Quadrupolar Nuclear Spin-Lattice Relaxation in InSb at Low and Medium Temperatures*

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Measurements of the nuclear spin-lattice relaxation rate of In^{115}, Sb^{121}, and Sb^{123} in InSb over the temperature range 3.8 to 300°K are reported. At temperatures exceeding 7°K, the dominant relaxation process is via quadrupolar coupling to the lattice vibrations. Below 7°K, the total relaxation rate is resolved into a sum of quadrupolar $(1/T_1^Q)$ and background impurity rates. For Sb^{121}, $1/T_1^Q$ is proportional to $T^{9.5\pm0.5}$ (T = temperature). A similar result is obtained for the other nuclei, but with reduced accuracy. This result disagrees with predictions based on the Debye model, but agrees with calculations based on a more accurate density-of-states function. Over the entire temperature range 4.2 to 300°K, the ratio $T_1^Q(Sb^{123})/T_1^Q(Sb^{121})$ is 1.45 ± 0.05, in agreement with theoretical predictions. The behavior of the ratio $T_1^Q(In^{115})/T_1^Q(Sb^{121})$ is quite different; it varies from 3.2 below 25°K to 1.4 at high temperatures. This change with increasing temperatures is attributed to the thermal excitation of optical phonons, which are more strongly coupled to In than to Sb nuclei.

I. INTRODUCTION

THE contribution of quadrupolar processes to nuclear spin-lattice relaxation in many nonmetallic solids at high temperatures has been widely studied both theoretically and experimentally. There appears to be, however, no prior report describing detailed experimental studies of the low-temperature behavior of this phenomenon. (For the purposes of this paper, we call the temperature range $T<0.05\Theta_D$ (T = temperature, Θ_D = Debye temperature) the low temperature range, and $0.05\Theta_D<T<0.5\Theta_D$ the medium-temperature range.)

Here we report an experimental study of the quadrupolar relaxation rate $(1/T_1^Q)$ of In^{115}, Sb^{121}, and Sb^{123} in InSb at low and medium temperatures (4–90°K). A theoretical interpretation at the simplest level for agreement with most of the experimental results is included.

The motivation for the work was twofold. First, the temperature dependence predicted for it at low temperatures by Van Kranendonk[1] using a Debye model for the phonon spectrum had not been tested. In addition, the importance of low-temperature quadrupolar relaxation with regard to a method of polarizing nuclei[2] in InSb needed to be assessed.

It is quite reasonable that nuclear quadrupolar relaxation at low temperatures has not been widely reported. There is a severe difficulty associated with such experiments, namely, at low temperatures the process is very weak.[1,3] It then follows that the measurements require a long time and the danger of competition from other processes is severe.[3–5] These problems have been mini-mized in the present work by employing a shortcut in the measurement method and a careful choice of sample-preparation techniques.

One of the major surprises (to us) of this work was the extent to which the temperature dependence of the relaxation rate deviates from that predicted by the Debye model[1,3] in the low-temperature range (4–10°K). This model predicts a rate proportional to T^7 below 7°K, whereas the observed rate between 4.5 and 7°K for the most accurate measurement is proportional to $T^{9.5\pm0.5}$. It is shown that the latter value is predicted theoretically if a more accurate phonon spectrum for transverse acoustic phonons is used in place of that given by the Debye model. This sensitivity of the relaxation rate to the phonon spectrum indicates that it may be a useful tool for checking gross features of phonon spectra.

Another unexpected result is a decrease in the ratio of the relaxation time of In to Sb which occurs at temperatures above 30°K. On the basis of a simple phenomenological model, it is argued that the effect is caused by the thermal excitation of optical phonons which are relatively more strongly coupled to the In nuclei than to the Sb nuclei. This coupling to optical phonons is analogous to that discussed by Wikner, Blumberg, and Hahn[6] for the alkali halides.

The order of presentation is as follows: First, a brief discussion of the experimental apparatus and procedures is given in Sec. II. It is followed by a presentation of experimental results in Sec. III. Section IV is devoted to an interpretation of the experimental results, which is prefaced by a brief review of the existing theories of quadrupolar relaxation relevant to our work. In the latter part of Sec. IV, the results which differ most with previous work are emphasized. Our conclusions are

[1] J. Van Kranendonk, Physica **20**, 781 (1954).

[2] W. G. Clark and G. Feher, Phys. Rev. Letters **10**, 134 (1963).

[3] R. L. Mieher, Phys Rev. Letters **4**, 57 (1960); R. L. Mieher, Phys. Rev. **125**, 1537 (1962).

[4] M. J. Weber, Phys. Rev. **130**, 1 (1963).

[5] C. V. Briscoe and C. F. Squire, Phys. Rev. **112**, 1540 (1958).

[6] E. G. Wikner, W. E. Blumberg, and E. L. Hahn, Phys. Rev. **118**, 631 (1960).

summarized in Sec. V. An Appendix is included to discuss theoretically some of the approximations used to arrive at the expression used for the temperature dependence of T_1^Q in the body of the paper.

II. EXPERIMENTAL DETAILS

Measurements of the nuclear spin-lattice relaxation time (T_1) were taken for the isotopes In^{115}, Sb^{121}, and Sb^{123} using a pulsed nuclear magnetic resonance (NMR) apparatus described elsewhere.[7] An NMR frequency of 7 MHz was employed with the magnetic field (H_0) adjusted to resonance at approximately 7.5 kG for In^{115}, 6.9 kG for Sb^{121}, and 12.7 kG for Sb^{123}.

In order to check on any contribution to T_1 from conduction electrons, several single crystal n-type InSb samples with different conduction electron concentrations (n_0=concentration at 77°K) were prepared. For two of them, very pure, uncompensated InSb supplied by Cominco Products, Inc., was used as starting material. They were doped with thermal neutrons[8] to $n_0 = 1 \times 10^{14}$ cm^{-3} and $n_0 = 3 \times 10^{15}$ cm^{-3}. A high-concentration sample, from Semitronics, had been doped with Te in the melt to $n_0 = 3 \times 10^{17}$ cm^{-3}. These concentrations were measured using standard Hall-effect techniques. Each sample was mounted in such a manner that it could be rotated 360° about the [01$\bar{1}$] axis oriented perpendicular to the applied magnetic field.

Measurements of T_1 when it was less than 5 min were made using conventional pulsed NMR techniques. However, when $T_1 > 5$ min, such measurements consume much time, and another method was used. Briefly, it was as follows: An NMR calibration sample with a short value of T_1 at low temperatures ($Na^{23}Cl$:Fe^{++}) was included with the InSb inside the receiver coil. At a temperature for which the InSb nuclei had a short value of T_1 (77°K), the relative amplitudes of the InSb and calibrator NMR signals at thermal equilibrium were measured. Since all species obey a Curie law, this ratio is independent of temperature. The thermal equilibrium NMR signal amplitudes for InSb at low temperatures were then inferred from the measured equilibrium signal amplitude of the calibrator and the previously measured amplitude ratios. Finally, the initial recovery of the InSb magnetization from zero toward its thermal equilibrium value (M_0) was measured by waiting a time Δt after saturation by a group of 90° pulses and observing the resultant value of the magnetization (ΔM). The relation

$$T_1 = \Delta t / \ln[M_0 / (M_0 - \Delta M)], \qquad (1)$$

valid for exponential recovery, was used to calculate T_1. With this method it was possible to measure relaxation times as long as 40 h in 1 h or less. Several checks of

the entire recovery to thermal equilibrium at high and low temperatures exhibited exponential behavior. Such behavior was assumed for all measurements.

The errors in our T_1 measurements came from several sources. The most important of these was usually the uncertainty in ΔM or M_0 caused by noise. Although the noise was about the same for measurements on all three isotopes, the signals, which depend on the magnetic moment and isotopic abundance, were not. This situation led to errors in T_1 which were different for the three isotopes. In many cases, T_1 was a rapidly varying function of the temperature; therefore, errors in temperature measurement also contributed some scatter in T_1.

