Corrections to First Annual Report

Pg. 4 In the last line of the third paragraph, "isotropic" should read "anisotropic".

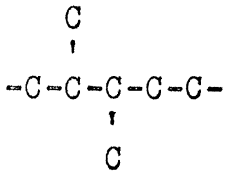
Pg. 11 In the eleventh line of the third paragraph, "when a small amount of $BaTiO_3$ is added" should read "when a small amount of $BaCO_3$ is added".

Pg. 11 In the fifth line of the last paragraph, the statement is made, "strontium and barium titanates have the same tetragonal structure at room temperature." Actually, $SrTiO_3$ has a cubic structure at room temperature. However, in the sense that $BaTiO_3$ and $SrTiO_3$ have similar TiO_6 octahedra in their structures, similarities are to be expected in their spectra.

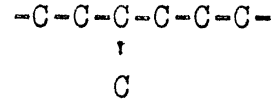
Pg. 27 In Fig. I, atom number five (5) is a titanium atom, and should be blacked in.

Pg. 39 In line 12 from the bottom, "Si-O bands" should read "Si-O bonds".

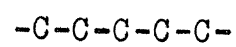
Pg. 52 In Table III, the representation of 2,3-dimethylpentane should be:



3-methyl hexane should be:



n-pentane should be:



Engineering Research Institute

University of Michigan

Ann Arbor

Quarterly Report No. 4

on

Infrared Studies of Crystals

(Period: 15 May 1952 to 15 August 1952)

G. B. B. M. Sutherland
Principal Investigator

R. T. Mara

W. G. Simeral

Project M957
Signal Corps, Department of the Army
Contract DA 36-039 sc-5581
SC Project 152B-0, DA Project 3-99-15-022
Squier Signal Laboratory, Fort Monmouth, N. J.
September 1952

Table of Contents

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on

Infrared Studies of Crystals

I. Purpose of the Research

The objectives of the research for the period covered by this report are essentially the same as those given in The First Annual Report, and therefore will not be repeated here.

II. Account of Work Done and Future Program

(A) BARIUM TITANATE (Mr. R. T. Mara): Preliminary work has begun on the 15-33μ region of the $BaTiO_3$ absorption spectrum. The spectrum of Sample No. 1067BT-7720-HJS-HDP is shown in Fig. I. It was stated in the First Annual Report that the band commencing at about 750 cm^{-1} may consist of two components. While Fig. I shows no indication of any doublet structure, the results are not as yet conclusive. It is difficult to locate the center of this absorption accurately from the spectrum shown in Fig. I; however, it appears to be in the neighborhood of 575 cm^{-1}.

The only other characteristic in this spectral range is an absorption beginning at about 470 cm^{-1}. This absorption is still present at 300 cm^{-1}. It may be noted that TiO_2 showed two bands in this range with maxima at 405 cm^{-1}, and 340 cm^{-1} (First Annual Report).

The $BaTiO_3$ sample used was supplied by the National Lead Co. through the Signal Corps. The spectrum in the 1-15μ region is almost completely clear of any impurity bands. It may therefore be assumed that this sample is chemically pure.

The sample was prepared in the manner described in the First Annual Report.

(B) MICA (Mr. R. T. Mara); Spectra have been taken of some mica samples in the 300-700 cm^{-1} range. A phlogopite spectrum is shown in Fig. I(a). The main characteristics in this region are the band near 625 cm^{-1} and the broad absorption centered at about 445 cm^{-1}. The sample used for Fig. I(a) contains 0.58% fluorine and 2.80% water by weight as ascertained by chemical analysis.

Preliminary investigations indicate that samples of varying fluorine and water content show some differences in their spectra. The spectrum of a phlogopite sample containing 6.74% fluorine and 1.06% water is shown in Fig. II (b). It is noted that the general absorption in the 600-700 cm^{-1} interval is less for the sample of lower OH content. Also, the center of the band has been shifted to about 650 cm^{-1}. Furthermore, the absorption in the 300-550 cm^{-1} interval is different for the two samples. In Fig. II(b) (low OH, high F) this region appears to be split into two absorption bands, one centered at about 480 cm^{-1} and the other at about 350 cm^{-1}. In addition, the general absorption near 300 cm^{-1} is large compared to the spectrum shown in Fig. II(a).

