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QUARTERLY REPORT NO. 1

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

In connection with the interpretation of the spectrum of brucite, the spectrum has been recorded of a single crystal of portlandite ($\text{Ca}(\text{OH})_2$).

In connection with the mica problem, the spectrum has been recorded of synthetic phlogopite from 300 cm^{-1} to 100 cm^{-1} . Also the effect of temperature on the spectrum of biotite was investigated. The theoretical treatment of the 3μ absorption bands of muscovite and biotite has been completed. Models of these crystals have been constructed in an attempt to see reasons for the differences in the OH group orientations in these two micas. The reflection spectrum of gypsum has been completed in the range 500 to 4000 cm^{-1} , for three different orientations of a single crystal.

The spectrum of a single crystal of barium titanate has been obtained between 1μ and 15μ .

III. PUBLICATIONS LECTURES etc.

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

At the Ohio State Symposium on Spectroscopy and Molecular Structure held at Columbus, Ohio, a joint paper was given on June 17, 1954 by Dr. Liang and Professor Sutherland entitled "The Location of the Hydrogen Atoms in Muscovite and Biotite." This paper contained some of the latest work on the theory of the spectra of muscovite and biotite

At the Gordon Conference on Infrared Spectra of Large Molecules held at Meriden, N. H., a paper was given on August 5, 1954 by Professor Sutherland entitled "Relation Between X-ray Results and Infrared Spectra of Large Molecules." This paper dealt (among other things) with the latest work on mica and on brucite and portlandite.

IV. FACTUAL DATA

A. Brucite Problem

The spectrum of portlandite ($\text{Ca}(\text{OH})_2$) in the form of a single crystal was recorded between 4500 cm^{-1} and 650 cm^{-1} (Fig. 1). The spectrum is identical with that of brucite ($\text{Mg}(\text{OH})_2$) in every detail (cf. Technical Report No. 2, Sept. 1954). This is a very important result. It proves that the fine structure in the 3μ region cannot be due to combinations of a single OH frequency with lattice frequencies of the heavier atoms since these would alter very significantly in going from an Mg_2O lattice to a Ca_2O lattice.

B. Mica Problem

The spectrum of synthetic phlogopite in the range 300 cm^{-1} to 100 cm^{-1} shows bands at 155, 162, 213 and 240 cm^{-1} . It is interesting to note that the bands at 213, 240 and 162 cm^{-1} were not observed in natural phlogopite but the band at 155 cm^{-1} is present in natural phlogopite and probably also in biotite where its maximum is at 148 cm^{-1} . This proves that the band near 150 cm^{-1} common to biotite and natural phlogopite is not due to an OH vibration since it is still present in synthetic phlogopite which contains no OH groups. The spectrum of biotite has been investigated in the region between 2500 and 4500 cm^{-1} at liquid nitrogen temperatures. The reason for this experiment was to see what light it would throw on the anomaly of the 2.72μ band mentioned in our last report (Quarterly Report No. 11, p. 2, March 1954). If our original picture is correct, the 2.72μ band ought to be absent unless the biotite

is tilted to make the cleavage plane oblique to the incident radiation. It was found that at low temperatures the 2.72μ band increased markedly in intensity for normal incidence. However, the 2.83μ band only increased very slightly at liquid nitrogen temperatures for normal or oblique incidence. On examining the 2.72μ band with the incident ray oblique to the cleavage plane, it was clear that there was little or no temperature effect on that component of the absorption which becomes active for oblique incidence. This indicates that the small absorption observed at 2.72μ for normal incidence is probably unconnected with the absorption which appears here on tilting. The exact origin of this extra absorption at 2.72μ , which is very sensitive to temperature, is still unknown. It is most probably due to a combination frequency.