For short values of T_1 (less than 5 min), measurements were made of M_0 at equilibrium and ΔM along the recovery curve. The former was measured several times and an average value correct to about 1% obtained. Scatter in a semilogarithmic plot of these data (Eq. 1) led to errors in T_1 ranging from 3 to 7%. Since the temperature dependence of T_1 for these times was close to T^3, our estimated error of 1% in T contributed a scatter in T_1 which was at most 3%.

Electrical noise was also an important source of error in measuring the long values of T_1. In addition, the rapid temperature dependence of T_1 (as high as $T^{9.5}$) caused errors in T_1 which could range as high as 10% because of errors in temperature measurement. The errors in M_0 were less than 5%. This figure is somewhat higher than the value obtained in the other measurements because of additional errors introduced by use of the calibrator sample. Errors in ΔM ranged from 3 to 10%.

Estimates of our errors in T_1 are indicated with error flags for most of the points on the graphs of experimental data. In the figures showing changes of T_1 over many orders of magnitude (Figs. 1 and 5), the estimated errors are approximately the size of the data points.

The temperature in this experiment ranged from 3.8 to 300°K. Over part of this range, the sample temperature was maintained through direct contact with three cryogenic fluids; liquid oxygen (90–55°K), liquid hydrogen (20–14°K), and liquid helium (4.22–3.8°K). Within the ranges of these liquids, the absolute temperature was kept constant to about 1% by using a manostat to regulate the vapor pressure over the liquid.

Temperatures between those available directly with the cryogenic fluids were obtained using a heat leak to a cold thermal reservoir and heater whose input power could be varied. The temperature was measured by a carbon resistance thermometer in thermal contact with the sample. This resistor was also used as the sensing element of a temperature regulating system, which operated as follows: The off-balance signal from a Wheatstone bridge (Millivac Instruments Model RM-267B) connected to the sensing resistor was fed via a dc amplifier (Dana Model 2200) to the regulating circuit of a dc power supply (H-Lab Model 6626A),

[7] W. G. Clark, Rev. Sci. Instr. 35, 316 (1964).
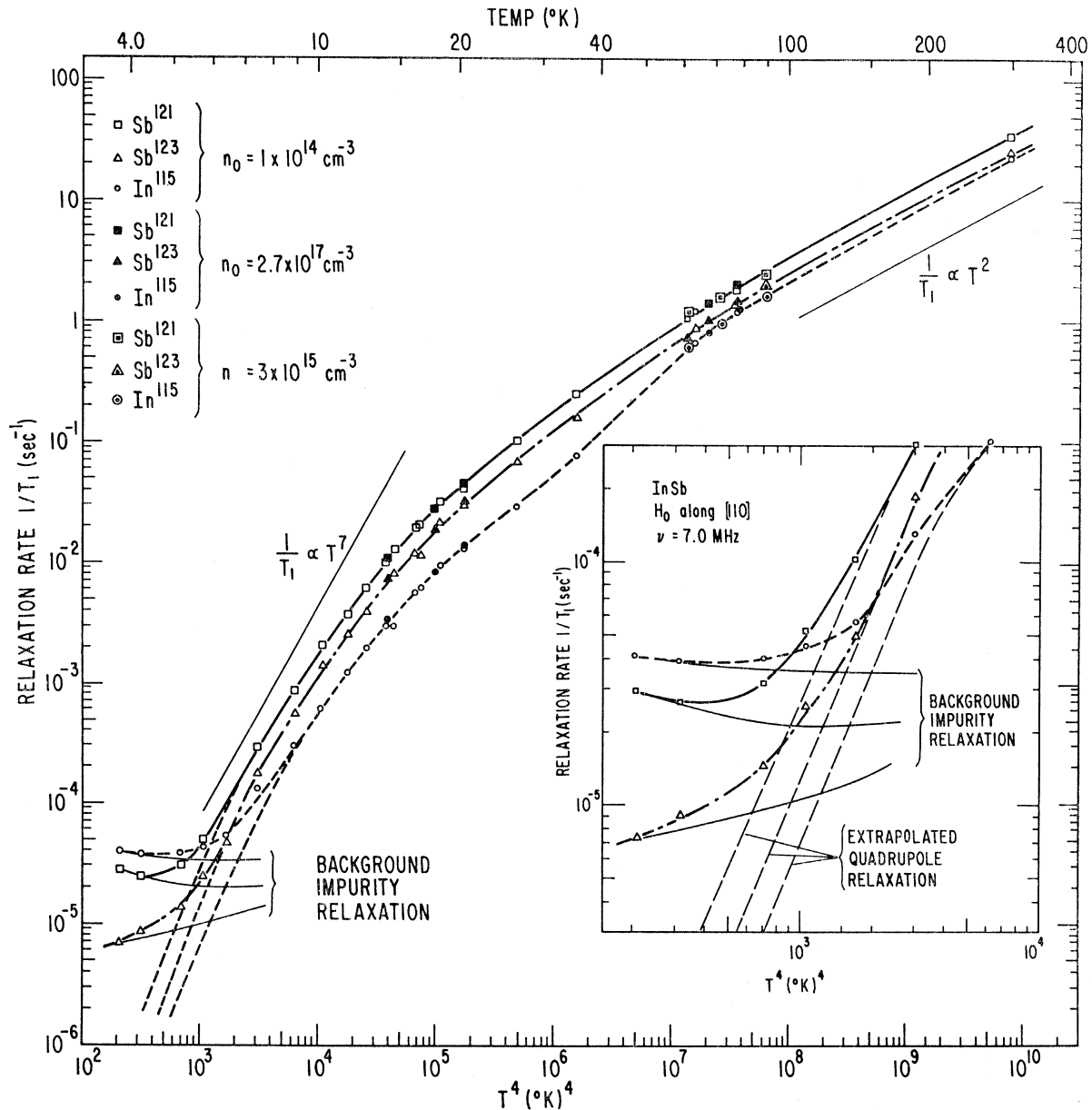[8] W. Gilbert Clark and R. A. Isaacson, J. Appl. Phys. 38, 2284 (1967).

FIG. 1. Experimental nuclear spin-lattice relaxation rate $1/T_1$ of In^{115}, Sb^{121}, and Sb^{123} in InSb as a function of the fourth power of the temperature T. The insert shows the resolution of the total relaxation rate into a quadrupolar relaxation rate $1/T_1{}^Q$ and a background-impurity relaxation rate. At the lowest temperatures shown, $1/T_1{}^Q$ for Sb^{121} varies as $T^{9.5\pm0.5}$. This temperature dependence is attributed to the structure of the low-frequency phonon spectrum in InSb.

which in turn powered the heater. With this system, temperature control to better than 1% over periods of several hours was obtained.

III. EXPERIMENTAL RESULTS

Measured values of the spin-lattice relaxation rate $1/T_1$ for In^{115}, Sb^{121}, and Sb^{123} in InSb as a function of temperature over the range 3.8–300°K with H_0 along the [110] direction are given in Fig. 1. (Logarithmic

scales and T^4 for the abscissas are employed to make the data presentable on a single graph.) Lines corresponding to $1/T_1 \propto T^7$ and $1/T_1 \propto T^2$ have been added for subsequent comparison with theoretical predictions. Also, a separation of $1/T_1$ into a background impurity relaxation component and a quadrupolar component is indicated. This resolution will be discussed shortly.

At 7.4, 11.5, and 18.8°K, measurements of T_1 for In^{115} and Sb^{121} were made as a function of the angle (θ) between the [100] direction and the magnetic

field direction, while keeping the magnetic field in the (01$\bar{1}$) plane. Experimental results for In^{115} and Sb^{121} at 7.4°K are shown in Fig. 2. It is seen that $1/T_1^{121}$ is independent of θ, while $1/T_1^{115}$ has a peak in the [100] direction. The curve for In^{115} has been resolved into a sum of quadrupolar and impurity contributions. (This resolution will be discussed shortly.) At 11.5°K (Fig. 3), $1/T_1$ is independent of θ for both In^{115} and Sb^{121}. The relaxation rates at 18.8°K (not shown) are also independent of θ.

