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# Lattice vibrations of solids

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Specific heat is one of the oldest techniques used in condensed matter physics. This paper reviews the contributions made through specific heat measurements to our understanding of lattice vibrations in solids, starting with the work of Petit and Dulong in 1819. Recently, specific heat measurements have revealed new information on the lattice vibrations in glasses, i.e., structurally disordered systems and certain highly disordered, yet crystalline, solids. These two classes of solids contain anomalous low energy excitations which completely mask the specific heat resulting from plane wave excitations at low temperatures. Measurements of thermal relaxations (time dependent specific heat) in these solids have also demonstrated the limits of the concept of temperature in these solids in the low temperature limit.

## I. INTRODUCTION

An instructor in physics must often feel frustrated as he tries to convey to the students the excitement a physicist experiences while attempting to unravel the secrets of nature. The material covered in introductory physics courses appears so thoroughly studied and well understood, that no room appears to be left for new discoveries. This impression is reinforced by a visit to a modern research lab. The experimental techniques used often appear just as complex as the problems that are being studied. The basic concepts, as they are discussed in the classroom, appear all but buried underneath the highly sophisticated methods of investigation. Fortunately, there exist exceptions, and it is the purpose of this paper to describe one of them. It is hoped that it will stimulate the reader to search for other, similar examples, which can be used to breathe life and actuality into the classroom discussion of the basic concepts of physics. The example to be discussed here, i.e., the study of lattice vibrations of solids by means of specific heat measurements, involves simple concepts, and basically straightforward experimental techniques. It is one of the oldest subjects of solid state physics, and has contributed repeatedly to our understanding of the solid state: yet it continues to present new puzzles, as we will try to show below.

## II. TEMPERATURE OF A SOLID; SPECIFIC HEAT

If a solid object, say a piece of rock salt or window glass, is said to have a certain temperature, it means that its constituent atoms or molecules perform motions around their equilibrium positions or orientations; the larger the amplitude of these motions, the higher the temperature. In order to describe, understand, and ultimately control phenomena which depend on the temperature, ways must be found to quantify this motion. This is no easy task, considering the structural diversity of solids, and the large number of atoms they contain—typically on the order of  $10^{22}$  in one cubic centimeter.

In the classical description of the thermal motion, each atom was considered to be a harmonic, three-dimensional oscillator, with six degrees of freedom, three of kinetic, and

three of potential energy. Each degree of freedom contains on the statistical average the energy  $(1/2)k_B T$ , where  $k_B$  is Boltzmann's constant and  $T$  is the absolute temperature. This model led to the thermal energy density  $w$ , contained in an object with the number density  $n$  of atoms:

$$w = 6n(1/2)k_B T, \quad (1)$$

or to a specific heat, defined as the derivative of  $w$  with respect to  $T$ :

$$\frac{dw}{dT} = n3k_B. \quad (2)$$

Usually, the specific heat is referred to the mass of the object, rather than to its volume, and is called  $C_v$ .

$$C_v = \rho n3k_B, \text{ where } \rho \text{ is the mass density.} \quad (3)$$

The subscript  $v$  indicates that the volume of the object is kept constant during the measurement. If the object is held in vacuum, as is usually done, one measures instead  $C_p$  (pressure  $p = \text{const.}$ ). The difference between  $C_v$  and  $C_p$  is usually small in solids, and for the present discussion shall be ignored.

If the specific heat is referred to the mole of a substance, Eq. (3) is written as

$$C_v = 3R, \quad (4)$$

where  $R = 8.31 \text{ J mole}^{-1} \text{ K}^{-1}$ . This is the rule of Dulong-Petit, proposed in 1819.<sup>1</sup> Thus, in the classical picture, the specific heat  $C_v$  is independent of temperature.

Measurements of the specific heat have been an important tool for the chemists and physicists of the 19th century. The technique is relatively simple: The sample (of mass  $m$ ) is kept in thermal isolation from its surroundings. A known amount of energy  $\Delta W$  is added (a heat pulse), usually by means of a small electric heater. A thermometer records the temperature rise  $\Delta T$ , see the inset of Fig. 1, and the specific heat

