be at least three bands in muscovite, and possibly four in biotite.

D. Gypsum

A full account of all the experimental work done on gypsum has been given in Technical Report No. 3 (June 1955).

E. Infrared Dichroism of Single Crystals in Converging Light.

When an absorption band in a crystal is observed with highly convergent radiation such as that for a microspectrophotometer, there are several kinds of error that may be observed in the spectrum. These errors would not be present for observations with parallel radiation.

In order to evaluate the effect of convergence on a crystal spectrum experimentally, an attempt has been made to observe a band in the hexagonal crystal of $CaCO_3$ with various angles of convergence of the incident radiation. The extinction coefficient of the band, however, as well as the refractive index must be known before the observations can be reconciled with the theory. Because of the intense absorption of the carbonate frequency chosen (895 cm^{-1}) the extinction coefficient can only be measured by reflection, since the transmission samples of about 0.3μ could not be prepared. The reflection spectrum is also advantageous to use because it gives the refractive index as well as the extinction coefficient according to the method of Robinson².

The reflection spectrum of a calcite crystal cut parallel to the optic axis has been measured accurately, and the data have been prepared for reduction to index of refraction and extinction coefficient on an electronic digital computer (MIDAC).

In the process of making the appropriate reflection measurements, it was necessary to make new selenium films for the infrared polarizers, and to make one new polarizer. It was also necessary to restore the linearity of the response for the Perkin-Elmer Model 12-C on which the reflection data were recorded.

V. CONCLUSIONS

A. Barium Titanate

No further work to report.

B. Brucite

No further work to report.

C. Micas

The grounds on which X-ray investigators have assigned the space group C_3^2 to single-layer biotite have been critically examined. It is concluded that although C_3^2 may be correct as a description of an idealized unit cell of biotite, it is probably incorrect when applied to the unit cell in detail. Thus the apparent conflict reported earlier between infrared and X-ray results is now satisfactorily removed. New observations on biotite and muscovite using a high-resolution vacuum spectrometer have revealed the presence of additional bands in the OH-stretching region, for both muscovite and biotite.

D. Gypsum

A full discussion of the conclusions reached on the work with gypsum has been given in Technical Report No. 3 (June 1955).

E. Infrared Dichroism of Single Crystals and Converging Light.

No conclusions can be made yet, since the data are incomplete.

VI. FUTURE PROGRAM

A. Barium Titanate

If time permits, some work will be done on large single crystals of barium titanate.

B. Brucite

The 2.7 micron region of the spectrum of brucite will be re-examined using very high resolving power.

C. Micas

High resolution work will be continued on the micas.

D. Gypsum

No further work is contemplated at present.

E. Infrared Dichroism of Single Crystals in Converging Light

This work will be continued so that the proper corrections can be made when using convergent beams in the microspectroscopy of small single crystals.

VII. PERSONNEL

The following have been engaged on the work reported here:

Professor G.B.B.M. Sutherland, Director (part time)
Dr. D. L. Wood (part time, unpaid)
Mr. D. E. DeGraaf (half time)
Mr. A. Dockrill (technician, part time)
Mr. M. Hass (part time)
Mr. R. Hede (part time)

References

- 1 S. B. Hendricks and M. E. Jefferson, J. Min. Soc. Am. 24, 729 (1939).
- 2 T. S. Robinson, Proc. Phys. Soc. B66, 969 (1953).

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