These variations cannot be considered significant at this time. A more extensive study is required before any correlations can be made between hydroxyl content and the form of the spectrum.

This spectral region (300-700 cm^{-1}) has also been investigated for some of the muscovite and biotite samples mentioned in the First Annual Report (see Figs. IV and IX of the Annual Report). These samples showed the 3.1μ and 7.05μ bands that were tentatively assigned to bonded OH frequencies. These two samples have spectra which are very similar to that shown in Fig. II(a), except that they appear to have a sharp band at 350 cm^{-1} superimposed on the broad 300-550 cm^{-1} absorption.

The spectra shown in Figs. I and II were obtained on a Perkin-Elmer Model 112 double pass instrument using a KRS-5 prism. Since the thermocouple available at this time has a KBr window, we were limited to frequencies above 500 cm^{-1}.

FUTURE PROGRAM: The investigation of the long wave length spectrum of $BaTiO_3$ will be continued. In conjunction with this, the chemically pure samples of $CaTiO_3$, $MgTiO_3$, and $SrTiO_3$ supplied by the National Lead Co. will be investigated.

A more complete set of observations will be made on the micas, that is, the spectra will be obtained of a series of phlogopites containing varying amounts of fluorine and hydroxyl groups. Also the samples showing the 3.1μ and 7.05μ bands (tentatively assigned as bonded OH frequencies in the First Annual Report) will be compared in the long wave length region with samples not displaying these bands.

Further, an attempt will be made to deuterate a mica sample. If the deuteration is successful, then a further check can be made on the OH assignments.

Polarization experiments on the micas will continue. We shall probably concentrate on the OH overtone at 1.4μ, since it seems to show the most extreme dichroism (see First Annual Report).

C. Diamond (Mr. W. G. Simeral): It is our purpose in this section of the report to discuss briefly the relation between the infra-red spectra of diamond, germanium and silicon. It is well known that all three of these substances have the same crystalline structure. For this reason, it is to be expected that the lattice vabrations of the three substances should be similar. Differences will arise from the different atomic masses and elastic constants associated with the individual substances.

In Fig. III are shown typical spectra of crystals of silicon, germanium, and Type I diamond. It has been possible to adjust the wavelength scales so that bands having similar origin will lie in corresponding positions along the horizontal scale. The correspondence is obvious for many of the bands, although the relative intensities of the bands differ between substances. The structure of the absorption near 30μ in germanium has not been reported in sufficient detail to allow close comparison with diamond. However, it can be seen that there are no bands in silicon or germanium which correspond to the narrow 7.3μ band in diamond. As noted in the First Annual Report, the 7.3μ band is in the so called Group II of infrared bands, while the broader bands having corresponding bands in silicon and germanium are either overtones or Group I bands.

H. M. J. Smith[1] has calculated the vibrational spectrum of diamond from its elastic constants, and the value of the strongest Raman line i.e. 1332 cm^{-1}. Using a general force field with only interaction between nearest neighbors, the distribution shown in Fig. IV(a) is obtained. The addition of central forces between second neighbors gives a different

distribution illustrated in Fig. IV(b). The second distribution, was used to calculate the variation of specific heat with temperature, and the result was in good agreement with experiment. The first distribution did not produce good agreement.

Y. Hsieh[2] has made a calculation for germanium which is similar to Smith's first calculation on diamond, i.e. he used only first neighbor interaction. The resulting distribution is shown in Figure V. This distribution gives good agreement with specific heat data.

When these calculated distributions are compared with the observed spectra, it is possible to identify various bands as fundamentals and others as overtones or combinations. Further discussion of these correlations will be given in the next report.