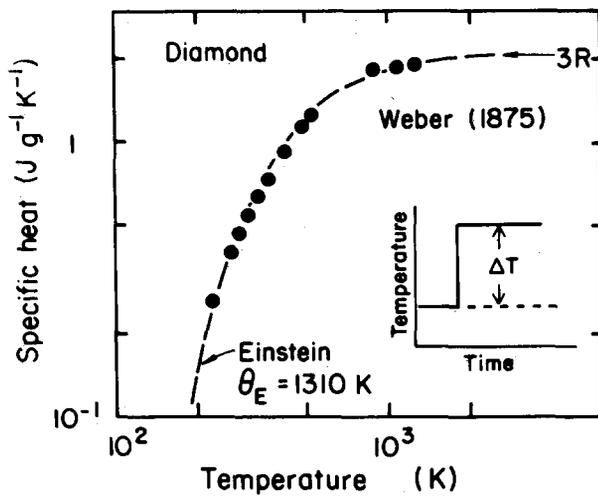


Fig. 1. Specific heat of diamond, after H. F. Weber (Ref. 2). The dashed line is Einstein's calculation (Ref. 3), adjusted horizontally for a best fit. In the limit of high temperatures, Einstein's  $C_v$  approaches the Dulong-Petit value,  $3R$ . The inset shows, schematically, the temperature rise of the sample to which a certain amount of heat has been added. In an actual experiment, the sample temperature will not rise abruptly, because of the time it takes for the heat to diffuse through the sample. Also, the sample temperature will return slowly to that of its surrounding, but these effects are easily accounted for.

$$C_v = \frac{1}{m} \frac{\Delta W}{\Delta T} \quad (5)$$

is calculated.  $\Delta T$  is chosen to be small in comparison to the sample temperature. Obviously, there are experimental problems, most importantly, that of achieving thermal isolation, but they can be resolved, and do not have to be discussed here.

### III. EARLY MEASUREMENTS OF THE SPECIFIC HEAT; THE MODELS BY EINSTEIN, BORN-VON KÁRMÁN, AND DEBYE

Measurements in the early part of the last century already showed deviations from the rule of Dulong-Petit, in that the specific heat was found to be less than  $3R$  in some solids. Moreover, it was found by H. F. Weber<sup>2</sup> as early as 1875, that  $C_v$  increased with increasing temperature. Figure 1 shows his data, taken on crystal diamond. Only in the limit of very high temperatures did the specific heat approach its expected value,  $3R$ . This most remarkable observation, which violated the classical concepts of the equipartition of energy, remained unexplained for over 30 years. Seven years after Planck had introduced the concept of electromagnetic quanta, in 1907, Einstein<sup>3</sup> offered the suggestion that the energy of mechanical harmonic oscillations in solids also had to be quantized in multiples of  $h\nu_E$ , where  $h$  is Planck's constant and  $\nu_E$  the (Einstein) frequency of oscillation. In Einstein's view, (these oscillators were the individual atoms, oscillating with the same frequency, independent of their neighbors, as sketched in Fig. 2(a). Einstein adjusted  $\nu_E$  to best fit Weber's data, see Fig. 1. From the relation  $h\nu_E = k_B\theta_E$ , he determined the characteristic (Einstein) temperature  $\theta_E$ . The good agreement

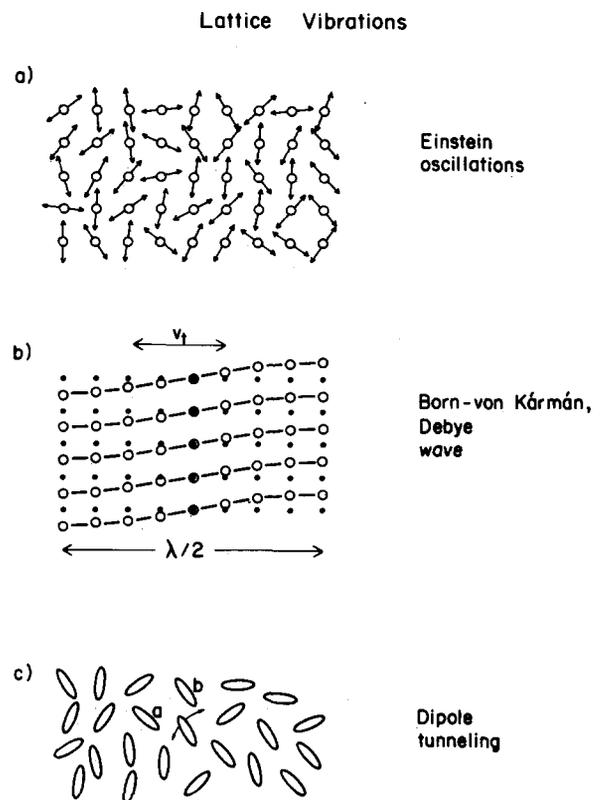


Fig. 2. Different models of lattice vibrations. (a) In Einstein's model, all atoms vibrate with the same frequency  $\nu_E$ , independent of their neighbors. (b) In the theory developed by Born-von Kármán and by Debye, the atoms perform collective motions described as transverse and longitudinal waves, propagating with the speeds of sound  $v_t$  and  $v_l$ , respectively. Shown is a transverse wave; the open circles indicate the instantaneous excursions of the atoms from their equilibrium positions (the solid dots). The wave can travel to the right or to the left (double arrow) with the velocity  $v_t$ . (c) In the tunneling model for amorphous solids, it is assumed that elastic dipole interaction will permit a small volume fraction of the solid to rearrange via tunneling even at the lowest temperature. In the picture shown, it is assumed that one dipole has two potential minima (see double arrow), one close to dipole  $a$ , one close to dipole  $b$ .

between theory and experiment established the *quantum concept* also for elastic vibrations.