It is interesting to note that two weak bands at 3.15μ (3174 cm^{-1}) and 3.27μ (3058 cm^{-1}) which are present as weak absorptions at room temperature become quite marked at high temperature (450°C) and are completely missing at low temperature (90°K) (Fig. 2). Two other bands at 2.33μ and 2.38μ (4290 cm^{-1} and 4200 cm^{-1}) show the reverse behavior in that their intensity is increased at low temperatures and slightly diminished at higher temperatures.

These four bands are presumably combination frequencies as shown in the table below:

μ	cm^{-1}	Differences in cm^{-1}	μ	cm^{-1}	Differences in cm^{-1}
2.33	4290	> 614	2.38	4200	> 524
2.72	3676	> 618	2.72	3676	> 502
3.27	3058		3.15	3174	

It should be remarked that no absorption has been found in biotite either near 615 cm^{-1} or 515 cm^{-1} but these frequencies may, of course, be forbidden as fundamentals and yet active in combinations with the 3676 cm^{-1} fundamental frequency.

The theoretical work on muscovite and biotite consisted largely of studying the selection rules for the space groups C_{2h}^4 and C_{2h}^6 which are applicable to these crystals. Various possible positions of the OH groups were tried but only one reasonable arrangement was found to give predicted results consistent with our experimental data (apart from the anomaly discussed above). A full account of this work is being given in the Final Report on Contract DA 36-039 sc-5581, since it is inappropriate to divide the theoretical treatment of the spectra of muscovite and biotite into two parts.

Accurate scale models have been constructed of the unit cells of muscovite and biotite in order to study more clearly the environment of the OH groups in the two cases. This work is continuing in an attempt to see why the OH configurations are so different in these two micas.

C. Gypsum Problem

The infrared spectrum of a single crystal of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has now been investigated very fully on the experimental side. The absorption spectrum has been obtained with the incident radiation normal to the best cleavage direction (i.e. normal to the (010) plane). The reflection spectrum has been obtained normal to the (010) plane, normal to the (-101) plane and normal to the (100) plane. The absorption spectra are now being derived from the reflection spectra following the method of Robinson and Price (Proc. Phys. Soc. 66, 969 (1953)). This is a very tedious process and so arrangements have been made with the Willow Run Research Center to have the computations done on their computing machine MIDAC. The programming has been completed during the past few weeks and it should now be a relatively easy matter to obtain the absorption spectra.

D. Barium Titanate Problem

The spectrum of a single crystal of BaTiO_3 (from the Bell Telephone Laboratories) has been obtained between 1μ and 15μ (Fig. 3). There is only one weak band observed at 8μ , followed by a steep rise in absorption at 9.5μ to a "cut off" which extends beyond 15μ . The thickness of the crystal was approximately 0.15 mm. It is interesting to note the resemblance between this spectrum and that recently reported by Noland (Phys. Rev. 94, 724 (1954)) for a single crystal of SrTiO_3 . The latter showed a steep cut off at 10μ and weak bands near 5.5μ and 7.5μ .

V. CONCLUSIONS

Brucite

The work on portlandite has confirmed our earlier conclusions on brucite that the hydrogen atoms do not appear to be in the positions deduced from X-ray measurements. The only alternative is that some new phenomenon has been uncovered in the infrared spectra of crystals which cannot be accounted for on present theories.

Muscovite and Biotite

The work on the effect of temperature on the bands near 3μ , together with the theoretical work, confirms our earlier conclusion that the OH groups have very different orientations in muscovite and biotite.

A band near 150 cm^{-1} common to biotite and natural phlogopite cannot be due to OH groups.

Gypsum

No conclusions can be drawn from this work until the observed data on the reflection spectra have been converted into absorption spectra.

Barium Titanate

The difference in the new band found at 8μ from that in SrTiO_3 at 7.5μ may be significant.

VI. FUTURE PROGRAM

The work on the micas will be prepared for publication in a scientific journal.

A full account of the work on brucite and portlandite will be prepared for publication.

The work on gypsum will be continued. After reduction of the data to absorption spectra, the interpretation of these spectra will be sought in terms of the presently accepted structure based on X-ray data. Particular attention will be paid to the determination of the orientation of the water molecules.

