

TABLE I. Position and width of  $\alpha$  and  $\beta$  bands, and intensity ratio between  $\beta$  and  $F$  bands at their peaks.

	$\alpha$			$\beta$			$\beta$ max./ $F$ max.
	Position $m\mu$	Position ev	Width ev	Position $m\mu$	Position ev	Width ev	
NaF	131.5	9.4 <sub>3</sub>	0.4	127.0	9.7 <sub>5</sub>	0.3 <sub>6</sub>	0.9
NaCl	173.0	7.1 <sub>6</sub>	0.3	168.0	7.3 <sub>8</sub>	0.3 <sub>1</sub>	0.9 <sub>0</sub>
KCl	178.5	6.9 <sub>5</sub>	0.2	169.5	7.3 <sub>1</sub>	0.1 <sub>8</sub>	0.8 <sub>5</sub>

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  $\beta$  band of NaCl and KCl a doublet structure with a separation of 0.10 ev,<sup>3</sup> 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

<sup>3</sup> 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  $m\mu$  (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- $m\mu$  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  $9 \times 10^{-6}$  in mole fraction. There was only slight absorption at 167  $m\mu$  by this crystal, far feebler than by Harshaw crystal used in the present study. The position of  $\beta$  band was found in the crystal at 168.5  $m\mu$  (7.3<sub>5</sub> ev). The doublet structure of the  $\beta$  band remained still unresolved at liquid nitrogen temperature.

## Center Law of the Lattice Vibration Spectra\*

JOHANNES N. PLENDL

*Electronic Material Sciences Laboratory, Electronics Research Directorate, Air Force Cambridge Research Center, Air Research and Development Command, Bedford, Massachusetts*

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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.<sup>1</sup>

\* 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).

<sup>1</sup> 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 ( $\nu_0$ ) (which is very close to the minimum of transmittance), or of maximum reflectance ( $\nu_r$ ), or the reststrahlen frequency ( $\nu_{\text{rest}}$ ).<sup>2</sup> However, for a number of substances, such as LiF, SiO<sub>2</sub>, 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"

<sup>2</sup> 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,  $\nu_{\text{rest}}$  is equal to the frequency of maximum reflectance ( $\nu_r$ ). In case of an unsymmetrical reflection curve, however,  $\nu_{\text{rest}}$  may differ somewhat from  $\nu_r$ , since the reststrahlen give an average frequency of any continuous spectral area of strong reflectance.

(designated as  $\nu_{\text{ctr}}$ ) and define it by

$$\nu_{\text{ctr}} = \frac{\int_0^{\infty} \nu f(\nu) d\nu}{\int_0^{\infty} f(\nu) d\nu}, \quad (1)$$

where  $\nu$ =frequency,  $f(\nu)$ =reflectance  $R$  or absorption coefficient  $K$ ,  $f(\nu)d\nu$ =a small area of the spectrum of reflectance or absorption.

In order to determine  $\nu_{\text{ctr}}$  correctly by Eq. (1), we need to know experimentally the entire spectrum of lattice vibrations of a solid either in reflectance or in absorption.<sup>3</sup> The absorption spectrum can be derived either from transmittance spectra at various layer thicknesses,<sup>4</sup> or from reflectance spectra at various angles of incidence.<sup>5</sup> Such data, however, are available only for a very few solids. Hence, in this study, we generally equate  $f(\nu)=R$ , and, according to availability, also  $f(\nu)=K$ . In this case, we denote  $R$ =reflectance in percent, and define  $K$  by the formula

$$J = J_0 e^{-4\pi K(d/\lambda)},$$

which represents the radiation intensity  $J$  of wavelength  $\lambda$  after traversing a layer of the thickness  $d$ . The limiting frequencies of the spectrum are conveniently defined as those frequencies at which  $f(\nu)$  becomes very small and remains so beyond them.

Obviously, the resonance lines occur at both sides of  $\nu_{\text{ctr}}$ , and the latter does not need to coincide with any one of the strong lattice resonance vibrations of the spectrum. In other words, there may or may not be a resonance line at  $\nu_{\text{ctr}}$  itself in the experimental spectrum, whether observed in reflectance, or in absorption, or as Raman type.

