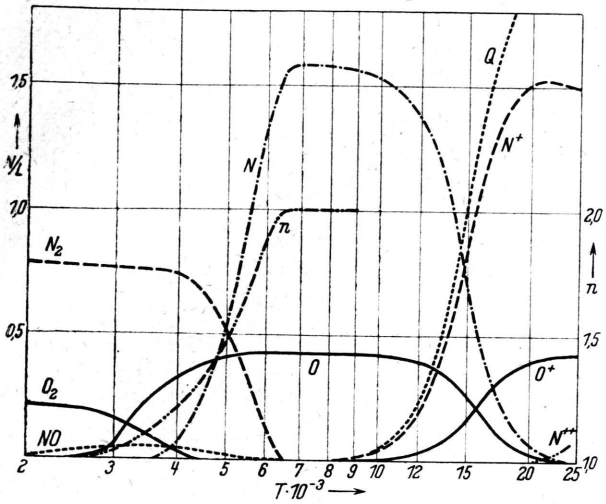

Abb. 2. Zusammensetzung der Luft bei konst. Druck $p_0 = 1$ atm. Teilchenanzahlen bezogen auf Zahl im Normalzustand.

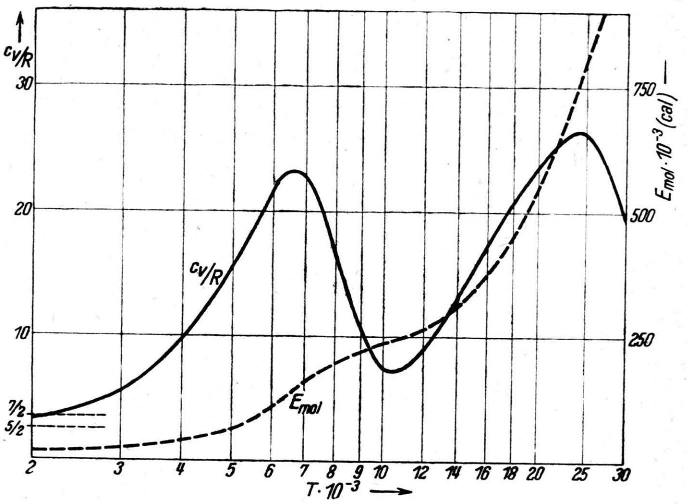

Abb. 3. Energie und spezif. Wärme der Luft bei konst. Dichte $V_0 / V = 1$.

Teilchenanzahlen und für den Anteil der Elektronenanregungsenergie numerisch durchgeführt werden. Abb. 3 enthält die so gefundene innere Energie und spezifische Wärme für Luft bei der relativen Dichte 1. Letztere wächst in den Gebieten der Dissoziation und der Ionisation etwa bis auf das 10-fache des Wertes bei Zimmertemperatur an. Ihr Verlauf hängt sehr empfindlich von der Zusammensetzung des Gases und von der Dichte ab, für reinen Stickstoff z. B. werden die Maxima etwa doppelt so hoch; mit zunehmender Dichte dagegen werden die Kurven immer ausgeglichener, infolge der Überlagerung der einzelnen Prozesse.

Hrn. Prof. Dr. R. Becker und Hrn. Prof. Dr. H. Schardin, auf deren Anregung hin diese Arbeit seinerzeit ausgeführt wurde, möchte ich an dieser Stelle meinen Dank aussprechen.

Lattice vibrations and specific heat of diamond

By W. V. Houston
The Rice Institute, Houston, Texas

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The low atomic heat of diamond at room temperature was one of the early noted striking exceptions to the law of Dulong and Petit. Einsteins[1] first application of quantum theory to this problem gave the qualitative explanation, and Born[2] in 1914 gave a detailed formulation in terms of normal modes of vibration for the diamond lattice. Apparently little further theoretical work along this line has been done, although Raman[3] has attempted to interpret the properties of diamond in terms of a small number of discrete frequencies instead of the very large number of the Born theory. In view of this situation it appeared of interest to make some further analysis of the spectrum indicated by Borns equations, and to compute the specific heat in terms of the observed Raman frequency of 1332 cm^{-1}. This involves an assumption for the ratio between the two force constants used by Born, but an indication of the proper value for this ratio comes from the measurements of Bhagavantam and Bhimasenachar[4].

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[1] A. Einstein, Ann. Physik **22**, 180 [1907].

[2] M. Born, Ann. Physik **44**, 605 [1914].

[3] C. V. Raman, Proc. Indian Acad. Sci. **13**, 1 [1941]; **14**, 65 [1942].