However, as specific heat measurements were extended to lower temperatures, it became clear that even Einstein's model was only an approximation. The data for copper, for example, shown in Fig. 3, collected by Nernst and Lindemann from a number of sources,<sup>4</sup> showed that  $C_v$  did not decrease exponentially with  $T$  at low temperatures, as predicted by Einstein's model. The existence of several oscillators with lower frequencies was indicated, but their nature defied a clear picture. A physical explanation was offered in 1912 by Born and von Kármán,<sup>5</sup> and by Debye.<sup>6</sup> Born and von Kármán demonstrated that Einstein's assumption of individual atoms oscillating independently from their neighboring atoms, was wrong and had to be modified. Their work led to the discovery of collective excitations, elastic waves, as sketched in Fig. 2(b). They have different wavelengths  $\lambda$  and frequencies  $\nu$ . Details of the vibrational spectrum of these waves depend on crystal structure and interatomic forces, but in the low frequency limit the den-

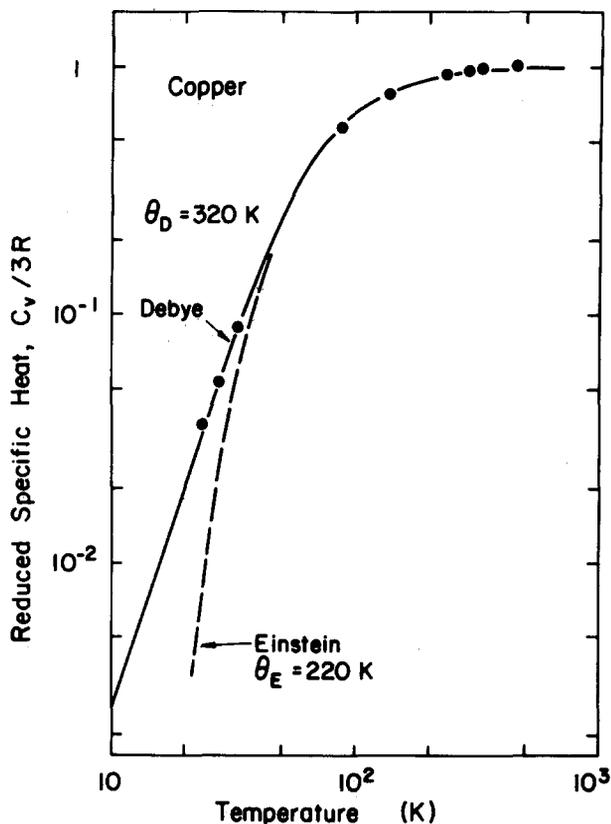


Fig. 3. Comparison of the models by Debye and by Einstein to the specific heat,  $C_v$ , of copper. Note that the Debye curve contains no adjustable parameters, while the Einstein curve is adjusted by shifting it along the  $T$  axis to fit the data.

sity of modes (i.e., the number of modes per frequency range and per volume) varies as  $\nu^2$ . Many of the details of the vibrational modes predicted by this model became known only much later, in particular as neutron scattering experiments could be used to detect these vibrations, and electronic computers became available to perform the calculations.

Debye chose the different approach of ignoring the atomic structure altogether. He assumed that all elastic waves travel with a frequency-independent speed of sound, the transverse waves with  $v_t$ , the longitudinal ones with  $v_l$ . He then counted the number density of normal modes (standing waves) which could exist in a three-dimensional elastic body very similar to the way in which Planck had counted the electromagnetic waves in a blackbody (for a two-dimensional object, like a drumhead, the elastic normal modes are easily visualized). The only point at which Debye acknowledged the atomic structure was when he limited the total number of normal modes to  $3n$ , where  $n$  is the number density of atoms in the solid. Thus, Debye's model used only the speeds of sound,  $v_t$  and  $v_l$ ,  $n$ , and the average mass  $m_a$  of the constituent atoms—and no adjustable parameters—to calculate the vibrational spectrum and from that the specific heat.  $v_t, v_l, n$ , and  $m_a$  were directly determined experimentally, and thus the good agreement between measured and calculated specific heat shown