As an example, Fig. 1 shows the determination of  $\nu_{\text{ctr}}$  from the reflectance spectrum of crystalline quartz ( $\text{SiO}_2$ ).<sup>6</sup> The easiest way to determine  $\nu_{\text{ctr}}$  [according to

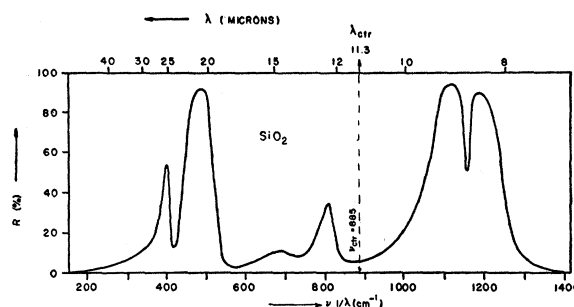


FIG. 1. Determination of  $\nu_{\text{ctr}}$  from the lattice vibration spectrum of crystalline quartz. This spectrum is shown in reflectance ( $R$ ) as a function of frequency ( $\nu=1/\lambda$ ). For the respective references see footnote 6. By cutting the area under the curve of the spectrum from cardboard and determining the point of equilibrium on the abscissa (as mentioned in the text) we obtain

$$\nu_{\text{ctr}} = 885 \text{ cm}^{-1} \quad \text{or} \quad \lambda_{\text{ctr}} = 11.3 \text{ microns.}$$

Eq. (1)] is to cut the area under the curve of the spectrum from cardboard and to determine the point of equilibrium by balancing it on a needle through a hole close to the abscissa. Trying at different points along the abscissa, we succeed at

$$\nu_{\text{ctr}} = 885 \text{ cm}^{-1} \quad \text{or} \quad \lambda_{\text{ctr}} = 11.3 \text{ microns.}$$

As the case of  $\text{SiO}_2$  shows, there is no resonance vibration at  $\nu_{\text{ctr}}$  itself.

Other examples for the determination of  $\nu_{\text{ctr}}$  are shown in Fig. 2 for  $\text{NaCl}$ , in Fig. 3 for  $\text{LiF}$ , and in Fig. 4 for  $\text{MgO}$ . These substances belong to the few solids where the spectrum of absorption is fully available, as is the spectrum of reflectance.<sup>6</sup> Both types of spectra are shown in Figs. 2, 3, and 4. In determining  $\nu_{\text{ctr}}$  in the manner mentioned above, and for each type of spectrum separately, we obtain

for  $\text{NaCl}$ :  $\nu_{\text{ctr}} = 188 \text{ cm}^{-1}$  or

$\lambda_{\text{ctr}} = 53 \text{ microns}$  for the absorption type, and

$\nu_{\text{ctr}} = 185 \text{ cm}^{-1}$  or

$\lambda_{\text{ctr}} = 54 \text{ microns}$  for the reflectance type;

for  $\text{LiF}$ :  $\nu_{\text{ctr}} = 410 \text{ cm}^{-1}$  or

$\lambda_{\text{ctr}} = 24.4 \text{ microns}$  for the absorption type, and

$\nu_{\text{ctr}} = 415 \text{ cm}^{-1}$  or

$\lambda_{\text{ctr}} = 24.1 \text{ microns}$  for the reflectance type;

for  $\text{MgO}$ :  $\nu_{\text{ctr}} = 525 \text{ cm}^{-1}$  or

$\lambda_{\text{ctr}} = 19.1 \text{ microns}$  for the absorption type,

$\nu_{\text{ctr}} = 515 \text{ cm}^{-1}$  or

$\lambda_{\text{ctr}} = 19.4 \text{ microns}$  for the reflectance type.

<sup>3</sup> For detailed representation of the experimental data of the lattice vibrations for a great number of solids, also comprehensive bibliography of pertinent literature, see H. H. Landolt-R. Boernstein, *Zahlenwerte und Funktionen aus Physik Chemie Astronomie Geophysik und Technik* (Springer-Verlag, Berlin, 1955), Vol. 4, Part 5, p. 546-666.

<sup>4</sup> See, for example, R. W. Wood, *Physical Optics* (Macmillan Company, New York, 1952), p. 102.

<sup>5</sup> J. Simon, *J. Opt. Soc. Am.* **41**, 336 (1951); also N. Neuroth, *Z. Physik* **144**, 85 (1956).

