α and β Bands in NaF, NaCl, and KCl

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By means of a vacuum spectrophotometer, α and β bands have been observed in NaF, NaCl, and KCl irradiated by soft x rays. At liquid nitrogen temperature, the positions of α band are 9.4_3 ev in NaF, 7.1_6 ev in NaCl and 6.9_5 ev in KCl, and the positions of β band are 9.7_5 ev in NaF, 7.3_8 ev in NaCl, and 7.3_1 ev in KCl. The doublet structure of β band in NaCl, expected by Fuchs' theory has not been detected. This may be due to the fairly wide band width of the component bands.

ALPHA and β bands, the absorption bands which appear in the tail of the fundamental absorption band in alkali halides when irradiated by x rays, were found in KI by Delbecq, Pringsheim, and Yuster.[1] These bands have since been investigated in many alkali bromides and iodides.[2] For alkali chlorides and fluorides, however, no work on these two bands seems to have been published, probably because the wavelengths of these bands are outside the range of ordinary quartz spectrograph.

The optical absorption in LiF, NaF, NaCl, and KCl was studied over the wavelength range from the fundamental absorption edge to F band by means of a vacuum spectrophotometer which had the maximum resolution of about 3 A and the available wavelength range from 105 mμ to 600 mμ. With the use of a cryostat, transmittance of the crystal specimens was measured with and without the irradiation of soft x rays at and above the temperature of liquid nitrogen.

Crystals used were all obtained from the Harshaw Chemical Company. With NaCl and KCl, weak absorption of OH was observed at 184 mμ and 202 mμ, respectively. KCl crystals, even the best of them, showed a strong absorption band at 167 mμ at liquid nitrogen temperature. At room temperature, this band is overshadowed by the fundamental absorption band and becomes undiscernible.

Both α and β bands were observed in NaF, NaCl, and KCl. When these crystals were irradiated by x rays (30 kv 25 ma; through 0.2 mm Be window) at liquid nitrogen temperature, the two bands appeared in all crystals, but when irradiated at room temperature the α band was undetectable.

The α band and β band in NaF, NaCl, and KCl were detected by the following evidences. For β band: (1) it is present in additively colored and in x-ray irradiated crystals, (NaCl); and (2) its intensity is proportional to the intensity of the F band, (NaF, NaCl, and KCl). For α band: (1) it is found a little lower than β band in energy; (2) it is stable at liquid nitrogen temperature, but not at room temperature; and, (3) it appears in β

(F) colored crystals if bleached at liquid nitrogen temperature.

The α band is distinctly separated from β band in the case of KCl. In NaF and NaCl, it is superposed on β band; its position was found from the change in band shapes when colored crystals were bleached at a low temperature. An example is shown in Fig. 1.

The position and other characteristics of α and β bands in NaF, NaCl, and KCl are shown in Table I.

The shape of β band in NaCl was carefully examined, but there was no apparent structure. (See Fig. 1.) With
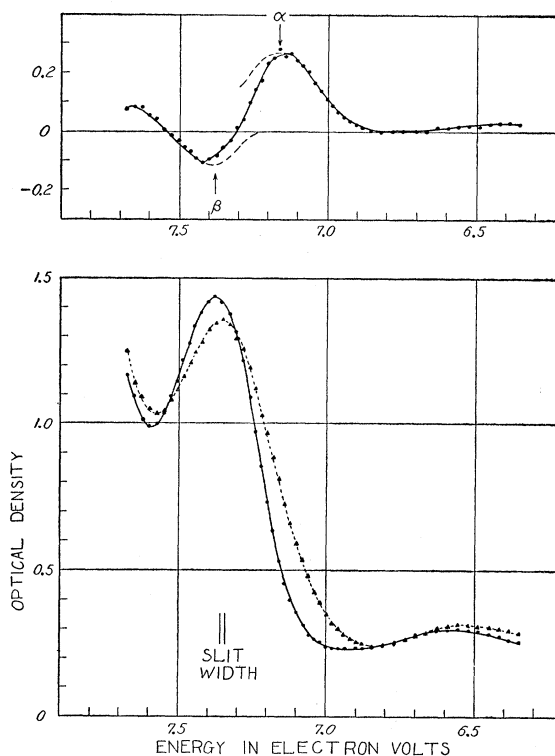

FIG. 1. β band in NaCl and appearance of α band by bleaching. Lower figure shows the optical density of a NaCl specimen. Full line—x-ray irradiated at room temperature and measured at liquid nitrogen temperature. Dotted line—bleached with white light for 90 minutes at liquid nitrogen temperature. Upper figure is the plot of the difference between these two curves showing the decrease of β band and the appearance of α band. The broken lines suggest the true shapes which were balanced up as the full line.