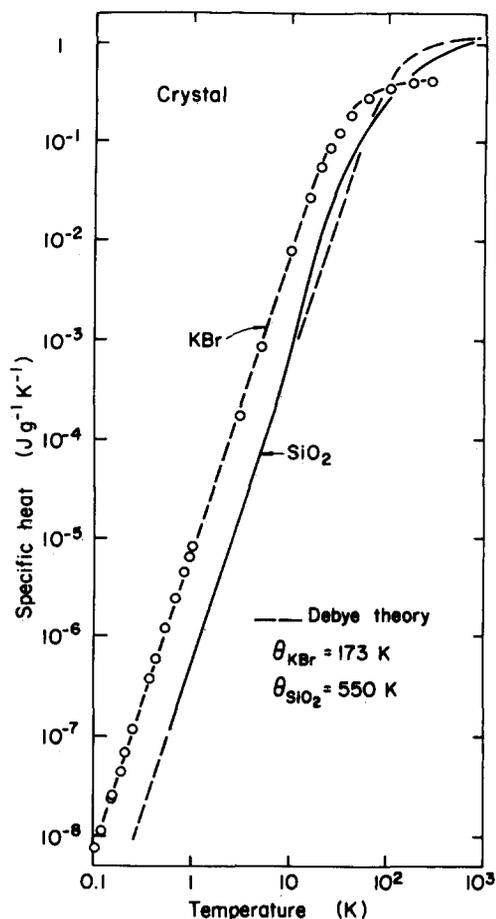


Fig. 4. Specific heat,  $C_v$ , of crystal KBr (Ref. 7) and  $\text{SiO}_2$  ( $\alpha$ -quartz, Ref. 8), compared to the Debye theory. For KBr, data points are used in order to distinguish the experimental results from the theoretical prediction which is based on elastic measurements. Note in particular that at low temperatures, the predicted  $T^3$  dependence is in excellent agreement with the experiment.

in Fig. 3 proved Debye's assertion of *sound waves as the elementary excitations of vibrations in solids*. Figure 4 shows two examples of the excellent agreement between experiment and Debye's prediction, obtained more recently over a much wider range of temperature.<sup>7,8</sup> The dashed curves are the Debye predictions based on elastic measurements (and  $n$  and  $m_a$ ). In the crystalline KBr, the agreement is excellent over the entire temperature range (note the perfect  $T^3$  dependence of  $C_v$  over two orders of magnitude in  $T$ ). In crystal quartz ( $\text{SiO}_2$ ) the difference between theory and experiment above a few K shows the limits of the continuum model for the waves which are thermally excited at these temperatures. In this range of wavelengths and frequencies, the more precise (and complicated) Born-von Kármán model must be used, i.e., knowledge of the atomic details is required. For example, if the specific heat in a certain temperature range exceeds that of the Debye calculation, it indicates that the density of modes of the lattice waves contributing to the specific heat is higher than predicted by the Debye model. These differences are by now well understood.

#### IV. SPECIFIC HEAT OF GLASSES, TUNNELING EXCITATIONS

In view of the repeatedly demonstrated success of Debye's model (or the more refined Born-von Kármán model), it is hardly surprising that for many decades the picture that all vibrational excitations in solids are waves, or phonons in the quantum picture, went without a challenge. The first evidence that something apparently was being overlooked came to light in 1958, when Flubacher, Leadbetter, Morrison, and Stoicheff<sup>9</sup> extended the earlier specific heat measurements on vitreous silica ( $\text{SiO}_2$ ), an amorphous solid, from 20 to 2 K, see Fig. 5. From speed of sound measurements O.L. Anderson<sup>10</sup> showed that even at the lowest temperatures of Flubacher *et al.*'s measurements,  $C_v$  exceeded the Debye prediction by a considerable amount (see the dashed curve labeled Debye in the figure). A similar discrepancy was found later in vitreous  $\text{GeO}_2$ .<sup>11</sup> The expla-

nation offered was that in these glasses some vibrational excitations existed besides the Debye-like plane waves, probably as a result of the disorder. These authors suggested localized, nonpropagating modes, and treated them as a collection of Einstein oscillators. Some of them had to have frequencies so low that the expected exponential drop-off of their contribution to the specific heat (see Fig. 1) could not be seen above 2 K.

An extension of the specific heat measurements to a variety of amorphous solids and to the temperature range below 2 K, first reported in 1971,<sup>8,12</sup> showed that the discrepancy between the measurements and the Debye prediction grew even bigger, as the temperature decreased. This is shown for silica in Fig. 5, see the curve labeled "10s" (the significance of this label, and of the other curves shown in this temperature range will be explained shortly). At 0.1 K, for example, the measured specific heat exceeded the Debye prediction by two orders of magnitude. In the low temperature limit,  $C_v$  varied approximately linearly with  $T$  and not as  $T^3$ ! It is now well established that this behavior is common to all amorphous solids.