<sup>6</sup> (1) In the case of  $\text{SiO}_2$ , the data of reflectance ( $R$ ) as a function of the frequency are taken from measurements by J. D. Hardy and S. Silverman, *Phys. Rev.* **37**, 179 (1931); K. Korth, *Z. Physik* **84**, 684 (1933); and W. Stein, *Ann. Phys.* **36**, 470 (1939). (2) In the case of  $\text{NaCl}$ , the data of reflectance ( $R$ ) as a function of the frequency are taken from measurements by L. Kellner, *Z. Physik* **56**, 215 (1929); M. Czerny, *Z. Physik* **65**, 600 (1930); R. B. Barnes and M. Czerny, *Z. Physik* **72**, 447 (1931); C. H. Cartwright and M. Czerny, *Z. Physik* **85**, 269 (1933); and A. Mitsuishi, H. Yoshinaga, and S. Fujita, *J. Phys. Soc. Japan* **14**, 310 (1959); the data of the absorption coefficient  $K$  as a function of the frequency are evaluated from transmittance data at variable layer thicknesses taken from measurements of the above authors. (3) In the case of  $\text{LiF}$ , the data of reflectance ( $R$ ) as a function of the frequency

are taken from measurements by K. Korth, *Nachr. Ges. Wiss. Göttingen Jahresber. Geschäftsjahr Math.-Physik Kl. 5*, 576 (1932); H. W. Hohls, *Ann. Phys.* **29**, 433 (1937); M. Klier, *Z. Physik* **150**, 50 (1958); G. Heilmann, *Z. Physik* **152**, 368 (1958); the data of the absorption coefficient  $K$  as a function of the frequency are taken from R. B. Barnes, *Z. Physik* **75**, 723 (1932); G. Heilmann, *Z. Physik* **152**, 368 (1958). (4) In the case of  $\text{MgO}$ , the data of reflectance and absorption as a function of the frequency are taken from measurements by J. C. Willmott, *Proc. Phys. Soc. (London)* **A63**, 389 (1950).

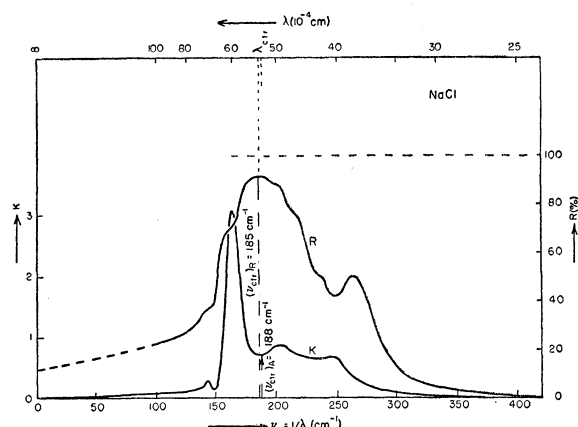


FIG. 2. Determination of  $\nu_{\text{etr}}$  from the lattice vibration spectrum of NaCl. Two types of this spectrum are shown: the absorption  $K$  (as an envelope) and the reflectance  $R$ , as a function of frequency ( $\nu = 1/\lambda$ ). The data of the absorption coefficient  $K$  are evaluated by the author from transmittance data at various layer thicknesses. For the respective references see footnote 6. By cutting the area under the curve of either type of the spectra from cardboard and determining the point of equilibrium on the abscissa (as mentioned in the text) we obtain

$\nu_{\text{etr}} = 188 \text{ cm}^{-1}$  or  $\lambda_{\text{etr}} = 53 \text{ microns}$  for the absorption spectrum, and

$\nu_{\text{etr}} = 185 \text{ cm}^{-1}$  or  $\lambda_{\text{etr}} = 54 \text{ microns}$  for the reflectance spectrum.

Although the two types of spectra are very different from each other, they show identical values of  $\nu_{\text{etr}}$  (considering the experimental inaccuracies of about  $\pm 3\%$ ). Also shown are the frequencies of maximum reflectance  $\nu_r$  and of maximum absorption  $\nu_0$ .