Finally, we wish to point out that the Group II bands in diamond (as characterized by the 7.3μ band) are not represented in the calculated distributions as shown in Figure IV. Consequently, it is not surprising that similar bands do not appear in silicon and germanium, since the Group II bands must have an origin different from the other infrared bands.

Bibliography:

1. H.M.J. Smith, Phil. Trans. Roy. Soc. A241, 105 (1948)

2. Y. Hsieh, Bull. Am. Phys. Soc. 27, 2, 15 (1952)

Future Program:

The construction of the vacuum ultraviolet spectrographic equipment has been completed. The equipment will be used to examine the absorption of diamonds in the wavelength region below 2000 A°.

Four diamonds which have already received 6 hours of neutron bombardment in the Oak Ridge pile have been returned for additional bombardment. Changes in the infrared spectrum have not yet occurred as a result of bombardment, but it is hoped that testing after each successive period of irradiation may enable us to detect any onset of structural alteration.

A new collection of 150 diamonds has been received on loan from Dr. Grenville-Wells, presently at Massachusetts Institute of Technology. She has investigated the x-ray and ultraviolet spectra of many of these stones. We propose to investigate the infrared spectra of selected stones from this collection which contains many especially interesting diamonds.

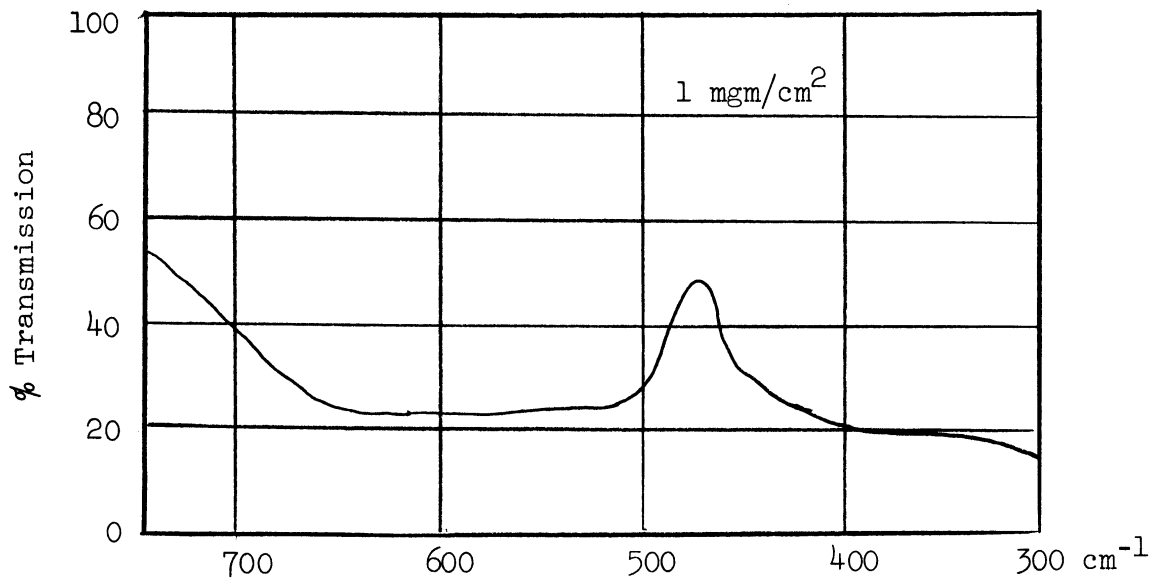


Fig. I. C.P. $BaTiO_3$, (Nat'l. Lead Co.) Sample No. 1067BT-7720-HJS-HDP

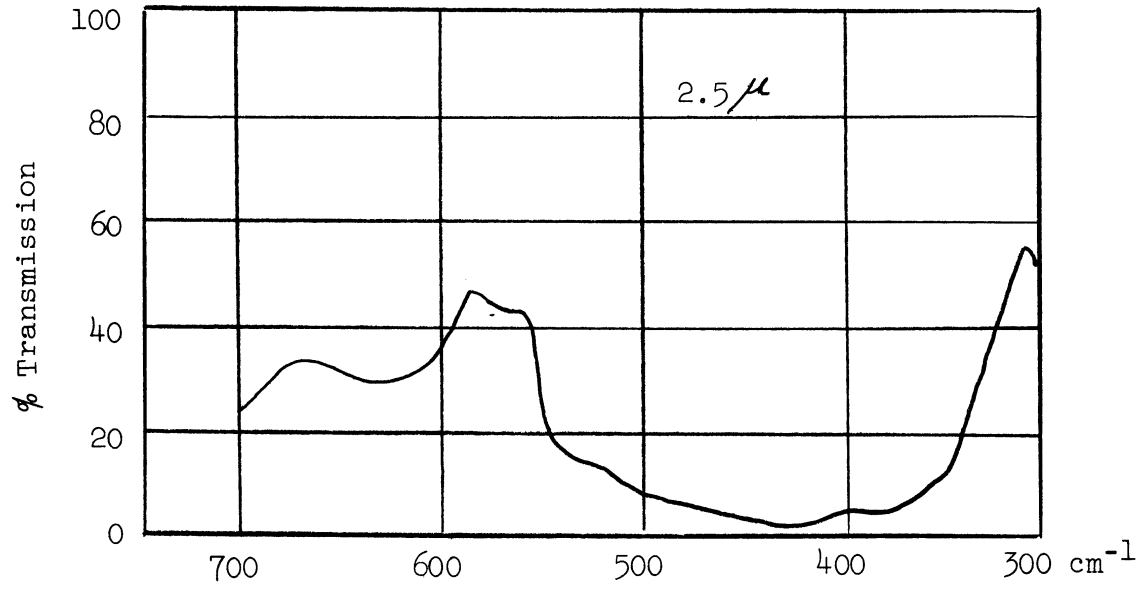


Fig. II (a). Phlogopite (0.58% F, 2.80% H_2O)