What could be the nature of elastic excitations with ener-

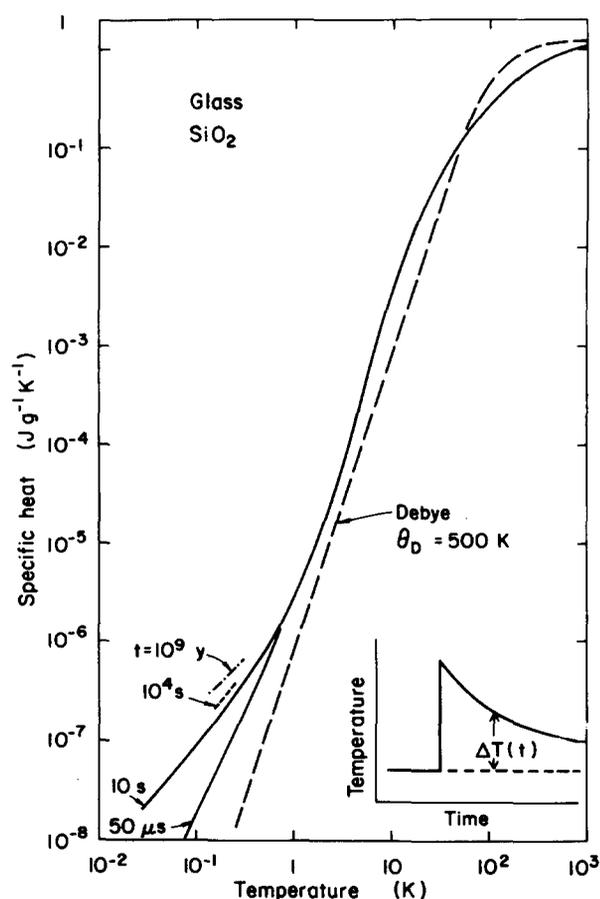


Fig. 5. Specific heat,  $C_v$ , of vitreous silica (Refs. 8,9,12), compared with the Debye theory based on elastic measurements (Ref. 10). The inset shows an effect observed only below 1 K: After a heat pulse has been added to the sample assumed to be perfectly thermally isolated from its surroundings, the temperature rise  $\Delta T$  decays logarithmically with time, as an increasing number of the slowly relaxing low energy excitations take up energy from the rest of the sample. As a consequence, the specific heat appears to increase with time. After  $50 \mu\text{s}$ , the heat is distributed only over the most rapidly relaxing excitations, and thus  $C_v$  appears small (Ref. 19). After 10 s (the usual time scale of specific heat measurements),  $C_v$  has become essentially independent of time, as shown with measurements after  $10^4$  s (Ref. 20), and an extrapolation to a time comparable to the age of the universe.

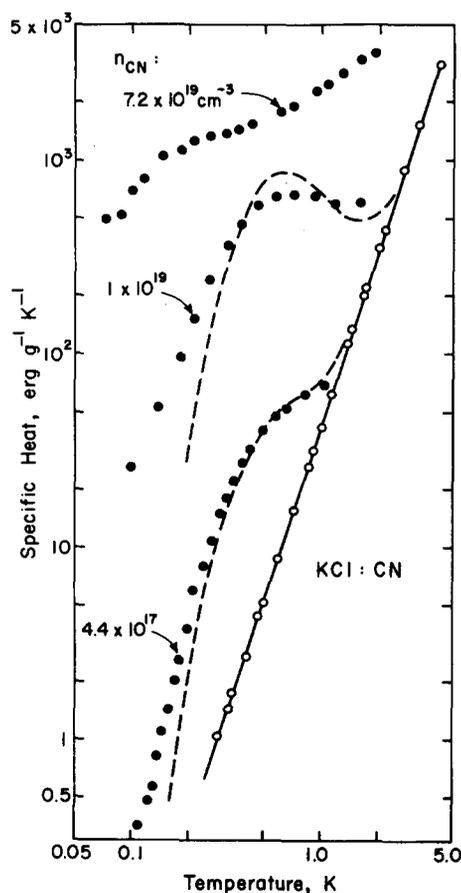


Fig. 6. Specific heat,  $C_v$ , of KCl containing three different concentrations of  $\text{CN}^-$  substituting for  $\text{Cl}^-$ . The number density of KCl molecules in pure KCl is  $n_{\text{KCl}} = 1.602 \times 10^{22} \text{ cm}^{-3}$ . Addition of  $\text{CN}^-$  in small concentration ( $< 0.1$  mole %) causes an anomaly centering around 0.5 K, which is caused by tunneling. The dashed curves represent theoretical predictions. At the highest concentration shown, interaction between the  $\text{CN}^-$  ions causes the anomaly to broaden (Ref. 13). This broadening is now believed to mark the transition to glasslike excitations in the crystal.

gies low enough so they could be thermally excited at 0.1 K? Born and von Kármán, and Debye had shown how this can happen if, in a collective excitation, many atoms oscillate practically in phase against an equally large number of neighboring ones, as in an elastic wave of long wavelength  $\lambda$  [see Fig. 2(b)]. But the density of states of these modes decreases rapidly with increasing  $\lambda$ , leading to the rapid drop-off of  $C_v$ , with the third power of  $T$ , as seen in crystals, and cannot lead to a linear temperature dependence. So, what other excitations can we think of?