The separation of $1/T_1$ into a background-impurity component[9] and a quadrupolar component is central to some of the conclusions we shall draw. It is therefore appropriate to anticipate Sec. IV and discuss it in some detail here. The identification of essentially all of the relaxation above about 8°K as quadrupolar (see Fig. 1) is easy. In that temperature range, the dependence of T_1 on temperature, spin, and quadrupole moment, and its independence of orientation, concentration, and sample origin conform very closely to that expected of quadrupolar relaxation (see Sec. IV).
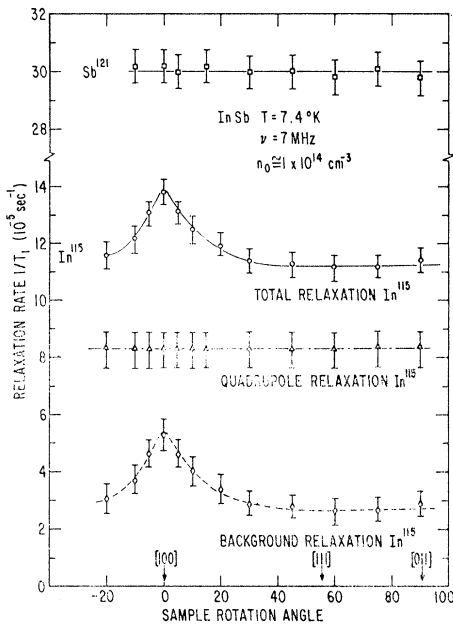
The separation below 8°K is somewhat more difficult.

FIG. 2. Experimental nuclear spin-lattice relaxation rate for In^{115} and Sb^{121} in InSb at 7.4°K as a function of angle between the magnetic field and the [100] axis for rotation about the [01$\bar{1}$] axis. The In^{115} relaxation rate (lower solid line) is resolved into an orientation-dependent background rate (lower dashed line) and an orientation-independent rate (upper dashed line) identified as of quadrupolar origin. The upper solid line (Sb^{121}) is attributed entirely to quadrupolar relaxation.

FIG. 3. Experimental nuclear spin-lattice relaxation rate for In^{115} and Sb^{121} at 11.5°K as a function of angle between the magnetic field and the [100] axis for rotation about the [01$\bar{1}$] axis. The entire relaxation rate is attributed to quadrupolar relaxation.

It is, nonetheless possible to find enough constraints on the separation to make it almost unique. The first constraint is the very rapid temperature dependence required of quadrupolar relaxation at low temperatures (see Sec. IV). The onset of this rapid temperature dependence is seen experimentally (Fig. 1) for Sb^{123} near 6°K. It then follows that the relaxation at 3.8°K is almost all due to the background impurity process. An experimental study of this background process in the range 1.3–4.2°K shows its temperature dependence to be rather weak,[10] a conclusion that is also supported by the extent to which the mechanisms responsible for the background relaxation are understood. It is, therefore, plausible to assume that the extrapolation of the background process up to 7.5°K should be done with a weak (proportional to T^x, where $|x| \lesssim 1$) temperature dependence. The resolution of Fig. 1 is based on these criteria.

The dependence of $1/T_1$ on θ for In at 7.4°K (Fig. 2) illustrates how the angular dependence of the background relaxation can be used as a check on the resolution of the total relaxation rate into quadrupolar and background components. Extensive investigations in the range 1.4–4.2°K have shown[8,10] that the impurity relaxation for In^{115} has the angular dependence of the impurity component in Fig. 2 with a peak-to-valley ratio of about 2:1. A measurement of this ratio at 4.2°K on the sample used here gave 1.9±0.1. If it is assumed that this behavior continues to 7.4°K, and the quadrupolar component is independent of θ, the resolution of Fig. 2 is obtained. Within the experimental error, this resolution agrees with that of Fig. 1.

Let us now summarize the more important characteristics of our measurements:

(a) The relaxation rate varies slowly with temperature below about 6°K, increases rapidly with temperature between 6 and 20°K, and increases more slowly above 20°K. The total rate is resolved into a background

[9] The assignment of the background process to impurities is based on a fairly extensive study of their origin and properties, to be reported elsewhere (Refs. 8 and 10). The impurities in question include conduction electrons, paramagnetic impurities, and perhaps other imperfections, but not phonons. We believe that in a perfect, insulating InSb sample, the relaxation attributed to impurities would not occur, and only the quadrupolar relaxation would be observed.
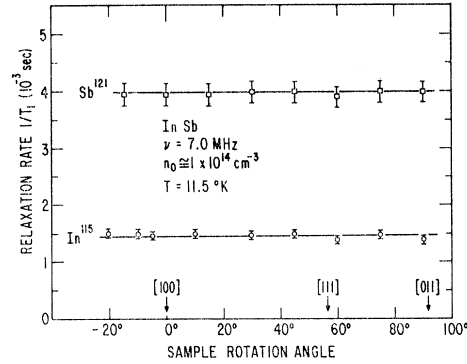
[10] F. Bridges and W. G. Clark, Bull. Am. Phys. Soc. 10, 700 (1965). A more complete report of this work is in preparation.

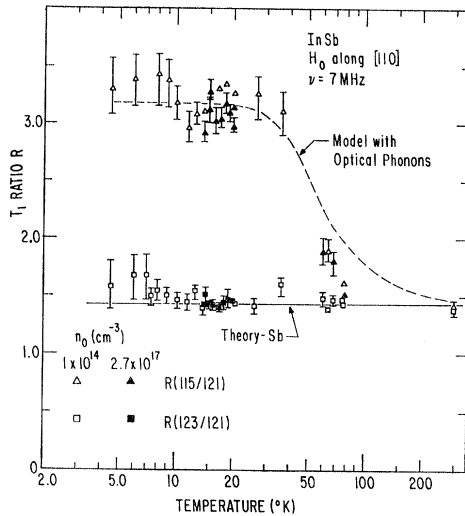FIG. 4. Experimental values of the ratio of quadrupolar nuclear spin-lattice relaxation rates for In[115] and Sb[121] [R(115/121)], and Sb[123] and Sb[121] [R(123/121)] as a function of temperature in InSb. The theoretical prediction (see Refs. 3 and 12) for R(123/121) is indicated by the solid line and the prediction for R(115/121) based on the excitation of optical phonons (see Sec. IV D) is indicated by the dashed line.

process which varies slowly with temperature and a quadrupolar process. The quadrupolar relaxation rate $1/T_1^Q$ for the Sb isotopes is proportional to $T^{9.5\pm0.5}$ in the temperature range 4.5–7°K, and gradually curves over to $1/T_1^Q \propto T^2$ above 100°K. The behavior of $1/T_1^Q$ for In[115] is similar, but not identical to that of Sb [see item (e)].

(b) There is no orientation dependence of T_1 at 10°K and above, but at somewhat lower temperatures an orientation dependence appears. This orientation dependence is attributed to the background relaxation, leaving $1/T_1^Q$ independent of θ.

(c) There is no dependence of $1/T_1^Q$ on n_0 for $n_0 = 1\times10^{14}$ cm^{-3}, 3×10^{15} cm^{-3}, and 3×10^{17} cm^{-3}. This indicates that T_1^Q is a property of the lattice.

(d) The ratio of relaxation times R(123/121) $\equiv$ $T_1^Q(123):T_1^Q(121) = 1.45\pm0.05$ for the two Sb isotopes is independent of T and n_0. This is illustrated by Fig. 4, where the different ratios are plotted as a function of temperature.

(e) The corresponding ratio (Fig. 4) for In[115] and Sb[121] [R(115/121)] does depend on temperature, making a smooth transition from 3.2 below 20°K to 1.4 above 100°K. An equivalent change is observed for R(115/123).