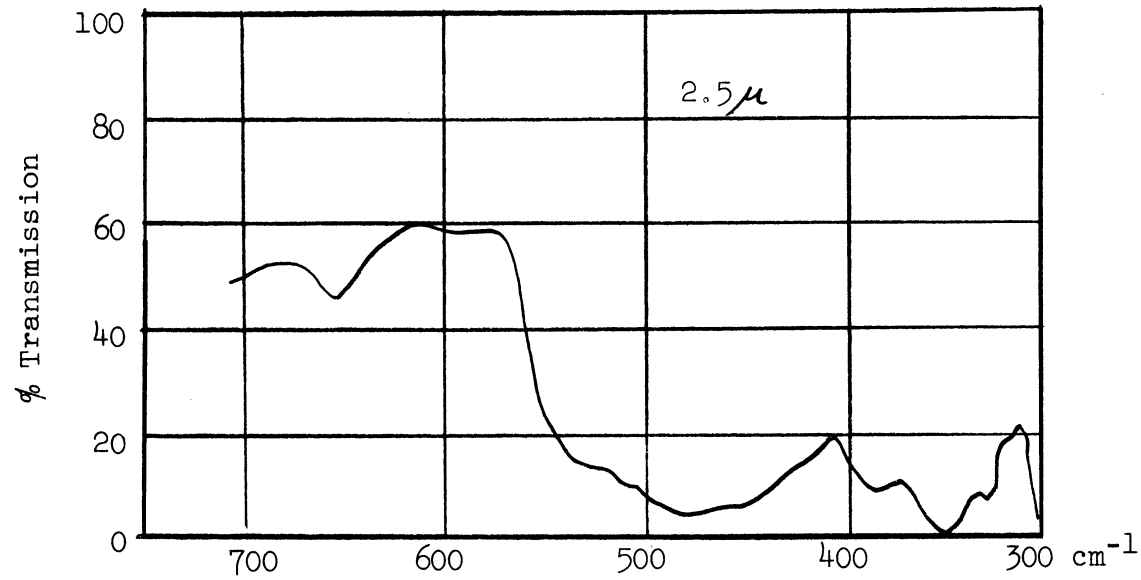
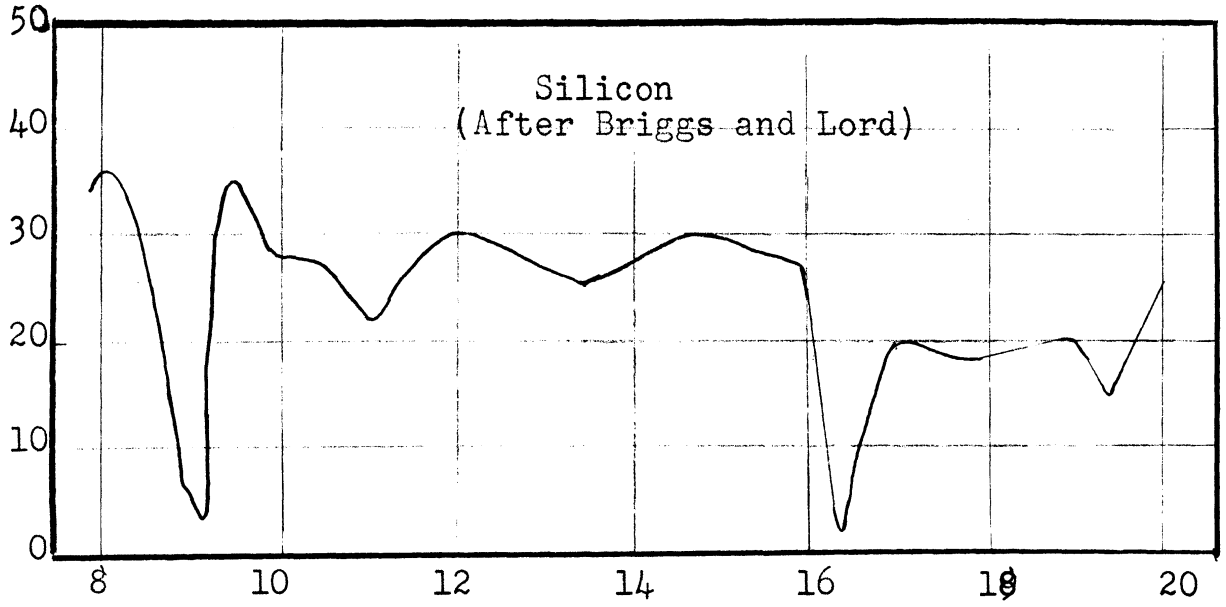