At this point, we have to digress for a moment, in order to explain a phenomenon that occurs in impure crystals: Certain, but by no means all, impurities can lead to significant increases of the low temperature specific heat, as demonstrated in Fig. 6 for an alkali halide crystal KCl containing small concentrations of an alkali cyanide, KCN.<sup>13</sup> When this phenomenon was first observed, it raised the same question we are now faced with here in glasses. In these doped crystals, the low excitation energies were explained as follows: The impurity ion, the CN<sup>-</sup> ion in this case, occupies a Cl<sup>-</sup>-ion vacancy of the host lattice. Since the CN<sup>-</sup>-ion is not spherical, but ellipsoidal, it has more than one equilibrium orientation (eight, in fact, along the diagonals of the chlorine vacancy it occupies, which has the form of a cube). One describes this situation by saying that the ion sits in a potential with eight minima. The wells are separated by barriers as shown schematically for two such wells in Fig. 7. A motion between these minima can occur not only as a thermally activated process *over* the barriers ( $V_0$ ), but also *through* the barrier, and this process is called tunneling. Tunneling is a phenomenon common for waves of all kinds. A well-known example is that called “frustrated total internal reflection,” when a light wave can penetrate a thin layer of a medium into which it should not be able to enter on the basis of Snell’s law. Hund<sup>14</sup> was the first one to extend this concept to matter waves. In a wave me-

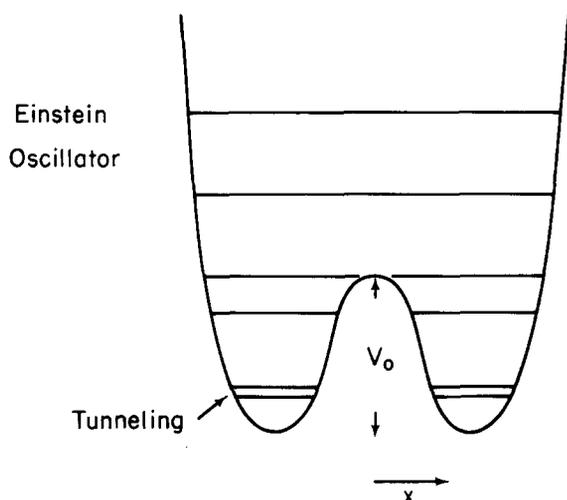


Fig. 7. Schematic representation of the potential energy function describing a particle with two equilibrium positions. For large energies, the potential is given by a parabola, and the energies of the oscillator are those of an Einstein oscillator. The states with the lowest energies are perturbed by the potential barrier  $V_0$ . The lowest oscillator state is split due to tunneling. If the particle is performing an angular (rocking) motion, the coordinate  $x$  designates an angle, and the highest motional states may become those of almost free rotation.

chanical calculation, he showed that in a double well potential the harmonic oscillator states are split; the energy splitting corresponds to the frequency  $\nu$ , with which the particle will tunnel back and forth between the two wells, times Planck’s constant  $h$ . The energy ( $h\nu$ ) decreases very rapidly (exponentially) with increasing barrier height. Thus, very small energies of excitation can be observed even with single particle motion of the impurity ions, and not only with collective, wavelike, excitations of the host. The excess specific heat observed in Fig. 6 in the doped crystals was caused by the thermal excitation of such *tunneling states*; this excess is, of course, proportional to the impurity concentration, and thus its magnitude is different for different levels of doping. The change in shape of the anomaly observed for the highest CN<sup>-</sup> concentration in Fig. 6 is evidence for interaction effects between neighboring CN<sup>-</sup> ions which will be discussed below.