Although the two types of spectra, reflectance and absorption, are very different from each other for each one of these solids (as is characteristic for the alkali halides),  $\nu_{\text{etr}}$  remains equivalent for both types, considering the over-all inaccuracy averaging  $\pm 3\%$ . According to expectation, however,  $\nu_{\text{etr}}$  is entirely different for the Raman type of spectrum (not shown here).

In regard to the reflectance spectra, the center frequency in many cases is close to the frequency of maximum reflectance ( $\nu_r$ ) as Figs. 2 and 4 show. This agreement, however, by no means applies to  $\text{SiO}_2$  nor to LiF, as Figs. 1 and 3 show. On the other hand, in regard to the absorption spectra,  $\nu_{\text{etr}}$  is close to a minimum in all four cases (Figs. 1 to 4); i.e.,  $\nu_{\text{etr}}$  does not coincide with any resonance line there.

Investigating the temperature dependence of  $\nu_{\text{etr}}$ , we determine (1) from the absorption spectra of LiF at various temperatures<sup>6</sup>:

$$\text{at } 293^\circ\text{K} \quad \nu_{\text{etr}} = 410 \text{ cm}^{-1},$$

$$\text{at } 593^\circ\text{K} \quad \nu_{\text{etr}} = 400 \text{ cm}^{-1},$$

$$\text{at } 893^\circ\text{K} \quad \nu_{\text{etr}} = 415 \text{ cm}^{-1};$$

(2) from the reflectance spectra at  $293^\circ\text{K}$ :  $\nu_{\text{etr}} = 415 \text{ cm}^{-1}$  with no change indicated at  $87^\circ\text{K}$ .<sup>6</sup>

In the case of LiF, this comparison shows that  $\nu_{\text{etr}}$  remains constant with varying temperatures, from the vicinity of liquid air temperature to somewhat below the melting point, considering the over-all inaccuracy of

data determination (about  $\pm 3\%$ , averaging  $\nu_{\text{etr}} = 410 \text{ cm}^{-1}$ ).

Thus, as far as the available data allow, we establish the following unique fact concerning the center frequency:

The "center of gravity" of the lattice vibration spectrum remains the same, whether determined from the reflectance or from the absorption type of spectrum. It also remains constant for varying temperatures [within a range in reduced temperatures (see below) from  $T/\theta = 0.14$  to  $1.45$  in the case of LiF, which is the only one examined so far].

### III. CENTER OF GRAVITY OF THE VIBRATIONAL SPECTRUM AND THE CHARACTERISTIC TEMPERATURE

Another frequency also peculiar for each substance, according to Debye, is defined by the characteristic temperature  $\theta$  as

$$\nu_0 = k/h\theta, \quad (2)$$

where  $k$  = Boltzmann's constant, and  $h$  = Planck's constant. The characteristic temperature can be determined from various data such as specific heat, or elasticity, compressibility, melting point, and electrical resistance.<sup>7</sup> But we restrict the term  $\theta$  to the representation of specific heat data only.

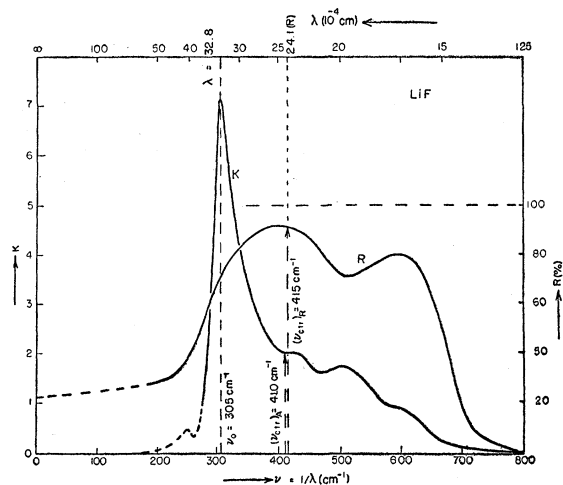


FIG. 3. Determination of  $\nu_{\text{etr}}$  from the lattice vibration spectrum of LiF. Proceeding in the same manner as mentioned in Fig. 2, we obtain

$\nu_{\text{etr}} = 410 \text{ cm}^{-1}$  or  $\lambda_{\text{etr}} = 24.4 \text{ microns}$  for the absorption spectrum, and

$\nu_{\text{etr}} = 415 \text{ cm}^{-1}$  or  $\lambda_{\text{etr}} = 24.1 \text{ microns}$  for the reflectance spectrum,

i.e., both quantities of  $\nu_{\text{etr}}$  are identical to each other, considering the experimental inaccuracies of about  $\pm 3\%$ . For the respective references see footnote 6.