[1] C. J. Delbecq, P. Pringsheim, and P. Yuster, J. Chem. Phys. 19, 574 (1951).
[2] W. Martienssen, Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. 1952, 111.

TABLE I. Position and width of α and β bands, and intensity ratio between β and F bands at their peaks.

	α Position mμ	ev	Width ev	β Position mμ	ev	Width ev	β max./F max.
NaF	131.5	9.43	0.4	127.0	9.75	0.36	0.9
NaCl	173.0	7.16	0.3	168.0	7.38	0.31	0.90
KCl	178.5	6.95	0.2	169.5	7.31	0.18	0.85

KCl no definite structure was found either, but the accuracy of measurement was not as good as with NaCl because of impurity band. According to the model used by Fuchs, one expects to find in β band of NaCl and KCl a doublet structure with a separation of 0.10 ev,[3] which however was not detected. The reason for the failure to uncover this fine structure may have been that the width of component bands in NaCl is fairly

[3] R. Fuchs, Phys. Rev. 111, 387 (1958).

wide. KCl will be better suited for the examination of the fine structure because of its narrower band width.

LiF was also investigated. Under x-ray irradiation either at room temperature or at liquid nitrogen temperature, a new absorption band of the width of about 0.6 ev was found at 111.5 mμ (11.1 ev). This new band can be bleached by light from a low-pressure mercury lamp, but its origin has not been ascertained.

Note added in proof.—Dr. K. Kobayashi of Tohoku University suggested to the authors that the 167-mμ band in KCl might be due to bromine impurity. He kindly sent the authors his specially made KCl crystal in which the bromine content was reduced to 9×10^{-6} in mole fraction. There was only slight absorption at 167 mμ by this crystal, far feebler than by Harshaw crystal used in the present study. The position of β band was found in the crystal at 168.5 mμ (7.35 ev). The doublet structure of the β band remained still unresolved at liquid nitrogen temperature.

Center Law of the Lattice Vibration Spectra*

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The lattice vibration spectra of a solid, as a whole, can be characterized by one single frequency, defined as the frequency of "the center of gravity" of the infrared spectrum, simply called "center frequency." The data of this frequency have been determined for many nonconducting solids (compounds) from the experimental spectra of lattice vibrations in reflectance as well as in absorption. A striking experimental phenomenon is discovered: The center frequency, whether determined from the reflectance or from the absorption type spectrum, is found to be equivalent and identical with Debye's characteristic frequency. This phenomenon is exhibited for a large variety of nonconducting compounds covering almost the entire range of the vibrational spectra of solids. Moreover, the center frequency remains constant with varying temperature. The equality of the center frequency of the infrared spectrum and the characteristic frequency from specific heat constitutes the "center law of the lattice vibration spectra."

I. INTRODUCTION

THE vibrational (infrared) spectrum of a substance is related to the forces that hold matter together in the solid state. The higher the region of resonance frequencies in the vibrational spectrum, the greater the cohesive forces. The full experimental spectra of lattice vibrations of various solids (commonly shown either in reflectance, or in transmittance, or again as the Raman type, but rarely in absorption), as a function of frequency, differ in range, in number of resonance frequencies, in intensities, and in line widths.[1]

* The gist of this paper was presented by the author at the Gordon Research Conference on Chemistry and Physics of Solids (Lattice Dynamics), August 18, 1959, at Meriden, New Hampshire. In its early stage, it was presented at the International Meeting of European Spectroscopists, Freiburg/Br., Germany, July 12, 1957 (unpublished).

[1] See, for example, R. B. Barnes et al., Infrared Spectroscopy: Industrial Applications and Bibliography (Reinhold Publishing Corporation, New York, 1944).

II. CENTER OF GRAVITY OF THE VIBRATIONAL SPECTRUM

In certain cases it is useful to characterize the experimental spectrum of lattice vibrations by one single frequency, such as the frequency of maximum absorption (ν_0) (which is very close to the minimum of transmittance), or of maximum reflectance (ν_r), or the reststrahlen frequency (ν_{rest}).[2] However, for a number of substances, such as LiF, SiO_2, diamond (I), etc., these frequencies are ambiguous. Thus in order to characterize the vibrational spectrum unambiguously and as a whole, we introduce the frequency of the "center of gravity"

[2] The reststrahlen frequency is the frequency selected from the infrared spectrum by multiple reflections on a number of polished plates of a crystal substance. In case of a symmetrical reflection curve, ν_{rest} is equal to the frequency of maximum reflectance (ν_r). In case of an unsymmetrical reflection curve, however, ν_{rest} may differ somewhat from ν_r, since the reststrahlen give an average frequency of any continuous spectral area of strong reflectance.