[4] S. Bhagavantam and J. Bhimasenachar, Nature [London] **154**, 546 [1944].

Born considered the central force between two nearest neighbors to be given by $A'/a\sqrt{3}$ times the departure from the normal distance, where $a\sqrt{3}$ is the distance between nearest neighbors. The force on an atom due to a departure from the equilibrium angle between the radii to two nearest neighbors was taken to be proportional to B'. He then let

$$A = \frac{1}{3a}\left(\frac{A'}{\sqrt{3}} - B'\sqrt{2}\right),$$

$$B = \frac{1}{3a}\left(\frac{A'}{\sqrt{3}} + \frac{B'}{\sqrt{2}}\right).$$

In terms of these constants the equations for the frequencies of the normal vibrations could be written

$$\begin{vmatrix} F + G_1 - \mu^2 & f_3 - ig_3 & f_2 + ig_2 \\ f_3 + ig_3 & F + G_2 - \mu^2 & f_1 - ig_1 \\ f_2 - ig_2 & f_1 + ig_1 & F + G_3 - \mu^2 \end{vmatrix} = 0\,. \quad (1)$$

In this

$$\mu = 4\pi^2\nu^2 m - 4A\,,$$

where m is the mass of an atom.

$$F = 4A^2(1 + \cos y \cos z + \cos z \cos x + \cos x \cos y)$$
$$G_1 = 8B^2(1 - \cos y \cos z)$$
$$G_2 = 8B^2(1 - \cos z \cos x)$$
$$G_3 = 8B^2(1 - \cos x \cos y)$$
$$f_1 = 4B\,(B - 2A) \sin y \sin x$$
$$f_2 = 4B\,(B - 2A) \sin z \sin x$$
$$f_3 = 4B\,(B - 2A) \sin x \sin y$$
$$g_1 = 4B^2 \sin x\,(\cos y - \cos x)$$
$$g_2 = 4B^2 \sin y\,(\cos z - \cos x)$$
$$g_3 = 4B^2 \sin z\,(\cos x - \cos y)\,.$$

This secular equation expresses the frequency ν in terms of 3 parameters, x, y, and z, which are proportional to the direction cosines of the associated plane wave. Born pointed out that all possible normal vibrations, and all possible frequencies, are represented by values of the parameters lying in a range of 2π. Hence one may consider the possible values as lying between $-\pi$ and π.

Further consideration of equation (1) shows that the six frequencies corresponding to (x, y, z) also correspond to $(x - \pi,\ y - \pi,\ z - \pi)$, so that each frequency is counted twice when all values of x, y, z lying in the cube are included. To avoid this duplication in calculation we may consider only that part of the cube between the origin and the plane $x + y + z = 3\pi/2$ for the octant in which x, y, and z are all positive. The corresponding planes in the other octants also bound the region to be considered.

Various methods of approximation to the vibration spectrum of a crystal have been used in recent years. Blackman[5] has made an extensive study of the properties of certain ideal lattices and Fine[6] and Leighton[7] have worked through two special cases by numerical and graphical methods. A recently described method[8] lends itself to possibly less laborious application than some of the others and has been applied to equation (1).

In this method the frequency spectrum is determined along several radii from the origin in the x, y, z space. If this process were carried out for radii in enough different directions, the total spectrum could be determined as accurately as is desired, but it is obviously impractical to analyze more than a few directions. Nevertheless by a judicious selection of these few directions, a fair approximation to the total spectrum can be obtained, and the few directions selected can be regarded as the first members of a convergent series.

The number of frequencies whose representative points lie on a given radius from the origin is a function of the frequency and of the direction. The direction may be expressed in terms of the polar coordinate angles Θ and Φ so that we have a function $F(\nu, \Theta, \Phi)$. This can then be expanded as an infinite series of spherical harmonics, each multiplied by a function of ν.

The series of spherical harmonics will contain only those terms having the symmetry of the lattice, and in a crystal such as diamond this condition eliminates many of the early members of the series. If only the first three terms are

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[5] M. Blackman, Reports on Progress in Physics, published by the Physical Society of London, 8, 11 [1942], contains references.

[6] P. C. Fine, Physic. Rev. **56**, 355 [1939].

[7] Leighton, Rev. mod. Physics **20**, 165 [1948].