<sup>7</sup> For detailed representation of the specific heat of solids, tables of  $\theta$  values and their discussion, also bibliography of pertinent literature, see the comprehensive articles by M. Blackman and G. Leibfried in *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), Vol. VII/1, pp. 325-382 and 104-324, respectively.

In reality, the Debye theory is not in perfect agreement with experiment.<sup>7</sup> Hence  $\theta$ , instead of being a constant, is a function of  $T$ . Within the practical range of temperatures, however, the deviation of  $\theta$  from the respective constant is but a few percent for many solids, although it may extend to a higher percentage for some solids. Nevertheless, it is customary to consider  $\theta$  as a constant. In this case  $\theta$  refers, in general, to the middle portion of the  $c_v$  curve (see Fig. 5), except for the very high  $\theta$  values (as for the diamond) where the lower portion prevails (since  $T/\theta$  is very small at room temperature).

The characteristic frequency ( $\nu_\theta$ ) was assumed by Debye as a maximum and cutoff frequency, in such a manner that above  $\nu_\theta$  no vibrations should exist, and below  $\nu_\theta$  a continuous frequency distribution represented by a parabola [ $f(\nu) \propto \nu^2$ ] should occur. The known experimental spectra of lattice vibrations of many solids reveal, however, that a considerable number of distinct resonance vibrations exist, without any preference for  $\nu_\theta$ , and that they are located at both sides of  $\nu_\theta$ . Hence the latter does not show up directly in the experimental spectrum; and this is the very same property which  $\nu_{ctr}$  exhibits.

A striking experimental phenomenon is discovered when we compare the characteristic frequency  $\nu_\theta$  with the frequency  $\nu_{ctr}$  for as many solid compounds as we have data on hand. It appears that both wavelengths  $\lambda_\theta$  and  $\lambda_{ctr}$  are equal throughout the entire range of vibrational spectra of solids.<sup>8</sup>

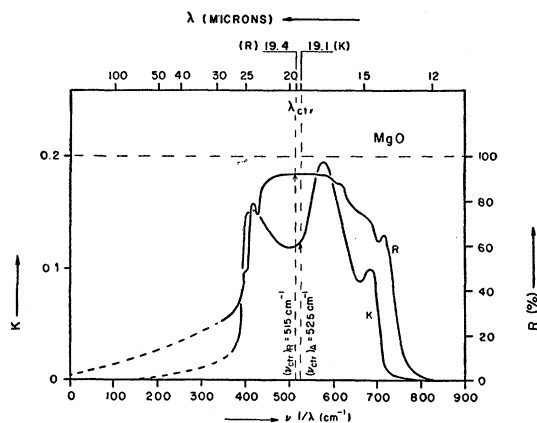


FIG. 4. Determination of  $\nu_{ctr}$  from the lattice vibration spectrum of MgO. Proceeding in the same manner as mentioned in Fig. 2, we obtain

$\nu_{ctr} = 525 \text{ cm}^{-1}$  or  $\lambda_{ctr} = 19.1$  microns for the absorption spectrum, and

$\nu_{ctr} = 515 \text{ cm}^{-1}$  or  $\lambda_{ctr} = 19.4$  microns for the reflectance spectrum, i.e., both quantities of  $\nu_{ctr}$  are identical to each other, considering the experimental inaccuracies of about  $\pm 3\%$ . For the respective references see footnote 6.

<sup>8</sup> The wavelength scale is chosen instead of frequencies because the original data in pertinent literature are mainly presented in wavelengths.

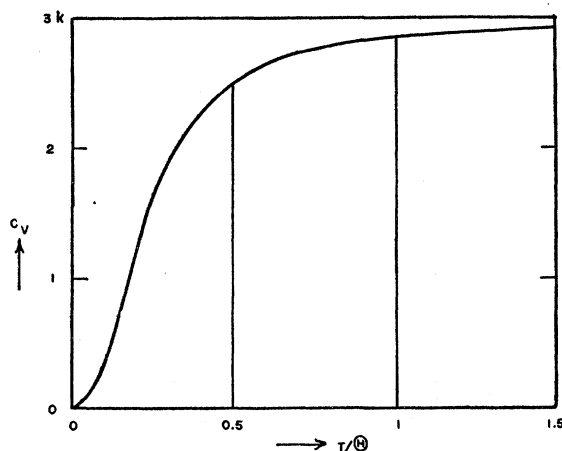


FIG. 5. Atomic heat capacity of simple solids (according to Debye).