Now we return to the amorphous solids. When the first evidence for a universal low temperature specific heat linear in  $T$  became known, it was suggested by Anderson, Halperin, and Varma,<sup>15</sup> and by Phillips,<sup>16</sup> that atomic tunneling could also occur in amorphous solids, even if they are chemically pure. They postulated that because of the disorder in these solids, a wide range of tunnel splittings would occur; it would lead to the uniform density of states (independent of the splitting) needed to explain the observed linear specific heat. However, the reason why tunneling occurred universally in *all* amorphous solids, irrespective of their microscopic composition, and would lead to linear specific heats of very similar magnitude in all cases, has remained an open question to this day. In spite of this shortcoming, this model has been extremely successful, not only in explaining existing experimental observations but also in predicting phenomena which were subsequently observed. Here we mention only one example: The model predicted a wide range of thermal relaxation times for the different tunneling states, since tunneling is very sensitive to the potential barrier. Thus, a heat pulse injected into a glassy sample would not lead to a temperature profile as shown schematically in the inset of Fig. 1, but rather to one of the kind shown in the inset of Fig. 5. As more states are “heated”, i.e., take up energy from their surroundings, the temperature of the thermally isolated sample decreases:  $\Delta T$  decreases with time, because the energy is spread over an increasing number of excitations. One way of describing this is by saying that the specific heat  $C_v$ , as defined in Eq. (5), is time dependent. According to the tunneling model in its simplest form,  $C_v$  should increase as the logarithm of time, i.e., it should increase by a constant amount for every decade of time that the sample has been held in isolation. This has indeed been verified by Lopenon *et al.*,<sup>17</sup> by Meissner and co-workers,<sup>18,19</sup> and by Zimmermann and Weber.<sup>20</sup> The data labeled  $50 \mu\text{s}$  in Fig. 5 were obtained by Knaak and Meissner<sup>19</sup>  $5 \times 10^{-5}$  s after application of the heat pulse. We omit here a discussion of the difficulties involved in measuring temperatures, and in assuring a uniform distribution of the heat throughout the sample, on such short time scales. Besides providing convincing evidence for the existence of intrinsic low energy *tunneling excitations in all amorphous solids*, these measurements have also shown that, strictly speaking, a specific heat does not exist in these solids at low temperatures, since a true thermal equilibrium cannot be reached on any finite time scale. This observation is of considerable interest from a

thermodynamic point of view, although, practically, it is of relatively minor importance: the short dashed line in Fig. 5 labeled  $10^4$  s shows by how little the specific heat changes between 10 s and approximately 3 h (three decades of time).<sup>20</sup> A logarithmic extrapolation of the experimental results to the age of the universe, only leads to the miniscule increase of the specific heat which is also indicated.

Thus, an extension of specific heat measurements to amorphous solids, in particular below 1 K, has led to significant new insights into the vibrational excitations of solids: In these solids, tunneling states, not plane waves, appear to contain the bulk of the thermal energy at low temperatures; furthermore, the concept of temperature itself has to be viewed with caution.

## V. ON THE UNIVERSAL NATURE OF TUNNELING STATES IN AMORPHOUS SOLIDS

As a final example of the use of specific heat measurements for the exploration of lattice vibration of solids, we want to return to the question of the universality of tunneling in amorphous solids, which we mentioned in the previous section. At the outset, it must be stated that the final answer is not yet available; however, some recent work has led to interesting suggestions.

As a perfectly ordered crystal, say of  $\text{SiO}_2$ , is disordered to its amorphous form, silica, it develops the low-energy tunneling excitations. One can hope that their physical nature may be clarified by searching for the onset of these states as the disorder in a crystal is gradually increased. Along these lines, much success has recently been achieved in alkali halide-alkali cyanide mixed crystals and also in alkali cyanide mixed crystals.

Pure alkali halide crystals have plane wave elastic excitations only, as shown in Fig. 4 for KBr as one example. In pure alkali cyanide crystals, the cyanide ions can rotate at their lattice sites at high temperatures. At low temperatures their long axes align along certain crystallographic directions. In this (antiferroelectric) phase, the elastic excitations are also plane waves only. When alkali cyanides are admixed to alkali halides in very small concentrations, the individual  $\text{CN}^-$  dumbbells retain their rotational mobility to the lowest temperatures, they tunnel between orientations, as was described in Sec. IV. As the cyanide concentration increases and their average separation shrinks, their interactions between one another will increase (they will tend to exert torques on one another). However, because of their random distribution throughout the crystal lattice, these interactions lead to an orientationally disordered state at low temperatures, if the KCN concentration exceeds approximately 10 mole %. This is shown schematically in Fig. 8 for a somewhat different case, namely the mixed crystal KCN-NaCN. In this crystal, only the alkali metal ions are randomly distributed. Yet, this randomness is enough to prevent the  $\text{CN}^-$  ions from ordering at low temperatures. One calls this state an "orientational glass state."<sup>21</sup> In this state, in which all ions occupy crystal lattice sites, and only the directions of some of their constituent molecules (e.g., the  $\text{CN}^-$  ions) are random, the low temperature specific heat has been found to be identical to that of (structurally) amorphous solids, as shown in Fig. 9 for a ~50-50 mixture of KBr and KCN.<sup>22</sup> Even the time dependence of the specific heat is the same as in glasses.