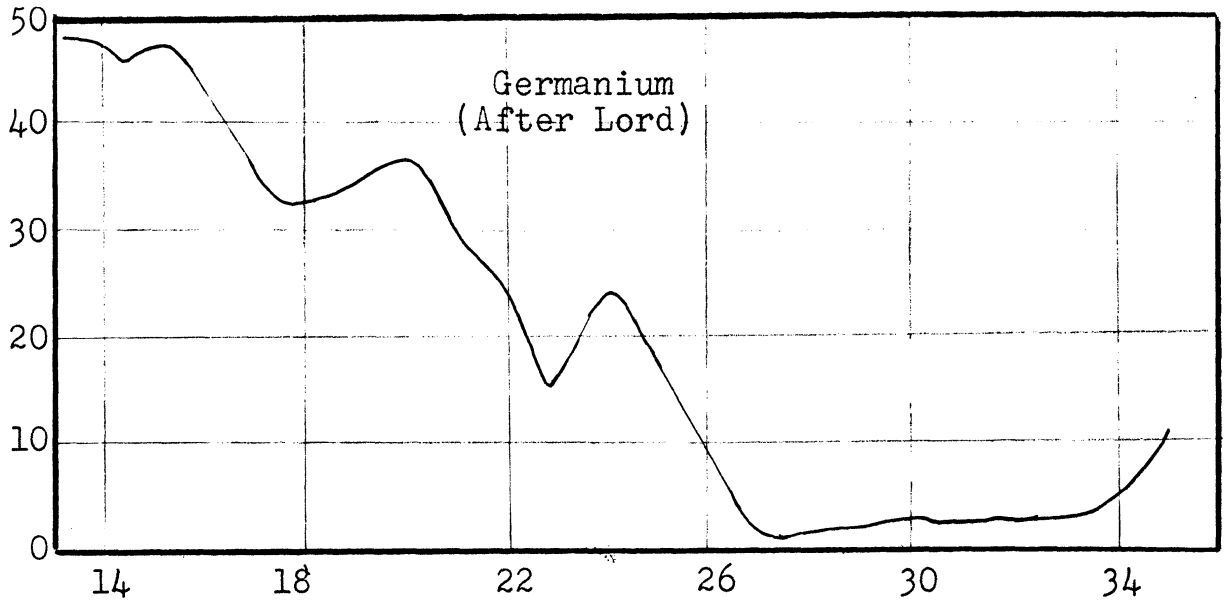