IV. INTERPRETATION

A. Existing Theory

Before discussing our experimental results, some of the pertinent points of the existing theory of quadrupolar relaxation in solids will be briefly sketched to establish a frame of reference. The first detailed theoretical calculations were made by Van Kranendonk.[1] He developed a theory of quadrupolar relaxation which assumed that the lattice could be described as an array

of point charges located at the lattice sites and that only nearest-neighbor interactions were important. It was also assumed in this calculation that the crystal structure was cubic and had inversion symmetry. The dominant process for quadrupolar relaxation was shown to be a first-order two-phonon process (Raman process) in which the nucleus makes transitions $\Delta m = \pm1$ (but not $-\frac{1}{2}\leftrightarrow\frac{1}{2}$), ±2, and a phonon is scattered such that the total energy is conserved. Electron cloud polarization effects were represented by a multiplicative Sternheimer antishielding factor (γ). Use of the Debye model to describe the spectrum of lattice vibrations yielded a temperature dependence for $1/T_1^Q$ which varied from $1/T_1^Q \propto T^7$ at low temperatures ($T\leq 0.02\Theta_D$) to $1/T_1^Q \propto T^2$ at high temperatures ($T\geq\Theta_D$). An angular dependence of the individual transition probabilities was also indicated.

Mieher[3] applied the Van Kranendonk formalism to a cubic lattice without inversion symmetry (such as InSb) and obtained similar results for the individual transition probabilities. He also showed theoretically that thermal equilibrium within the spin system[11] and use of the Debye approximation gives the following result:

$$\frac{1}{T_1^Q} = \frac{2I+3}{I^2(2I-1)}\frac{1}{40}(e^2Q\gamma)^2\frac{24}{\pi d^2 v^3 a^3}\frac{3305 T^{*2}E(T^*)}{r^{10}}, \quad (2)$$

where I is the nuclear spin, Q is the nuclear quadrupole moment, d is the mass density, v is the velocity of sound, a is the lattice constant ($a=6.48$ Å for InSb), r is the nearest-neighbor distance, $T^*=T/\Theta_D$, and $E(T^*)$ is a complicated function of temperature defined by Van Kranendonk. Equation (2) shows explicitly the dependence of $1/T_1^Q$ on I and Q (for all lattices) is independent of the magnetic field orientation, and has the same temperature dependence as the Van Kranendonk theory. Substantial agreement between Eq. (2) and experiments on zincblende lattices at moderate and high temperatures was also obtained by Mieher.[3] More recently, Zak[12] has shown by symmetry arguments that in the spin temperature limit, for cubic lattices (such as the zincblende structure possessed by InSb), $1/T_1^Q$ is independent of the orientation of the magnetic field with respect to the crystalline axes. His result is independent of the model used to represent the spin-phonon coupling.

The models discussed by Van Kranendonk[1] and Mieher[3] neglected the difference between the contributions of the optical and acoustical phonon modes. The importance of optical phonons as a contribution to T_1^Q at high temperatures has been emphasized by Kochelaev,[13] Wikner et al.,[6] Weber,[4] and Joshi et al.[14]

The effect of optical phonons is to introduce an

[11] This assumption is valid for InSb over the temperature range covered in this work (see Ref. 3).
[12] J. Zak, Physica **30**, 401 (1964).
[13] B. I. Kochelaev, Zh. Eksperim. i Teor. Fiz. **37**, 242 (1960) [English transl.: Soviet Phys.—JETP **10**, 171 (1960)].
[14] S. K. Joshi, R. Gupta, and T. P. Das, Phys. Rev. **134**, A693 (1964).

extra contribution to $1/T_1{}^Q$ which is negligible at low temperatures (because of their high excitation energy), but which may be important at high temperatures. The temperature variation of this contribution to $1/T_1{}^Q$ is expected to have the same high-temperature dependence as the acoustical contribution, i.e., proportional to T^2. It need not, however, have the same relative coupling strength for different nuclei in a polyatomic substance as the acoustical phonons.[4,6,14]

B. Discussion of Experimental Results

In this section we examine the extent to which our experimental results are in agreement with existing theories based on a Debye spectrum of acoustical phonons, as represented by Eq. (2) and its adjoining comments. The question of absolute values of $T_1{}^Q$, which depends on the size of γ, will be ignored, and the discussion limited to relative comparison, such as the temperature dependence, angular dependence, etc., of $T_1{}^Q$.

First, consider the properties for which Eq. (2) is a satisfactory description. Experimentally, there is no angular dependence to $T_1{}^Q$, as predicted by Eq. (2). Since this result is expected on the basis of general symmetry arguments, it would be very surprising if it did not occur.

It is found experimentally that $T_1{}^Q$ is independent of n_0, indicating that $T_1{}^Q$ is a property of the pure lattice. This independence of n_0 also appears in Eq. (2), which is derived for an ideal lattice. (The reason that no dependence of $T_1{}^Q$ on n_0 is observed at all but the lowest temperatures is that n_0 is too small for conduction electronic processes to compete effectively with the Raman process,[10] a situation which holds all the way to the melting point of InSb.[15])

Next we note that existing theory predicts, and experiments on AlSb at 77°K have verified,[3] that

$$R(123/121) = \left(\frac{Q_{121}}{Q_{123}}\right)^2 \frac{I^2_{123}(2I_{123}-1)(2I_{121}+3)}{I^2_{121}(2I_{121}-1)(2I_{123}+3)}. \quad (3)$$

This result follows from the work of Mieher[3] and Zak.[12,16] Substitution of the values[17] $I_{121}=\frac{5}{2}$, $I_{123}=\frac{7}{2}$,

[15] W. G. Clark and W. W. Warren (to be published).

[16] The simple form obtained for $R(123/121)$ in Eq. (3) rests on the assumption that the part of the spin-phonon coupling which depends on the details of the phonons is the same for both Sb[121] and Sb[123]. Because of the mass difference between the two isotopes, the assumption is only approximately correct. We have estimated the correction to Eq. (3) due to this isotopic mass difference using the following model. The lattice vibrations are represented by those of a one-dimensional monatomic lattice with restoring forces proportional to the separation between nearest neighbors. Antimony atoms with the naturally occurring isotopic abundance are distributed at random to fill all sites of the lattice. The fractional difference in mean-square displacements of the two isotopes is then found to be on the order of $\langle \Delta m^2 \rangle / \langle m \rangle^2$ or less, where $\langle \Delta m^2 \rangle$ is the mass dispersion and $\langle m \rangle$ is the mean value of the mass for Sb. From this result the correction to $R(123/121)$ is found to be on the order of $6\langle \Delta m^2 \rangle / \langle m \rangle^2$ or less, i.e., on the order of 0.04% or less. Since the effect is so small, it has been neglected elsewhere in this paper.

[17] Our numerical values were obtained from *Nuclear Data Sheets*, compiled by K. Way *et al.* (Printing and Publishing Office, National Academy of Sciences-National Research Council, Washington 25, D.C., 1962), Appendix 1.

and $Q_{121}/Q_{123}=0.79$ into Eq. (3) yields $R(123/121) = 1.47$, which agrees with the experimental result

$$R_{\text{exp}}(123/121) = 1.45 \pm 0.05.$$

Again, it would be surprising if this result were not obtained, because its theoretical foundation is independent of the detailed model for the coupling between the phonons and the nuclear quadrupole moment.[16] The extent to which this relationship is observed over a wide range in temperature (see Fig. 4) constitutes a strong argument for the assignment of the antimony relaxation as quadrupolar.

Finally, the temperature dependence of T_1 above 100°K obeys the relationship $(1/T_1) \propto T^2$, as predicted by Eq. (2). Subsequent work[15] shows this to be the case up to the melting point of InSb.

Now we turn to the experimental results for which Eq. (2) is inadequate.

The first of these is the temperature dependence of $1/T_1{}^Q$ at low temperatures. For example, Eq. (2) predicts $1/T_1{}^Q \propto T^7$ between 4.5° and 7°K, whereas the experimental result is $1/T_1{}^Q \propto T^{9.5 \pm 0.5}$ for the Sb isotopes. (The exponent for In is the same, but with a much larger error because of more effective competition from the background relaxation.) A modification to Eq. (2) which accounts for the temperature dependence of $T_1{}^Q$ in the low-temperature range is discussed in the next section.