[8] W. V. Houston, Rev. mod. Physics **20**, 161 [1948].

considered, the series for a cubic lattice is

$$F(\nu, \Theta, \Phi) = f_0(\nu)\frac{1}{\sqrt{4\pi}}P_0(\cos\Theta)$$

$$+ f_1(\nu)\left\{\frac{3}{\sqrt{4\pi}}P_4(\cos\Theta) + \frac{1}{56\sqrt{4\pi}}P_4^4(\cos\Theta)\cos 4\Phi\right\}$$

$$+ f_2(\nu)\left\{\frac{13}{\sqrt{4\pi}}P_6(\cos\Theta) - \frac{\sqrt{13}}{720\sqrt{4\pi}}P_6^4(\cos\Theta)\cos 4\Phi\right\}. \tag{2}$$

When any such series is integrated over all values of Θ and Φ to get the entire spectrum, the result is

$$N(\nu) = \sqrt{4\pi}\, f_0(\nu)\,. \tag{3}$$

The three functions in equation (2) can be evaluated in terms of the distributions along any three non-equivalent directions in the crystal. It appears convenient to take for these $x = y = 0$, or $\Theta = 0$; $x = z$, $y = 0$, or $\Theta = \pi/4$, $\Phi = 0$; and $x = y = z$, or $\Theta = \cos^{-1} \cdot 1/\sqrt{3}$, $\Phi = \pi/4$. If the spectra along these directions are designated by F_1, F_2, and F_3, respectively

$$N(\nu) = \frac{4\pi}{469}\left\{162\, F_1(\nu) + 208\, F_2(\nu) + 99\, F_3(\nu)\right\}. \tag{4}$$

The problem is then to evaluate these three functions.

Assuming $B/A = 1/\sqrt{2}$ and inserting the values of $x = y = 0$ in equation (1) it can be shown that one root along the z-axis is given by

$$\mu^2 = 16\, A^2(\Phi^2 - 1)^2 = 16\, A^2 \cos^2 z/2\,. \tag{5}$$

where $\Phi = \pi\nu\sqrt{m/A}$. This dimensionless ratio Φ will be used in place of the frequency itself. Then

$$z = 2\cos^{-1}[\pm(\Phi^2 - 1)]\,. \tag{6}$$

z must lie between 0 and π, and the argument of the inverse cosine must be positive. Hence for $\Phi < 1$ the positive root is taken, and for $1 < \Phi < \sqrt{2}$ the negative root is used. For each value of z there are two possible frequencies. The lower is usually called an acoustical vibration and the higher an optical vibration.

The maximum possible frequency corresponds to $\Phi = \sqrt{2}$ and $z = 0$. This turns out to be the maximum frequency for all radii and is the upper limit of the frequency spectrum. The spectral distribution along the z-axis is given by $z^2\, d\Phi/dz$, which has the form

$$z^2\frac{d\Phi}{dz} = \frac{4\left\{\cos^{-1}[\pm(\Phi^2 - 1)]\right\}^2}{(2 - \Phi^2)^{1/2}}. \tag{7}$$

Expression (7) represents the spectrum of the longitudinal vibrations for which $x = y = 0$. A similar expression can be obtained for the two transverse vibrations, and the sum then gives the frequency spectrum for this one radius. Figure 1 shows this distribution.

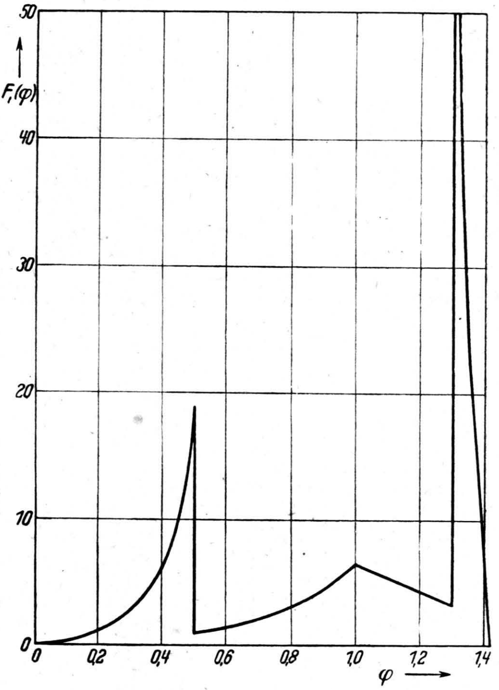

Fig. 1. Frequency spectrum of those normal vibrations whose propagation vectors lie along the z-axis. The dimensionless ration Φ is proportional to the frequency.

All frequencies between $\Phi = 0$ and $\Phi = \sqrt{2}$ are represented in the longitudinal vibrations, but the transverse vibrations have acoustical frequencies only between 0 and 0,5412 and optical frequencies only between 1,3066 and $\sqrt{2}$. The size of this gap in the spectrum is determined by the ratio B/A.