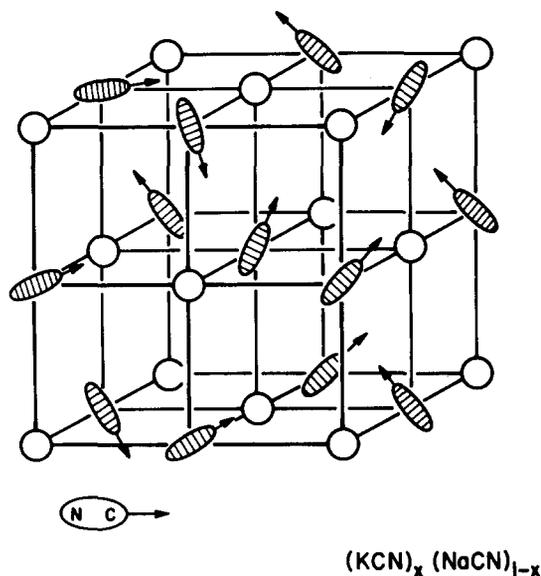


Fig. 8. In the mixed crystal  $(\text{KCN})_x (\text{NaCN})_{1-x}$  ( $x \sim 0.5$ ), the  $\text{CN}^-$  ions freeze at low temperature into random orientations. This is called an orientational glass. An orientational glass is also observed in  $(\text{KBr})_{1-x} (\text{KCN})_x$  ( $x \sim 0.5$ ).

The physical nature of these tunneling states has been explained<sup>22,23</sup>: Most of the  $\text{CN}^-$  ions are indeed immobile at the lowest temperatures, frozen into the random orientations. Only one in  $\sim 10^5$  ions finds itself in such an environment that the effects of the neighboring ions largely cancel each other, leaving this ion free to tunnel. The tunnel splittings, however, have different magnitudes for different ions (the onset of this spreading can be noticed in Fig. 6 for the highest  $\text{CN}^-$  concentration, 0.5%). The distribution of tunneling states shows up as a linear specific heat. Although it has not yet been possible to calculate the distribution of tunnel splittings from first principles, it has been derived experimentally from dielectric measurements (the  $\text{CN}^-$  ion carries an electric dipole moment), and has been shown to agree quantitatively with the distribution needed to explain the specific heat results.

How can these findings help to understand the tunneling states in amorphous solids? A look at Fig. 2(c) shows how we think it may do this. Because of the random distribution of its atoms, we propose that an amorphous solid has to be viewed as consisting of essentially densely packed groups of atoms which exert torques on each other. These quasimolecular groups have random orientations (think of a bag filled with beans), and their mutual interactions cause most of the groups to be immobilized at low temperatures. Only a small fraction, on the order of one to ten part per million, remains free to change the orientation by tunneling, because of the particular arrangement of its neighbors. With the aid of this picture, we have circumvented the differences one would expect to result from the different microscopic structures of amorphous solids, e.g., the chain structure of polymers versus the random dense packing of amorphous metals. By postulating the amorphous solid to consist of a random distribution of elastic dipoles, we have generated a solid which resembles the orientational glasses, with which they share the tunneling states. Obviously this

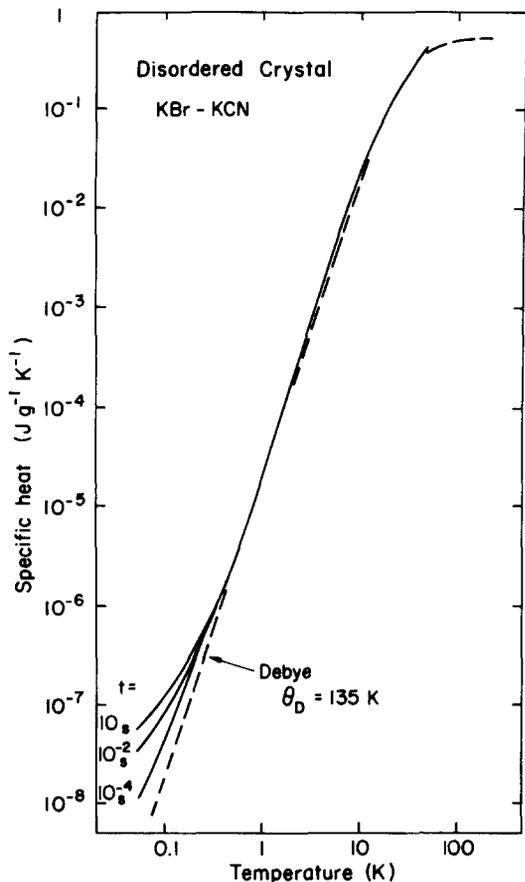


Fig. 9. The low temperature specific heat of the orientational glass  $(\text{KBr})_{1-x}(\text{KCN})_x$  ( $x \sim 0.5$ ) shows the same temperature and time dependence as do structural glasses. Reference 22.

is only a model we invented to guide us in further experiments. At the very least it demonstrates how we hope that a study of carefully disordered crystalline solids may help to unravel the mystery of the low energy excitations in glasses.

## VI. SUMMARY AND CONCLUSIONS

For over 100 years, measurements of the specific heat have contributed to our understanding of the lattice vibrations of solids. To the plane wave excitations, which describe fully the lattice vibrations in perfect crystals, tunneling excitations have had to be added to describe the

amorphous solid. Their physical nature is not yet understood, but the investigation of crystals with a controlled disorder promises to shed some light on this question.

## ACKNOWLEDGMENTS

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