Fig. II (b). Phlogopite (6.74% F, 1.06% H_2O)





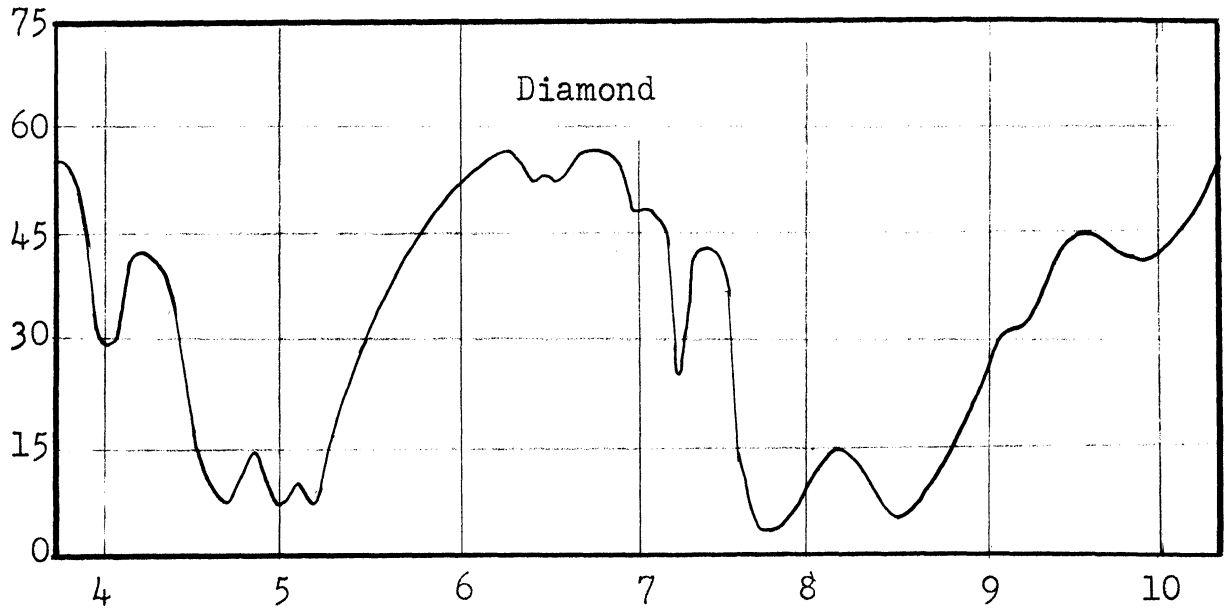
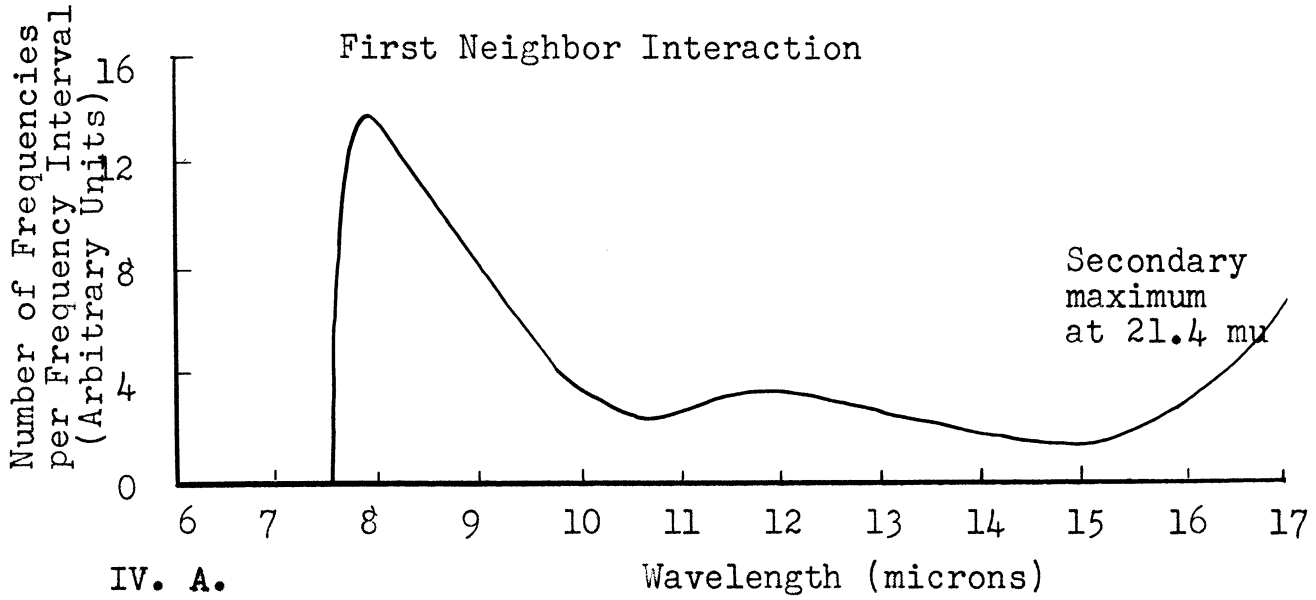