The second way in which our experimental results do not agree with the prediction of Eq. (2) is the temperature dependence of $R(115/121)$ in Fig. 4. An alternative representation of this phenomenon is the different dependence of $1/T_1{}^Q$ on T for Sb and In in Fig. 1.[18] Equation (2), on the other hand, predicts the temperature dependence of $1/T_1{}^Q$ is the same for all species, i.e., $R(\text{In/Sb})$ should be independent of T.

From a naive (i.e., nearest-neighbor point-charge model) viewpoint, the observed temperature dependence of $R(\text{InSb})$ is surprising, because the environment of both In and Sb in InSb is in some respects quite similar. An In nucleus is at the center of a tetrahedron of Sb nuclei, whereas an Sb nucleus resides at the center of an identical tetrahedron of In nuclei. Furthermore, the masses of all the isotopes are so close that one does not expect the effect of atomic mass on phonon amplitudes to cause an important difference in the spin-phonon couplings.[16] In Sec. IV.D, it is shown that a somewhat more realistic viewpoint, which goes beyond the point-charge model and makes a distinction between acoustic and optical phonons, can explain our experimental result.

[18] If the change in $R(115/121)$ with decreasing value of T were to smaller values, it could be argued that some nonquadrupolar relaxation mechanism which affected only the In was responsible for the change in R at medium temperatures. However, since the Sb relaxation is established as quadrupolar (see Sec. II) and the observed effect on In is a reduction of the relaxation rate relative to Sb, it is not possible to invoke additional relaxation mechanisms to explain it.

C. Application of Calculated Phonon Spectrum at Low Temperatures

It was pointed out in the preceding section that the observed low-temperature variation of $1/T_1{}^Q$ is somewhat faster than that predicted using the Debye model for the phonon spectrum. Here, we show that the use of a more realistic acoustic phonon spectrum brings the theoretical predictions into agreement with our experimental results over the temperature range 4–10°K, and predicts $1/T_1{}^Q \propto T^7$ at still lower temperatures. The treatment given below represents a useful simplification of a much more detailed calculation of the temperature dependence of $T_1{}^Q$ in the diamond and zincblende lattices. The more general result, which appears in an accompanying publication by one of us (F.B.),[19] extends the range of close ($\sim$12%) agreement between theory and the experimental values of $T_1{}^Q$ for the Sb nuclei up to about 60°K.

As discussed in the Appendix, the temperature dependence of $1/T_1{}^Q$ at low temperatures is given approximately by

$$\frac{1}{T_1{}^Q} = \text{const} \times \int_0^\infty \frac{\rho_{\text{TA}}{}^2(\omega)\omega^2 d\omega}{\sinh^2(\hbar\omega/2kT)}, \qquad (4)$$

where ω is the phonon frequency, $\rho_{\text{TA}}(\omega)$ the density of transverse acoustic phonon states, and $\hbar$ and k are Planck's and Boltzmann's constants, respectively.

In order to evaluate Eq. (4), we shall use Phillips' values[20] for $\rho_{\text{TA}}(\omega)$. However, before presenting the results of this calculation, two remarks based on a detailed examination of Eq. (4) will be made. First, it can be seen from Phillips's work that up to about 40% of the Debye frequency, essentially all of the modes are transverse acoustic. Since we have restricted the discussion to these modes, it is valid only at temperatures low enough that the denominator of the integrand in Eq. (4) makes any contribution from higher energy modes (longitudinal acoustic and optical) negligible. This upper bound on the temperature is about 10°K. The second point is that since $\rho_{\text{TA}}(\omega) \propto \omega^2$ for very small values of ω, there will be an extreme low-temperature regime for which the prediction of the Debye model, i.e., $1/T_1{}^Q \propto T^7$ will hold.[1] This occurs for temperatures less than 3°K.

The temperature dependence of $1/T_1{}^Q$ obtained by the method just described is shown as the solid line on Fig. 5. The result obtained from treatments based on the Debye model[1,3] (dashed lines) and some of our experimental data for Sb[123] are included for comparison. First consider the result obtained with Phillips' density of states. (Since our interpretation is concerned with the temperature dependence of $1/T_1{}^Q$ and not with

absolute values, the theoretical curve has been adjusted vertically to fit the data near 6°K, where the uncertainty in the quadrupolar contribution to $1/T_1$ is small.) It is seen that the fit between this theory and our experiments is good to about 15% over the three decades in $T_1{}^Q$ covered by the temperature range 4.2–10°K. (Although the theoretical result is valid only up to 10°K, it has been plotted to 17°K.) We believe this agreement between the theory and our experiments strongly supports our interpretation of the low temperature dependence of $1/T_1{}^Q$.

It is instructive to compare our experimental results with the predictions of the simpler model[1,3] based on a dispersionless substance with a Debye phonon spectrum. These predictions are represented by an alternating dashed line in Fig. 5, which has been fitted to the experimental value of $1/T_1{}^Q$ at 300°K. Although the high-temperature behavior of $1/T_1{}^Q$ ($1/T_1{}^Q \propto T^2$)[3,15] is adequately fitted by this model, it is seen that it underestimates $1/T_1{}^Q$ by as much as one order of magnitude in the intermediate temperature range. The other dashed line in Fig. 5 is an extrapolation of the T^7 region obtained with $\rho_{\text{TA}}(\omega)$ to temperatures above 3°K. It illustrates the large difference between results obtained with $\rho_{\text{TA}}(\omega)$ and those obtained using a Debye spectrum.
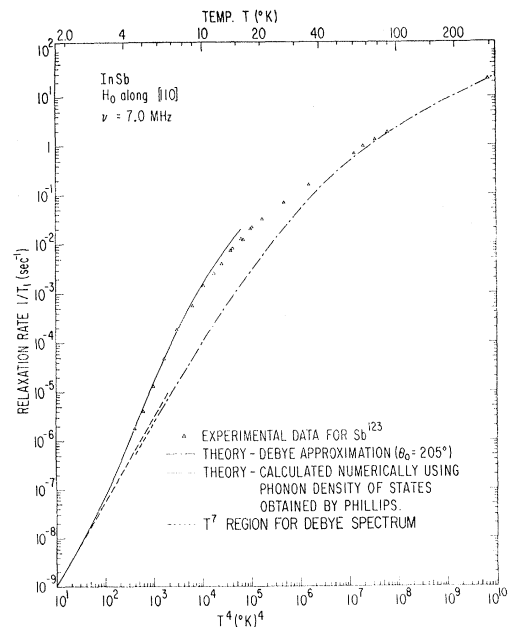

FIG. 5. Theoretical and experimental quadrupolar relaxation rates for Sb[123] in InSb as a function of the fourth power of the temperature. The solid line is obtained from Phillips's density of states (Ref. 20) and Eq. (4) of the text. Use of van Kranendonk's theory (Ref. 1) and a Debye spectrum for the phonons gives the alternating dashed line, which has been adjusted to fit the experimental value at 300°K. The dashed line at low temperatures corresponds to using a Debye spectrum that has been made to agree with Phillips's density of states in the low-frequency limit. Experimental points corresponding to the resolution of Fig. 1 are indicated by triangles.

[19] F. Bridges, following paper, Phys. Rev. 164, 299 (1967).

[20] J. C. Phillips, Phys. Rev. 113, 147 (1959). For the purposes of this paper, we shall adopt the phonon spectrum for InSb to be approximately that of gray tin with a small correction in Debye temperature as suggested by Phillips.