The differences between the spectra of BaTiO_3 and SrTiO_3 will be further investigated, especially at longer wavelengths.

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. Haas (part time)
Mr. A. Dockrill (part time)

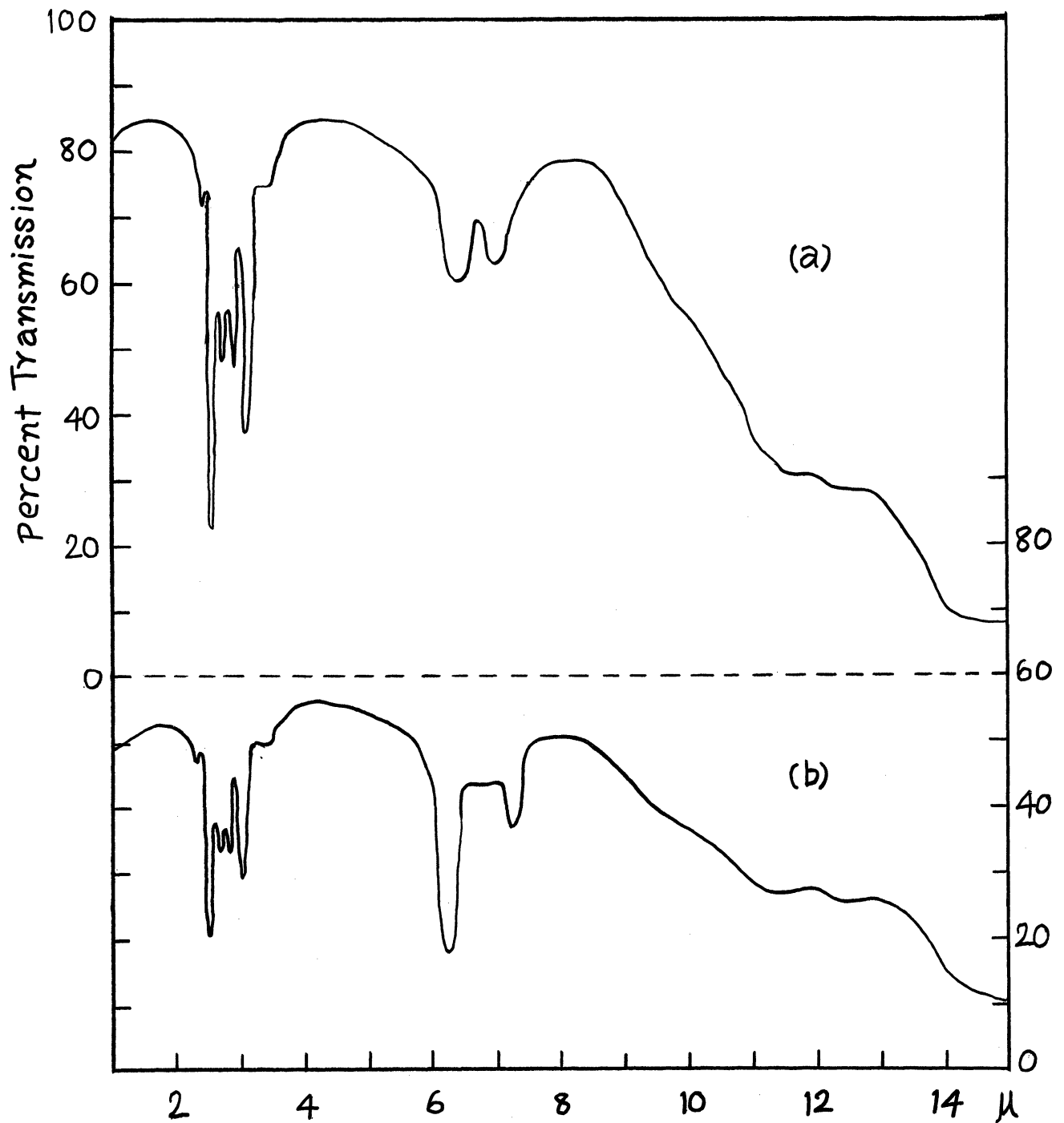


Fig. 1. Spectra of single crystal of Portlandite $\text{Ca}(\text{OH})_2$ with incident beam parallel to the C-axis, (a) 100 microns thick, (b) same sample which has been exposed to source radiation and atmosphere for a long period (NaCl prism dispersion).