Fig.III :- Infrared Transmission vs Wavelength (microns) for crystals of the diamond structure.

H.B.Briggs, Phy. Rev. 77, 727 (1950)
R.C.Lord , Phy. Rev. 85, 140 (1952)



IV. A.

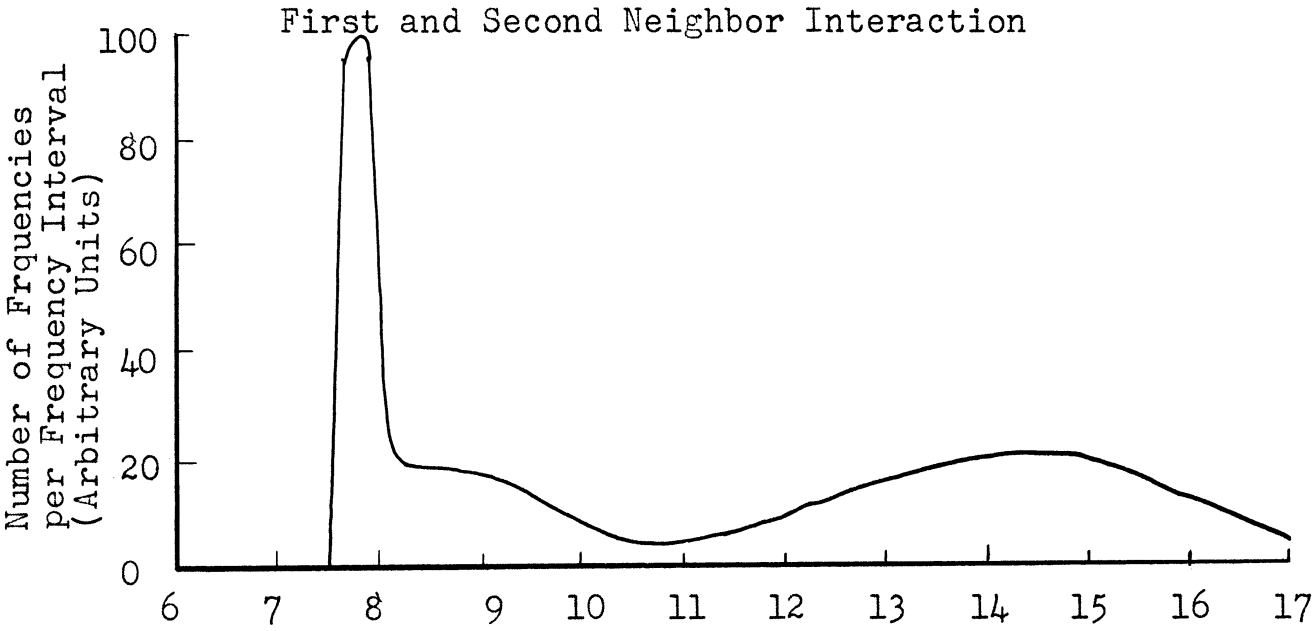