There is another approach to explaining the low-temperature behavior of $1/T_1{}^Q$ that is worth noting here, namely, to treat the lattice modes in the Debye approximation, but allow Θ_D itself to be a function of temperature. This approach is used widely in discussions of the specific heats of solids at low temperatures and is incorporated, for example, in part of Phillips's treatment of diamond-type lattices.[20] The application of this approach to quadrupolar relaxation in InSb is accomplished by including the temperature dependence of Θ_D in Van Kranendonk's function[1] $T^{*2}E^*(T^*)$ $[T^*=T/\Theta_D(T)]$. Measurements of $\Theta_D(T)$ for InSb are available from specific heat data.[21] If these values of $\Theta_D(T)$ are substituted into $T^{*2}E^*(T^*)$, one finds a temperature dependence of $T_1{}^Q$ for the Sb nuclei which is indistinguishable from the experimental values between 6 and 15°K, and which agrees with the experimental values within 35% all the way to 250°K. We believe this agreement to be fortuitous, however, because the functional dependence of the specific heat on the lattice dynamics is different from that of the quadrupolar relaxation rate. (This fact has already been pointed out by Mieher[3] and by Weber.[4]) There is, therefore, no *a priori* reason why $\Theta_D(T)$ obtained from specific-heat measurements should be applicable to our quadrupolar relaxation rate measurements.

D. Optical Phonons

We now present arguments in support of attributing the change in $R(\text{In}/\text{Sb})$ (see Fig. 4) over the temperature range 30–100°K to the thermal excitation of optical phonons.[4,6,13,14]

At the phenomenological level, what is needed to explain the temperature dependence of $R(\text{In}/\text{Sb})$ is an appropriate set of high-energy phonon modes which are more strongly coupled to the In nuclei relative to the Sb nuclei than are the low-energy lattice modes. The value of $R(\text{In}/\text{Sb})$ at low temperatures would be governed by the thermal excitation of low-energy phonons. At intermediate temperatures, the onset of thermal excitation of high-energy phonon modes would then change R toward values characteristic of high temperatures.

Let us calculate the temperature dependence of $R(\text{In}/\text{Sb})$ using a model based on several simplifying assumptions. First, it will be assumed[4,13] (Einstein model) that all optical phonons have the same fre-

quency $(\bar{\omega}_0)$. Reference to the phonon densities of states published by Phillips[20] illustrates that this is a good approximation for InSb. Furthermore, the observations that the $k=0$ optical phonon energy is[22] $\omega_0 = 3.44 \times 10^{13}$ rad sec^{-1} for InSb and the average optical phonon energy is about 5% less than its value[20] at $k=0$ lead us to $\bar{\omega}_0 \equiv k\bar{\Theta}_0/\hbar = 1.25 k\Theta_D/\hbar$ for use with the Einstein model. The second assumption will be that the ratio of relaxation rates due to acoustical phonons is independent of temperature. This assumption is plausible because the experimental data up to about 30°K are attributed to acoustical phonons, the majority of which can be shown to have become effective for relaxation at 30°K. It will also be assumed that mixed processes involving one acoustical and one optical mode can be ignored because of energy conservation in the Raman process (see density of states in Ref. 20).

Under these conditions, the total relaxation rate (W) for a given isotope is the sum of an acoustical part (W_A) and an optical part (W_0), each of which is a function of T:

$$W(T) = W_A(T) + W_0(T). \tag{5}$$

If all the optical modes are at about the same frequency, $W_0(T)$ separates into a product of two factors,[23] $\sinh^{-2}(\hbar\bar{\omega}_0/2kT)$ and a sum over the optical modes that is independent of temperature (w_0), i.e.,

$$W_0(T) = w_0 \sinh^{-2}(\hbar\bar{\omega}_0/2kT). \tag{6}$$

Hence,

$$R(T) = T_1{}^{115}/T_1{}^{121} = W^{121}(T)/W^{115}(T)$$
$$= W^{121}(T)/[W_A{}^{115}(T) + w_0{}^{115} \sinh^{-2}(\hbar\bar{\omega}_0/2kT)]. \tag{7}$$

At low temperatures, $R(T)$ assumes the constant value

$$R_L = W_A{}^{121}(T)/W_A{}^{115}(T), \tag{8}$$

whereas at high temperatures it assumes the constant value

$$R_H = W^{121}(300°\text{K})/W^{115}(300°\text{K}). \tag{9}$$

In the latter case,[13] the contribution of both the acoustic and optical phonons varies as T^2.

The solution of Eqs. (7)–(9) in terms of the experimental values of $W^{121}(T)$, R_L, R_H, and the optical phonon frequency is (since $W^{121}(T) \propto T^2$ for $T > \Theta_D$)

$$R(T) = \frac{R_L W^{121}(T)}{W^{121}(T) - [(R_H - R_L)/R_H](\bar{\Theta}_0/2\Theta_D)^2 W^{121}(\Theta_D) \sinh^{-2}(\hbar\bar{\omega}_0/2kT)}. \tag{10}$$

With the substitutions $R_L = 3.2$ (Fig. 4), $R_H = 1.4$ (Fig. 4), $\bar{\Theta}_0 = 1.25\Theta_D$, $\Theta_D = 200°\text{K}$,[20] $\bar{\omega}_0 = 3.27 \times 10^{13}$ rad sec^{-1}, and the experimental values of Fig. 1 for $W^{121}(T)$, the dashed curve of Fig. 4 is obtained.

Comparison of this result of the model with the

experimental points of Fig. 4 shows quantitative agreement except that in the range around 80°K the model predicts values of R that are as much as 20% larger

[21] Y. Ohmura, J. Phys. Soc. Japan **20**, 351 (1965).

[22] R. B. Sanderson, J. Phys. Chem. Solids **26**, 803 (1965).
[23] This can be seen, for example, if one writes down explicitly the temperature dependence of Eq. (A1).

than the data. Considering the crudeness of the model, we believe that this discrepancy is not a serious challenge to the conclusion we wish to draw, namely, that the temperature variation in R is caused primarily by the thermal excitation of optical phonons. The only other phonons with a high enough density to be important occur[20] at frequencies of about $0.5\bar{\omega}_0$. An attempt to explain the effect with them would push the major portion of the change in R to too low a temperature.

The model just described also allows us to estimate the importance of the optical modes for In[115] in the high-temperature range. From Fig. 1 it is seen that the change in slope of the Sb curves is very slight in the region where $R(\text{In/Sb})$ is changing. This suggests that the change in R is due almost exclusively to a relative increase in the In[115] rate. Because of the smoothness of the Sb curves, we estimate that the contribution of optical phonons to Sb relaxation lies between zero and 15% of the total. If we take the limiting cases of zero or 15%, the solution of Eqs. (5), (8), and (9) then indicates a contribution of optical phonons to the In[115] relaxation rate above 300°K of 56 and 63%, respectively. In either case, it is seen that the contribution of optical phonons to In[115] relaxation is important at high temperatures.

There remains the question of why the optical phonons should have a relatively stronger coupling to the In nuclei than the Sb nuclei. The answer to this probably lies along the lines of the model discussed by Wikner, Blumberg, and Hahn[6] for alkali halides. In their model, an important contribution to the electric field gradient responsible for relaxation of a nucleus comes from the electric dipole moment induced on its neighboring ions by optical phonons. The nuclei surrounded by ions with a large polarizability are then relatively more strongly coupled to the optical phonons than the ones whose neighbors have a small polarizability. The details of extending this type of approach to a covalent substance with a large dielectric constant like InSb appears to be, unfortunately, a rather complicated problem, and will not be attempted in this paper.

V. CONCLUSIONS

Our measurements of $1/T_1{}^Q$ for In[115], Sb[121], and Sb[123] in InSb over the temperature range 4–300°K can be put into two categories: those that agree with theoretical calculations based on a nearest-neighbor point-charge interaction and a Debye model for the phonon spectrum, and those that do not. The first category includes our observation that $1/T_1{}^Q$ is independent of the orientation of the magnetic field,[3,12] and that the ratio of Sb relaxation rates has the correct value[3,12] independent of T.

One experimental result in disagreement with the model mentioned above is the low-temperature behavior of $1/T_1{}^Q$ ($1/T_1{}^Q \propto T^{9.5\pm0.5}$). By employing the calculated density of phonon states for InSb,[20] a theoretical pre-diction in agreement with our observations at low temperatures is obtained.