The equality of center frequency with characteristic frequency is shown in Table I for eighteen nonconducting solids (compounds) for which complete data on both the lattice vibrations and the characteristic temperatures are available.<sup>9</sup> The substances of Table I belong to six different lattice structures and cover the range from  $\lambda_{ctr} = 120$  microns, as for CsBr, to  $\lambda_{ctr} = 5.9$  microns, as for the diamond (I).<sup>10</sup> This is almost the entire range of the vibrational spectra of solids (measured in center frequencies).

In detail: Table I includes thirteen solids (Numbers 1, 5, 8 to 12, and 14 to 18) for which sufficient experimental data are available to determine  $\lambda_{ctr}$  correctly (besides  $\lambda_\theta$ ).<sup>11</sup> In comparing the  $\lambda_{rest}$  of these solids with  $\lambda_{ctr}$ , it appears that ten of them show almost the same quantity for both  $\lambda_{rest}$  and  $\lambda_{ctr}$ , whereas the remaining three (Numbers 14, 15, and 18) have double values of  $\lambda_{rest}$  which are far apart from each other (in the frequency scale).<sup>12</sup> In the latter case,  $\lambda_{rest}$  remains ambiguous. Hence we conclude that both  $\lambda_{rest}$  and  $\lambda_{ctr}$  are very close to each other, provided that  $\lambda_{rest}$  has one value only. We now make use of this fact for another variety of solids (Numbers 2 to 4, 7, and 13) for which  $\lambda_{rest}$  is known (single values of course), but not the complete infrared spectrum, in order to determine  $\lambda_{ctr}$  correctly. Thus, in approximating  $\lambda_{ctr}$  by  $\lambda_{rest}$ , we in-

<sup>9</sup> Considering the over-all inaccuracy of data determination which averages  $\pm 3\%$  for  $\nu_{ctr}$ , but varies from  $\pm 2$  to  $\pm 10\%$  for  $\theta$ .

<sup>10</sup>  $\lambda_{ctr} = 5.9$  microns applies to the ordinary diamond of type (I).

<sup>11</sup> Most data of the characteristic temperatures are taken from the comprehensive articles by G. Leibfried and M. Blackman in *Handbuch der Physik* (see reference 7), pp. 104–382; also from K. Lonsdale, *Acta Cryst.* 1, 142–149 (1948). The data of the reststrahlen wavelengths are taken mainly from C. Schaefer and F. Matossi, *Das Ultrarote Spektrum* (Springer-Verlag, Berlin, 1930). The values of  $\lambda_{ctr}$  are determined mainly from data on lattice vibrations compiled in H. H. Landolt-R. Boernstein, *Zahlenwerte und Funktionen aus Physik Chemie Astronomie Geophysik und Technik* (see reference 3). See also the comprehensive bibliography there, pp. 663–666.

<sup>12</sup> Double values of  $\lambda_{rest}$  indicated by double maxima of reflectance apply to LiF, SiO<sub>2</sub>, double maxima of absorption to the diamond (I). The double maxima of each one of these solids are equally strong and may or may not be symmetrical to  $\nu_{ctr}$ .

TABLE I. Comparison of the characteristic frequency with the frequency of the center of gravity.

