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INFRARED STUDIES OF CRYSTALS II

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Principal Investigator

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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, gypsum and diamond.

II. ABSTRACT

This report summarizes the progress which has been made during the past three months on the preparation of our previous results for publication. No new experimental work has been done.

III. PUBLICATIONS AND CONFERENCES

No publications have been made during the period covered by this report. A conference was held at Ann Arbor with Dr. H. Kedesdy and Mr. A. Schwarz on Wednesday, January 31st at which the arrangements for the termination of this contract were discussed. It was agreed that during the remainder of the time preparation of the previous work for publication should be given top priority. Some of the current problems in infra-red research at the Signal Corps Laboratory were discussed, especially the estimation of oxygen in silicon.

IV. FACTUAL DATA

A. BARIUM TITANATE AND MICAS

Nothing new to report.

B. BRUCITE

The whole of the work on brucite and portlandite is being prepared for publication. The theory of the anomalous bands is being investigated by Dr. K. Hecht. The following note is being submitted to the Journal of the Optical Society:

Crystal Structure of Brucite and Portlandite in Relation to Infrared Absorption

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The infra-red spectrum of brucite ($Mg(OH)_2$) shows an unexpected band with a very interesting fine structure in the region between 2.3μ and 3.5μ. When we first reported this phenomenon [1], the conclusion was drawn that the unit cell in brucite must be larger than that found from X-ray analysis [2] and that the positions of the hydrogen atoms had been incorrectly deduced.[3] This conclusion was questioned by Petch and Megaw [4] who reinvestigated the crystal structure of brucite and also that of the isomorphous crystal, portlandite ($Ca(OH)_2$), finding no evidence in either case for a unit cell larger than that found in the earlier X-ray work. Petch and Megaw [4] also reported that the infra-red spectrum of portlandite exhibited features very similar to those found in brucite. Since the crystals of portlandite used in these observations was much more nearly perfect than the brucite crystals, it was clear that the anomalous fine structures could not have arisen from the use of an imperfect crystal.

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The basis for our conclusion that the unit cell in brucite must contain more than two hydroxyl ions was that the fine structure was shown to be due essentially to hydrogenic vibrations and since it seemed unlikely that much of it could be due to the combination of OH stretching with OH deformation modes [5], it was assumed that more than one OH stretching fundamental was being observed. Recently we have examined the infra-red spectrum of brucite at the temperature of liquid nitrogen and we find that all of the bands on the low frequency side of the center of the band disappear. This shows that these bands are combination difference frequencies arising from energy levels due an exceptionally low OH deformation mode and that it is possible to explain the spectrum (in principle at least) without invoking a larger unit cell or changing the equilibrium positions of the hydrogen atoms from those proposed originally by Bernal and Megaw.[3] The possibility that a low frequency "libration" of the OH ion might be responsible for the fine structure was also pointed out by Hexter [6] who had observed an analogous effect in the spectrum of crystalline iodoform. Our observations at low temperature confirm Hexter's suggestion, although the full explanation of the fine structure still presents many difficulties. These will be discussed in a future and fuller presentation of this work.

It should be added that the hydrogen atoms in portlandite have recently been located by Petch [7] using refined X-ray analysis. Also Elleman and Williams [8] have located the protons in brucite by nuclear magnetic resonance. In each case the work confirms the Bernal-Megaw structure.

We are grateful for financial support from the U. S. Army Signal Corps under Contract DA-36-039 sc-56736.

[1] R. T. Mara and G.B.B.M. Sutherland, J. Opt. Soc. Am. 43, 1100 (1953).

[2] G. Aminoff, Geol. Foren. I Stockholm Forh. 41, 407 (1919).

[3] J. D. Bernal and H. D. Megaw, Proc. Roy. Soc. (London) A 151, 384 (1935).

[4] H. E. Petch and H. D. Megaw, J. Opt. Soc. Am. 44, 744 (1954).

[5] R. T. Mara, Ph.D. Dissertation, University of Michigan (1954).

[6] R. M. Hexter and H. Cheung, Ohio State Symposium on Molecular Structure 1955 p.22. Also private communication from R. M Hexter.

[7] H. E. Petch, Phys. Rev. 99, 1635 (1955).

[8] Private Communication from Professor Dudley Williams.

C. DIAMOND

Nothing especially new to report.

D. GYPSUM

The manuscript of the paper on gypsum is almost complete. It has taken much longer than was anticipated to get this material into shape. A copy of the manuscript will be included in the Final Report since there is not sufficient time for it to be reproduced in full (with diagrams) for this report.

V. CONCLUSIONS

Nothing new to report.

VII. FUTURE PROGRAM

Work will continue on the preparation of manuscripts for publication.

VIII. PERSONNEL

The following people have been engaged on the work reported here:

Professor G.B.B.M. Sutherland (part time)

Dr. K. Hecht (part time)

Mr. A. Dockrill (part time on model construction and preparation of diagrams)

Mrs. C. Walker (part time on typing and secretarial work).