At each limiting frequency the spectrum actually becomes infinite although the area under the curve, which represents the total number of modes of vibration, remains finite. These infinite peaks in the partial spectra are real. They represent the actual situation along a particular direction in the x-y-z space. Since, however, these peaks may occur at different points for spectra corresponding to different directions, the final result of combining all of them is to fuse groups of many sharp peaks into lower and broader maxima. Nevertheless, rather pronounced peaks seem to be a characteristic feature of the diamond spectrum and to be responsible for the fact that the specific heat curve can be approximated about as well with one or two properly chosen discrete frequencies as with a continuum.

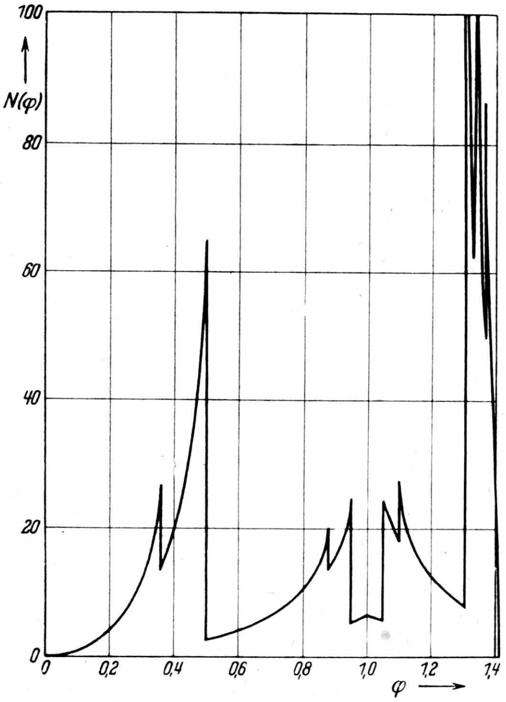

Fig. 2. Total frequency spectrum of the vibrations of the diamond lattice.

In a similar manner the spectra along the other two selected directions can be evaluated. Along $x = z$, $y = 0$ the limiting value of z (or x) is $3\pi/4$, and the maximum radius is $\sqrt{2} \cdot 3\pi/4$. These three vibrations cannot be classified as transverse and longitudinal. Considerations of symmetry show that the motion of one vibration is perpendicular to the x-z-plane, and the motions of the other two lie in it.

Along the direction $x = y = z$ there are again two transverse and one longitudinal vibration for each value of z $(= x = y)$. The limiting value of z is $\pi/2$ corresponding to a maximum radius $\sqrt{3} \cdot \pi/2$.

Figure 2 shows the total spectrum in which the three branches are combined with the coefficients of equation (4). The separation between the optical and the acoustical branches is quite clear, and the rather narrow range of frequencies occupied by the optical branch is striking. The exact width and shape of the minimum between the two branches is dependent upon the assumed value of B/A, but the general features are independent of this ratio. It is also striking that all eighteen curves superimposed to make Figure 2, show $\Phi = \sqrt{2}$ as the maximum frequency. This means that all long wavelength vibrations in the optical branch, whether transverse or longitudinal, have the same frequency.

The change of frequency in Raman scattering will correspond to a wavelength in the vibration spectrum that is long compared with the interatomic distances. It will correspond essentially to $r \to 0$ or to a frequency either $\Phi = 0$ or $\Phi = \sqrt{2}$. Since the very low frequency cannot be observed, the Raman displacement of 1332 cm^{-1} is to be associated with $\Phi = \sqrt{2}$. With this datum to determine the scale of Φ the atomic heat can be evaluated by numerical integration of the spectrum in Figure 2. The result is shown in Figure 3

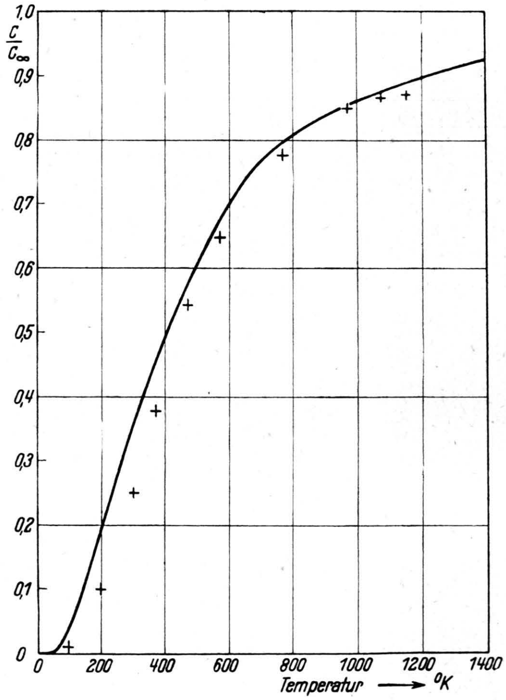

Fig. 3. Ratio of the specific heat at the temperature T to the specific heat at an infinitely high temperature. The crosses (+) indicate experimental values taken from the International Critical Tables.