No.	Substance	Structure	$\theta$ °K	$\lambda_\theta$ microns	$\lambda_{\text{ctr}}$ microns	$\lambda_{\text{rest}}$ microns
1	CsBr	(cesium chloride)	120	120	120	125
2	RbI	(rocksalt)	115	125	...	117
3	AgBr	(rocksalt)	130	111	...	113
4	RbBr	(rocksalt)	130	111	...	105
5	KI	(rocksalt)	155	93	98	94
6	KBr	(rocksalt)	170	85	85	82.5
7	AgCl	(rocksalt)	180	80	...	81.5
8	KCl	(rocksalt)	225	64	65	63.5
9	NaCl	(rocksalt)	275	53	53(A) 54(R)	52
10	NaF	(rocksalt)	440	33	34	35
11	ZnS	(zinc blende)	450	32	32	31
12	CaF <sub>2</sub>	(fluorite)	470	31	31	31.5
13	CaO	(rocksalt)	510	28	...	27.5
14	LiF	(rocksalt)	620	23.5	24.4(A) 24(R)	17 and 26
15	MgO	(rocksalt)	740	19.5	19.1(A) 19.4(R)	20
16	SiC	(zinc blende)	1200	12	12	12
17	SiO <sub>2</sub>	(quartz)	~1300	~11	11.3	8.8 and 21
18	C—C(I)	(diamond I)	2340	6.1	5.9	4.5 and 8.0

crease the number of comparable solids in Table I from thirteen to eighteen. In this manner, we assemble a large variety of nonconducting solids for which we definitely possess the data required for checking the results.

For more than 30 years, as a matter of fact, it has been known that the quantities of  $\lambda_\theta$  and  $\lambda_{\text{rest}}$  are almost equal for a few solid compounds, such as NaCl, KCl, and CaF<sub>2</sub>. More recently, the  $\theta$  values of a few additional

ionic crystals were estimated by reststrahlen data. It was considered remarkable, however, that in these cases only the  $\theta$  values determined by the reststrahlen frequency agree quite well with the average  $\theta$  values from specific heat, whereas neither the "natural frequency," corresponding to the main resonance of absorption, nor any one of the strong secondary resonance frequencies seems to have any direct relation to  $\theta$ . This was the more remarkable as the reststrahlen frequency was considered obsolete. Consequently, the good agreement of the average  $\theta$  values from specific heat with the  $\theta$  values from reststrahlen data was regarded as due to "a combination of favorable circumstances" only, but not based on direct relation between the two quantities.<sup>13</sup> This conclusion, moreover, was emphasized by the lack of agreement observed in LiF, SiO<sub>2</sub>, and the diamond (I).<sup>12</sup> However, if we introduce the center frequency instead of the reststrahlen frequency we observe identity between both  $\lambda_{\text{ctr}}$  and  $\lambda_\theta$ , throughout all the solids listed in Table I. Thus it is  $\nu_{\text{ctr}}$  that should be deemed the true "natural frequency" of the vibrational spectrum.

The tight equality between the two frequencies,  $\nu_{\text{ctr}}$  and  $\nu_\theta$ , can best be seen in Fig. 6 where  $1/\lambda_{\text{ctr}}$  is plotted against  $1/\lambda_\theta$  (both in wave numbers) for all substances of Table I. The deviation from the bisector, which stands for the deviation from equality of both frequencies, is very small indeed and remains within the over-all inaccuracy of data determination.<sup>9</sup> As Table I and Fig. 6 equally indicate, we attain the following unambiguous and obvious relation:

*The characteristic frequency (defined by the characteristic temperature) and the center frequency (defined by the "center of gravity" of the lattice vibration spectrum) of nonconducting solids are identical with one another.*

<sup>13</sup> See M. Blackman, *Handbuch der Physik* (see reference 7), pp. 375-376.

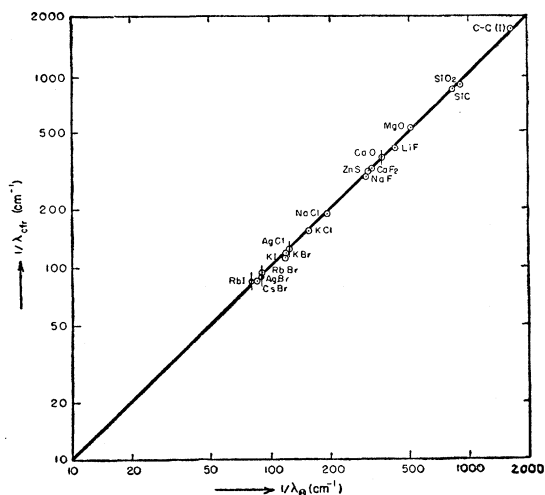


FIG. 6. Identity of the characteristic frequency with the center frequency (applying the data of Table I). Both frequencies  $1/\lambda_\theta$  and  $1/\lambda_{\text{ctr}}$  are plotted against one another and in logarithmic scales. They cover almost the entire range of the vibrational spectra (also of the characteristic temperatures) of solids. The deviation from the bisector (small as it is) stands for the deviation from the identity of both frequencies. The data are mean values, and their average inaccuracy is indicated by the size of the circles, the radius of which corresponds to about  $\pm 3\%$  (this radius being a constant in the logarithmic scales). Small vertical lines through some of the circles indicate solids where the center frequencies are determined by reststrahlen data.

