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UNIVERSITY OF MICHIGAN
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NINTH QUARTERLY REPORT

ON

INFRARED STUDIES OF CRYSTALS

(PERIOD: 16 August 1953 to 15 November 1953)

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COVERING THE PERIOD

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I. INTRODUCTION

Purpose of the Research

This has been outlined previously and need not be repeated. The objectives are essentially as stated in the Second Annual Report (June 1953). Emphasis during the past quarter has been placed almost entirely on the mica problem.

Personnel

The following have been engaged on the work reported here:

Prof. G.B.B.M. Sutherland, Director (Part time)
Mr. G. Allen (Half time)
Mrs. C. Y. Pan Liang (Half time)
Mr. A. Dockrill (Part time as laboratory technician)

II. ACCOUNT OF NEW RESEARCH DONE

(A) Mica Problem

General

The OH band near 2.8μ has been studied in a systematic manner in muscovite, biotite and phlogopite in order to substantiate the tentative conclusion in the Second Annual Report (June 1953) that the OH directions are not the same in all micas.

Observations have been made with polarized and unpolarized radiation on the variation of the intensity of this band as the mica sheet is rotated about the a and also about the b axis.

Similar observations have been made on some other bands but so far only the 1.38μ band of muscovite shows marked effects.

The spectra of muscovite, biotite and phlogopite have been extended from 30μ to 100μ.

The present general conclusion from these observations is that the OH groups in biotite and phlogopite have rather similar environments and orientations which differ very markedly from those obtaining in muscovite. The spectra of biotite and phlogopite are very similar over the whole range from 2μ to 100μ but differ markedly from that of muscovite over the same range. For instance, under moderate resolving power the 2.8μ band is split into two components in biotite and phlogopite but is single in muscovite. With incident radiation normal to the cleavage plane, this same band is markedly polarized parallel to the b axis in muscovite whereas in biotite and phlogopite neither component of the doublet shows appreciable dichroism. Moreover, the small dichroism observable under moderate resolving power is opposite to that shown by muscovite. Other differences will be apparent from the following account of the work on the individual types of mica.

Biotite

The intensities of the two components of the OH band at 2.73μ and 2.83μ have been measured carefully over almost

the whole possible range of values of tilt angles about the a and b axes using unpolarized radiation. The 2.73μ component increases steadily in intensity in both cases as we pass from normal incidence (perpendicular to cleavage plane) to within 15° of grazing incidence. In addition, this band is found to be very strongly polarized perpendicular to the axis about which the biotite is tilted. It is clear that the resultant change of electric moment associated with this band must be nearly parallel to the c axis. The intensity of the 2.83μ band decreases very slowly with the tilt angle about either the a or the b axis for unpolarized radiation.

An attempt was made to account for these results by considering two possible in phase and out of phase combinations of the stretching frequencies of 4 OH groups, oriented in certain directions within the unit cell. The first combination gave a resultant moment entirely along the c axis for normal incidence but with a component perpendicular to the axis of tilt (and proportional to the sine of the angle of refraction) for oblique incidence. This accounts qualitatively (and even in a fair quantitative manner) for the observations on the 2.73μ band. The other combination gives a resultant moment for normal incidence which is the same along the a and b axes but for oblique incidence the component perpendicular to the tilt axis should decrease (proportionately with the cosine of the angle of refraction); the component parallel to the tilting axis should remain unchanged. Computations indicate that the total intensity of such an absorption should decrease very slowly as the angle of incidence is increased and rather good agreement was obtained with the experimental results on the 2.83μ band. However, when confirmation was sought using polarized radiation, it was found that whereas for normal incidence the theory predicted no dichroism, the 2.83μ band (when examined with a LiF prism) exhibited some polarization perpendicular to the b axis. The theory predicts that as the angle of incidence is increased this band should show polarization parallel to the axis about which the biotite is tilted. Qualitative confirmation of this prediction was obtained in that the perpendicular polarization decreased as the tilt angle increased and changed to weak parallel polarization for a 45° angle of incidence.

It appears therefore that the tentative theory is along the right lines but will require some modifications before exact agreement can be obtained with experiment.

Phlogopite

The OH band near 2.8μ has been investigated under high resolving power with a LiF prism, although not in such a detailed manner as the corresponding band in biotite. It exhibits considerable similarity in its behavior. For normal incidence, this band shows two components with maxima at 2.72μ and near 2.8μ; of these, the one at 2.8μ is the more intense. As in biotite, the 2.72μ band is very weakly polarized perpendicular to the b axis and so is the 2.8μ band. When the angle of incidence is increased to 40° (tilting about the b axis), the intensity of the 2.72μ band is greatly increased but the 2.8μ band is virtually unaffected. This parallels the behavior of the 2.73μ and 2.83μ bands in biotite. Similarly it is found that for oblique incidence the 2.72μ band is strongly polarized perpendicular to the tilting axis while the 2.8μ band is only weakly polarized. There is one new effect in phlogopite in that tilting appears to bring up an entirely new band at 2.74μ which has the same dichroism as the 2.72μ band.

Muscovite

It has already been mentioned that the main OH band shows no splitting under moderate resolving power (NaCl prism) having a single maximum near 2.75μ. This still remains true under the higher resolving power of a LiF prism, although there are signs of a shoulder on the long wave side. Tilting about the a or the b axis produces certain variations in the intensity of this band for unpolarized radiation. However, a careful investigation using polarized radiation reveals many interesting new facts. These will be described in detail in the next report, since some of them are so puzzling that they may be due to polarization effects in the spectrometer and this must be investigated. It can be stated however that this band is always markedly polarized parallel to the b axis in contrast with biotite and phlogopite. This indicates that the resultant dipole moment change makes a large instead of a small angle with the c axis.

(B) Brucite and Diamond Problems

Work is continuing on the preparation of these results for publication. No new results to report.

III. FUTURE PROGRAM

Work will continue on the micas so that the OH positions can be located more precisely. The theoretical interpretation of the brucite results will be pursued so that a full technical report on that work can be completed. The spectrum of gypsum will be studied.