together with a number of experimental values taken from the International Critical Tables. The points representing observations all lie below the theoretical curve, but in view of the fact that the scale of Φ is determined from an entirely independent observation, the agreement lends support to the theoretical point of view. An atomic heat curve based on a single frequency equal to the Raman frequency lies very much lower than the points and is a much poorer representation of them.

It is true, of course, that the experimental points can be represented, over a wide range of temperature, by a Debye curve or an Einstein curve if the characteristic frequencies are suitably selected. In fact, if two or three discrete frequencies are selected for the purpose, a very good fit can be obtained. It must be emphasized, however, that the curve in Figure 3 involves no adjusted constants. The only uncertain constant is the ratio B/A, and this was selected on the basis of recent measurements of elastic constants[4]. It is probable that an improved fit could be obtained by using a different value for this ratio. A value more nearly equal to the $^1/_2$ preferred by Born in 1914, or even smaller, would lower the curve in the intermediate region.

Some precision measurements of the atomic heat of diamond in the liquid helium range of temperature would be very valuable in appraising the correctness of the vibration spectrum. Presumably there would be no electronic heat to obscure the energy of the lattice vibrations, and a comparison over such a wide range of temperature would minimize the possibility of spurious apparent agreement with simplified formulae.

It gives me great pleasure to be able to join with others in extending greetings to Professor Sommerfeld on the occasion of his 80'th birthday.

Varianten zum chemischen Austauschverfahren, Anreicherung von ^{34}S

Von KLAUS CLUSIUS* und HANS HAIMERL

(Z. Naturforschg. **3 a**, 611—616 [1948]; eingegangen am 4. Juni 1948)

Herrn Geheimrat Arnold Sommerfeld zum 80. Geburtstage gewidmet

Beim chemischen Austauschverfahren gehen bei der üblichen „offenen“ Arbeitsweise große Mengen wertvollen Ausgangsmaterials (NH_4NO_3 für ^{15}N, NaCN für ^{13}C und Na_2SO_3 für ^{34}S) verloren. Man kann durch Übergang zu „geschlossenen“ Systemen diesen Mangel beheben, was besonders für die Verarbeitung technischer Isotopenkonzentrate Interesse hat. Dann werden nur billige Arbeitschemikalien — Natronlauge und Schwefelsäure für alle drei Isotope — verbraucht. In manchen Fällen dürften sich auch diese noch einsparen lassen.

In einer 20 m langen Austauschkolonne wird mit einem geschlossenen System das Isotop ^{34}S durch die Reaktion

$$H^{34}SO_3{}'_{\text{fl}} + {}^{32}SO_{2\,\text{gas}} \rightleftarrows H^{32}SO_3{}'_{\text{fl}} + {}^{34}SO_{2\,\text{gas}}$$

angereichert. Der mit Schwefelsäure beschickte Auskocher auf der schweren Seite wird durch einen Lösungsvorrat mit alkalischem Absorptionsturm auf der leichten Seite ergänzt. Die von Hrn. Dr. W. Paul, Göttingen, durchgeführte massenspektrographische Analyse ergab einen Endwert von 10,2% ^{34}S und 1,5% ^{33}S gegenüber der natürlichen Konzentration von 4,18% ^{34}S und 0,74% ^{33}S.

Auf die Bedeutung der Gewinnung von reinem ^{32}S zum Anschluß des chemischen Silberatomgewichts, das praktisch als Substandard allen modernen chemischen Atomgewichtswerten zugrunde liegt, an das physikalische Standard-Atomgewicht von ^{16}O wird hingewiesen.

Aufgabenstellung

1. Das von Urey und seinen Mitarbeitern entwickelte chemische Austauschverfahren zur Anreicherung seltener Isotope verbindet die Vorzüge großen Materialdurchsatzes und kontinuierlicher Arbeitsweise. Dem gegenüber stehen die Nachteile seiner Störanfälligkeit, die, im Gegensatz zum Trennrohr, eine dauernde Überwachung erfordert, und des Verbrauches großer Chemika-

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* Zürich, Rämistr. 76.