Consequently, we conceive the center frequency as the optical (infrared) value of the characteristic frequency.

As we know, the spectrum of lattice vibrations as a whole contributes to the specific heat of a solid. In order to represent the entire spectrum in this case unambiguously and effectively by one single frequency, we may imagine the spectrum to be concentrated in its center of gravity and thus the accordant frequency to be identical with the characteristic frequency from specific heat.

#### IV. CENTER LAW OF THE LATTICE VIBRATION SPECTRA

As we conclude from Fig. 6, the center frequencies of the lattice vibration spectra of nonconducting solids can be determined simply by their characteristic temperatures. Introducing this fact into Eq. (2), we obtain

$$\nu_{ctr} = k/h\theta. \quad (3)$$

This relation expresses the equality of the characteristic temperatures with the center of gravity of the lattice vibration spectra in absorption as well as in reflectance. It states:

*The higher the characteristic temperature of a solid, the higher also the frequency region of the vibrational spectrum.*

Applying Eq. (3), we may now determine the centers of the vibrational spectra in absorption and reflectance for nonconducting solids from characteristic temperature data, or vice versa. The reciprocal case applies to a number of solids whose vibrational spectra we know but incompletely. Among these substances are, e.g., BN,

BeO, Al<sub>2</sub>O<sub>3</sub>, etc., with structures different in some cases from those of Table I. Other and more important applications of the center law, concerning the study of the solid state in general, will be treated in successive papers.

#### V. CONCLUSION

The accepted percentage of impurities in the investigated nonconducting solids (averaging close to 1%) may cause small deviations in some of the experimental data. However, no changes, beyond the over-all inaccuracies of the experimental data, are to be expected, either in the center frequency or in the characteristic frequency, provided the small impurities do not influence the electrical conductivity of the materials to any substantial degree.<sup>14</sup>

In the past, for various reasons, many experimental data in the far infrared have not met the standards that would be desirable. Hence comparisons made in our study are hampered in many respects by this fact. It is exactly the purpose of this paper to stimulate extensive and more accurate work within the experimental aspect of this field, in order to provide confirmation or modification of our results.

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<sup>14</sup> The influence of electrical conductivity on the data, in semiconductors and metals, will be considered separately in a subsequent paper.

## Optical Mode Scattering Contribution to Electrical Resistivity in Zirconium Hydride\*

PAUL W. BICKEL AND TED G. BERLINCOURT  
*Atoms International, Canoga Park, California*  
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Electrical resistivity measurements on fcc ZrH<sub>1.54</sub> and fct ZrH<sub>1.96</sub> between 1.2°K and 400°K have revealed a sizeable optical mode scattering contribution. Excellent fits to the data are obtained using a simple additive combination of Grüneisen and Howarth-Sondheimer functions for the respective acoustical and optical mode scattering contributions. The corresponding acoustical and optical mode characteristic temperatures are in good accord with values derived from earlier inelastic neutron scattering experiments.

RECENT neutron scattering experiments<sup>1-5</sup> have shown that hydrogen atoms occupy tetrahedral lattice sites in fcc and fct zirconium hydride (approx-

mately ZrH<sub>1.5</sub> to ZrH<sub>2</sub>), and further that these hydrogen atoms behave much like independent simple harmonic or "Einstein" oscillators. A value of 0.133 eV (average of two neutron scattering determinations) was obtained for the level spacing of these Einstein or optical modes, and a value of approximately 0.02 eV was obtained for the high-frequency cutoff of the acoustical modes. These energies correspond to an Einstein characteristic temperature  $\theta_E = 1550^\circ\text{K}$  for the optical branch and a characteristic temperature of approximately 230°K for the acoustical branch. The purpose of this note is to describe electrical resistivity measurements on zirconium

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