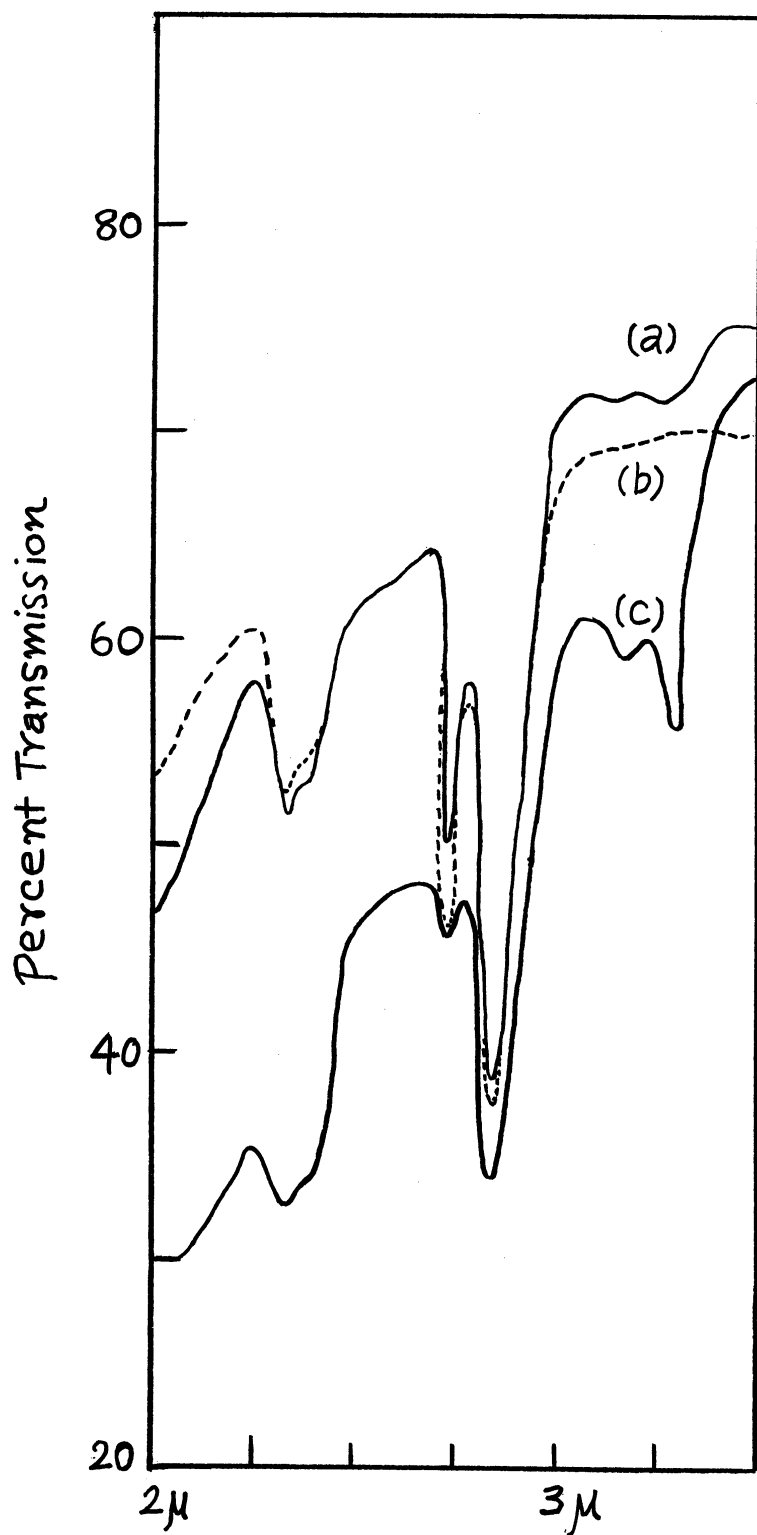


Fig. 2. Spectra of Biotite crystal with incident beam perpendicular to cleavage at (a) room temperature (b) liquid nitrogen