The other experimental result not in agreement with theoretical predictions[1,3] of the above mentioned model is the temperature dependence of $R(115/121)$. This phenomenon is attributed to the thermal excitation of optical phonons.

These experiments and the attempts made to explain them suggest to us several topics for further work. On the experimental side, it would be useful to make more careful measurements in the temperature range 10–60°K to see if $R(115/121)$ and/or $1/T_1{}^Q$ displays any structure related to the peak in the density of states for longitudinal acoustic phonons.[20] (The data of Fig. 4 suggest that such a structure may be present.) It should also be worthwhile to extend the measurements to other substances. On the theoretical side it appears that an improved calculation of $1/T_1{}^Q$ is now called for. It should include a more exact and complete treatment of the k dependence of the matrix elements than is done in the Appendix, and it should be able to explain from first principles the temperature dependence of $R(115/121)$. We suspect that the latter point requires including details of the band structure of InSb and the motion of atoms more distant than the nearest neighbors.

ACKNOWLEDGMENTS

APPENDIX

The major purpose of this Appendix is to indicate the extent to which the use of Eq. (4) is justified for calculating the temperature dependence of $T_1{}^Q$ in the range 4–10°K for InSb.[24]

Before doing so, however, we point out the motivation for, and physical significance of, the approximation implied by Eq. (4). The basis for these remarks will be developed later on.

The temperature dependence of $T_1{}^Q$ comes from integrating a two-phonon, wave-number-dependent matrix element over the normal modes of the crystal.[1,3] At temperatures low enough that only long-wavelength phonons are important, the wave number dependence of the matrix element becomes particularly simple. In InSb the densities of states for these phonons also correspond to those of the Debye model,[20] i.e., proportional to the square of the frequency, so that one expects its prediction[1,3] for the low-temperature de-

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[24] Equations similar to Eq. (4) have been used elsewhere (Refs. 3, 4, and 14) to discuss the temperature dependence of quadrupolar-relaxation experiments.

pendence of $T_1{}^Q$ $(1/T_1{}^Q \propto T^7)$ to be observed. This situation applies to temperatures below 3°K, where $T_1{}^Q$ has not been measured. In the temperature range 4–10°K, however, the majority of the phonons important for quadrupolar relaxation have short wavelengths, are grouped into branches with unequal dispersion relations, and have a frequency spectrum which differs significantly from that of the Debye model. To treat this situation exactly, even in the framework of the nearest-neighbor point-charge model,[1] would be extremely complicated. Equation (4) appears to be a reasonable compromise in this situation. It is worth noting that Eq. (4) is formally equivalent to using the long-wavelength approximation for the matrix elements, using the exact density of states for the phonon modes,[20] assuming that the dispersion curves for all acoustic branches are equal and isotropic, and including only the vibrations of nearest neighbors.

Now consider this approximation in greater detail. Since many of the steps duplicate work presented elsewhere, this discussion will be rather brief. The relevant process[1] is a spin transition from the state m to the state $m+\mu$, accompanied by the scattering of a phonon from the state with wave vector $\mathbf{k}$, polarization index p, and frequency ω to the state $\mathbf{k}'$, p', ω' via the quadrupolar spin-lattice Hamiltonian[1,3,25,26] $\mathfrak{IC}_{SL}$. According to conventional time-dependent perturbation theory, the transition probability per unit time for all such spin flips $(W_{m,m+\mu})$ is

$$W_{m,m+\mu} = (2\pi/\hbar^2) \sum_{p,p'} \iint_0^{k_{max}} d^3k\,d^3k'$$

$$\times \delta(\omega-\omega') |\langle n(\mathbf{k}, p), n(\mathbf{k}', p'), m+\mu |$$

$$\times \mathfrak{IC}_{SL} | n(\mathbf{k}, p)+1, n(\mathbf{k}', p')-1, m\rangle|^2, \quad (A1)$$

where the usual approximation that ω and ω' are much greater than the nuclear resonance frequency has been used,[1] the limit k_{max} indicates integration over the first Brillouin zone, and $n(\mathbf{k}, p)$ is the number of phonons in the state $\mathbf{k}, p$.

Evaluation of Eq. (A1) is in general very difficult because, among other things, the dispersion relation for a real lattice, $\omega = \omega(\mathbf{k}, p)$, is a complicated functional relationship to put into the δ function. Therefore, we let the phonon spectrum of InSb (as discussed by Phillips[20]) be a guide to the further simplification of Eq. (A1). The low-energy portion of this phonon spectrum is given by the solid line in Fig. 6, where the

[25] M. H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

[26] The quadrupolar Hamiltonian includes as a multiplicative factor terms depending on the antishielding factor, lattice constant, and velocity of sound (Ref. 1). Contributions to the temperature dependence of $1/T_1{}^Q$ from thermal changes in these factors will be ignored here because (a) the major emphasis of this work is on low temperatures, where such changes are expected to be small, and (b) experimental values of $1/T_1{}^Q$ up to the melting point (Ref. 15) show no evidence that such effects are important in InSb.
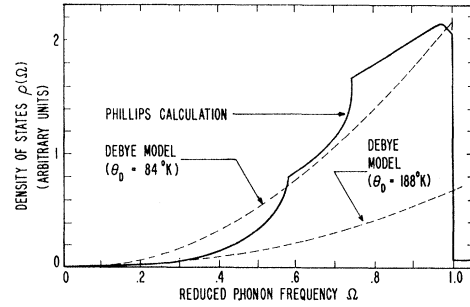

FIG. 6. Density of phonon states in InSb as a function of frequency. The solid line was plotted from numerical values in Ref. 20. The lower dashed line corresponds to a Debye spectrum $(\rho \propto \Omega^2)$ that has been made to fit the solid line in the limit of small Ω, whereas the upper dashed line corresponds to a Debye spectrum with the same number of states up to $\Omega = 1$ as the solid line.

density of phonon states ρ is plotted as a function of reduced phonon frequency $\Omega = \omega/\omega_{max}$, where ω_{max} is the frequency at which the large drop in ρ occurs. Two different Debye-model spectra (dashed lines) related to ρ have been included; the lower $(\Theta_D = 188°K)$ has the same total number of states and fits the solid line at low values of Ω, where $\rho(\Omega) \propto \Omega^2$; the upper has both the same integrated number of states and cutoff frequency as $\rho(\Omega)$. Almost all of the modes represented by $\rho(\Omega)$ are from the two transverse acoustic (TA) branches in InSb. The sudden drop in ρ at $\Omega = 1$ corresponds to the maximum frequency of these modes. The small value of ρ immediately above $\Omega = 1$ is the contribution of the longitudinal acoustic mode. Its contribution to ρ at these frequencies is so small that its presence henceforth will be neglected, i.e., at low frequencies only the two TA modes will be considered.

The next simplifying assumption is based on the observation that the dispersion curves for the TA modes differ only on the order of 50% on changing from one to the other or from one direction to another in the Brillouin zone.[20] We therefore approximate the exact dispersion curves by a single dispersion curve that is isotropic. We require, however, that this approximate dispersion curve give the calculated density of states. Since the transition probability for the relaxation process involves integrations over all directions of $\mathbf{k}$ and a wide range of ω, substituting this average dispersion curve for the exact ones is probably a good approximation.

The form of the average dispersion curve is easily obtained by equating the number of states with energies less than ω to the number of states in the corresponding sphere in k space. In terms of the reduced wave vector $\kappa = k/k_{max}$, one obtains

$$\kappa = A\left[\int_0^\Omega \rho(\Omega')\,d\Omega'\right]^{1/3}, \quad (A2)$$

where A is a constant. The resulting dispersion curve (obtained by numerical integration) is represented by
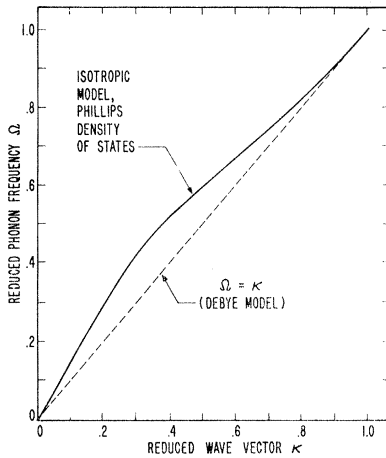
FIG. 7. Dispersion curves for the isotropic model (see text) and the Debye model.

the solid line in Fig. 7. It is interesting to see how close this curve is to that of the Debye model (dashed line), in which a constant velocity of sound is assumed. We shall refer to the approximation just outlined as the isotropic model.