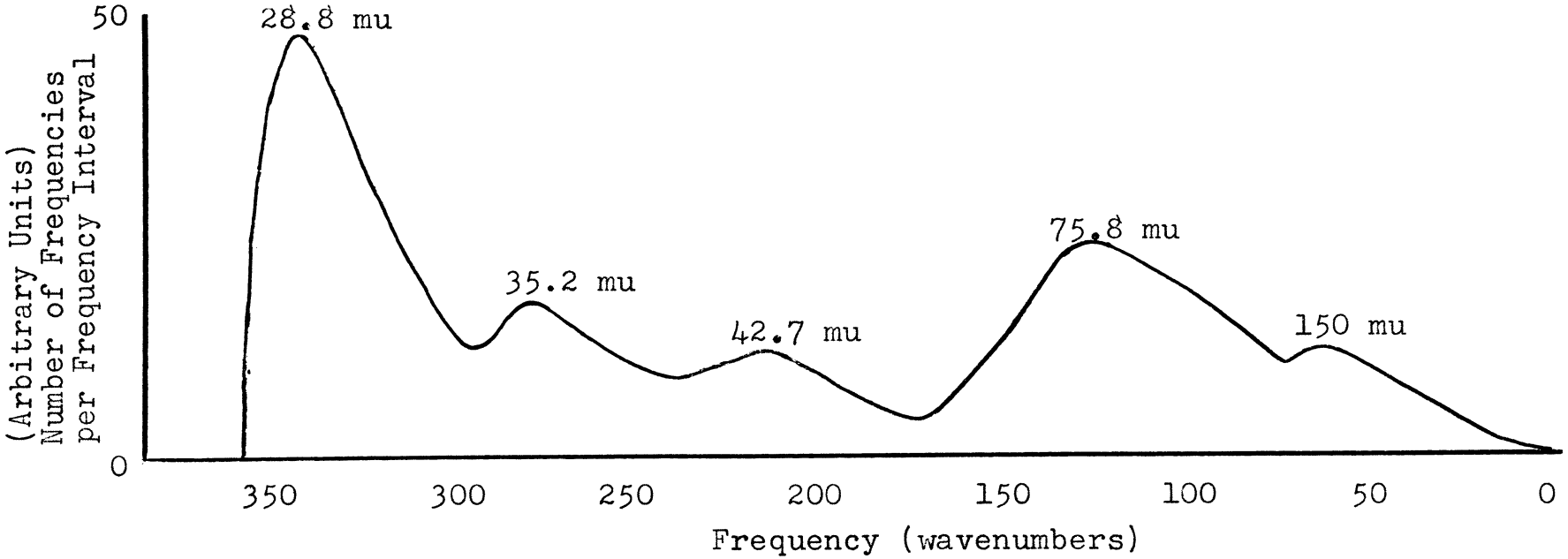


Fig.IV.B:-The Frequency Distribution of Diamond as Calculated by Smith.



Note: Maxima marked in microns.

Fig. I :- The Frequency Distribution of Germanium as Calculated by Hsieh using first neighbor interaction.