temperature (c) 450° C. (NaCl prism dispersion).

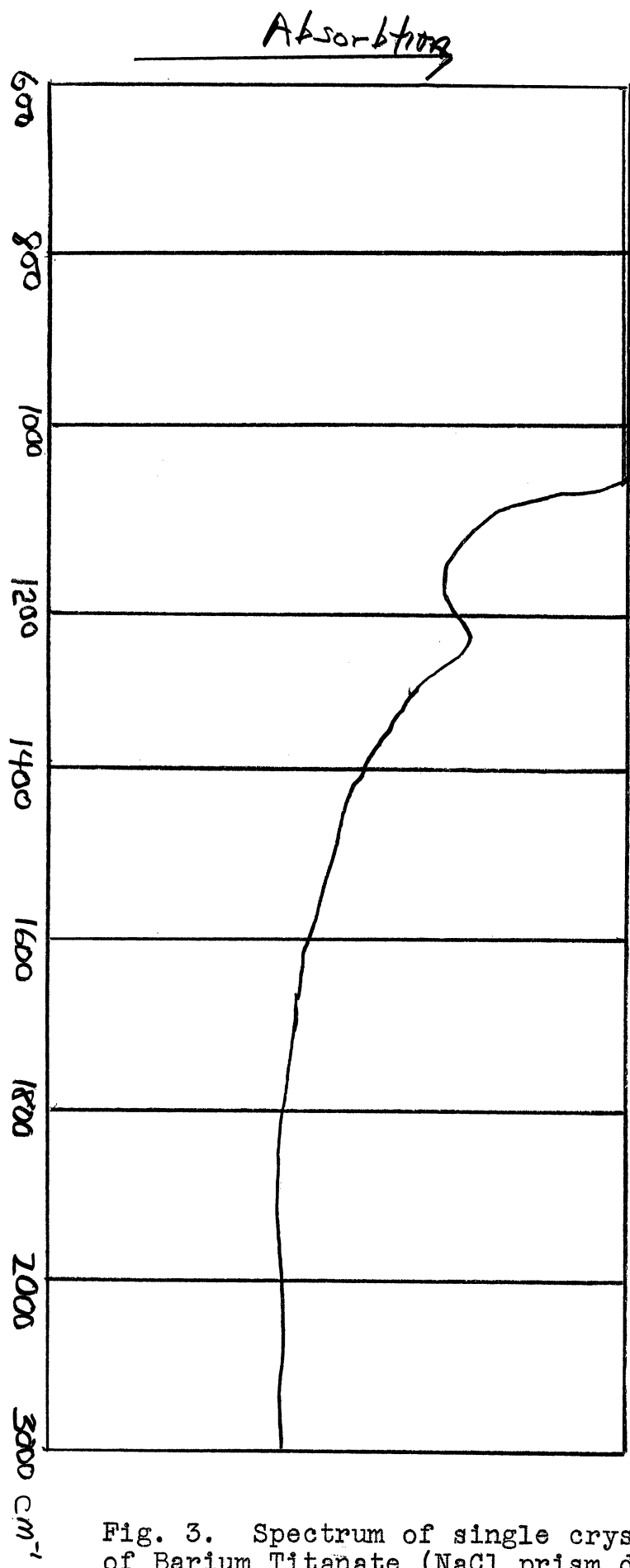


Fig. 3. Spectrum of single crystal of Barium Titanate (NaCl prism dispersion).