Given the isotropic model, there is one more obstacle to using the relatively simple matrix elements discussed by Van Kranendonk[1] and by Mieher.[2] In their works, an orthogonality relation employing equal dispersion curves for all three acoustical modes is used to simplify the summations over polarization indices. Here, we shall assume that because of the large amount of directional averaging which occurs in the matrix elements, their dependence on κ is essentially the same for two isotropic modes as for three.

On the basis of the last assumption, use of the k dependence of the matrix elements obtained by Mieher[3] is justified. In his notation, the k dependence of $|\langle m+\mu \mid \mathfrak{K}_{SL} \mid m\rangle|^2$ is given by

$$M_\mu(ka) = N_{\mu 1}[L_1(ka) + L_3(ka) + L_5(ka)]$$
$$+ N_{\mu 2}[L_2(ka) + L_4(ka) + L_6(ka)], \quad (A3)$$

where $N_{\mu n}$ is a numerical coefficient, a is the lattice constant, and $L_n(ka)$ are functions defined by Mieher. The linear combination of matrix elements which gives $1/T_1^Q$ is proportional to[3,12]

$$M_1 + 4M_2 = (N_{11} + 4N_{21})(L_1 + L_3 + L_5)$$
$$+ (N_{12} + 4N_{22})(L_2 + L_4 + L_6). \quad (A4)$$

Substitution of Mieher's values for $N_{\mu n}$ into Eq. (A4) shows the second term on the right is about 4% of the first; it will therefore be neglected. This leaves us with the sum $(L_1 + L_3 + L_5)$ for the k dependence of the square of the matrix element. It is easily shown that

$$H\mid^2 \equiv \tfrac{1}{4}(L_1 + L_3 + L_5) = [1 - (\sin\tfrac{1}{4}\sqrt{3}ka)/\tfrac{1}{4}\sqrt{3}ka]^2. \quad (A5)$$

With the simplifying assumptions just outlined, the temperature dependence of T_1^Q is given by

$$(T_1^Q)^{-1} = D \int_0^{\omega_{max}} \frac{\rho_{TA}^2(\omega)\mid H\mid^2 d\omega}{\omega^2 \sinh^2(\hbar\omega/2kT)}, \quad (A6)$$

where D is a constant and the denominator of the integrand comes from the thermal equilibrium values of the phonon creation and annihilation operators which are a part of $\mathfrak{K}_{SL}$.[1,3]

We now consider the effect of the k dependence of $\mid H\mid^2$ on the integral for three different approximations. The first is to assume that only small values of k are important (i.e., a very low temperature). In this case, $\mid H\mid^2 \propto k^4$ and $\omega = vk$, where v is the velocity of sound for long-wavelength phonons. Substitution of this result into Eq. (A6) yields Eq. (4), the equation on which our calculations were based. It should be noted that if $\rho_{TA}(\omega)$ appropriate to the Debye model had been used (i.e., $\rho_{TA}(\omega) \propto \omega^2$), the temperature dependence of T_1^Q discussed by Van Kranendonk[1] and by Mieher[3] would be obtained. The second and third approximations are to include the k dependence of $\mid H\mid^2$ [Eq. (A5)] all the way to the zone boundary, but to assume a relation between ω and k that is either (a) $\omega = vk$ or (b) the dispersion curve for the isotropic model (Fig. 7).

The effect of the three approximations is illustrated in Fig. 8, where $\mid H\mid$ is plotted as a function of reduced phonon frequency Ω. It is seen there that the frequency dependence of $\mid H\mid$ is almost the same for all three approximations. Since our ultimate interest is to explain an order-of-magnitude discrepancy in the temperature dependence between measured values of T_1^Q and the prediction of the Debye model, the differences between
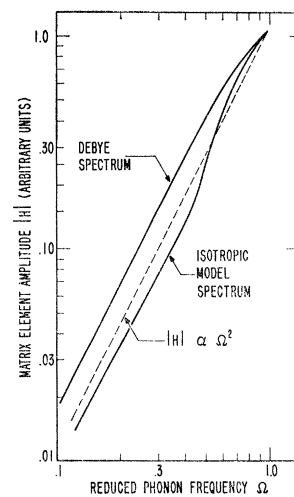

FIG. 8. Amplitude of the matrix element $\mid H\mid$ [see Eq. (A5)] as a function of phonon frequency. The dashed line is obtained by extrapolating the long-wavelength dependence to all wavelengths. The solid lines show the exact frequency dependence for dispersion curves appropriate to the Debye and isotropic models (see Fig. 7).

the three approximations is not important. We have therefore chosen the simplest form of $|H|$ for our calculations.

The approximations just discussed lead to a relatively simple expression for $1/T_1^Q$ [Eq. (4)], which provides a satisfactory fit to our data up to about

10°K. To go beyond this requires a much more detailed examination of the k dependence of $\mathcal{H}_{SL}$. This has been done by one of us (F.B.)[19] in a treatment which incorporates the normal modes of a tetrahedron with an atom at its center into a discussion of quadrupolar relaxation in the diamond and zincblende lattices.

Calculation of the Temperature Dependence of the Nuclear Quadrupolar Spin-Lattice Relaxation Rate for InSb Using the Normal Coordinates of a Tetrahedron*

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A calculation of the temperature dependence of the nuclear quadrupolar relaxation rate (two-phonon Raman process) for diamond and zinc-blende lattices at temperatures below $0.4\Theta_D$ (Θ_D = Debye temperature) is reported. It is assumed that in this temperature range the relaxation is caused primarily by acoustic phonons; therefore, the effects of the optical phonons are neglected. The calculation is carried out using the normal coordinate expansion of the Hamiltonian which is obtained in this paper. The matrix element for the phonon transitions is calculated for all values of the wave number k (assuming a spherical Brillouin zone) without the assumption of degeneracy between the transverse acoustic and longitudinal acoustic modes. Using this calculation of the matrix elements and a realistic density of phonon states, the calculation of $1/T_1$ has a temperature dependence that differs from that predicted by the Debye model over most of the temperature range. At low temperatures the Debye model predicts $1/T_1 \propto T^7$, whereas between 3 and 8°K the present calculation predicts $1/T_1 \propto T^{9.3}$. This calculation agrees (within 12%) with the experimental data for Sb[123] (InSb) over five orders of magnitude in $1/T_1$.

I. INTRODUCTION

A NUMBER[1–8] of theoretical and experimental investigations of the nuclear quadrupolar spin-lattice relaxation rate in solids have been published. The first detailed calculation was carried out by Van Kranendonk[1] for the NaCl-type lattice, in which he assumed the ions to be point charges. He showed that the two-phonon (Raman) process was the dominant relaxation mechanism. In this calculation, the temperature dependence was obtained by assuming a Debye model for the lattice vibrations. Subsequent investigations[2–6] have considered the effects of some covalency in alkalide halides, the use of more realistic phonon spectra, and the effect of optical modes at high temperatures.

For zinc-blende lattices (such as InSb), Mieher[7] has

calculated the relaxation rate for the two-phonon process using Van Kranendonk's method. He assumed that the covalency effects and antishielding effects could be accounted for by a multiplicative constant γ. Using the Debye and point-charge models (with a point charge γe), he obtained the same temperature dependence obtained by Van Kranendonk. In addition, he calculated the spin dependence and found that the total relaxation rate was independent of the magnetic field orientation. More recently, Zak[8] has done a general calculation for cubic lattices and has obtained generally the independence of the relaxation rate on orientation found by Mieher. Recently, an experimental investigation of the nuclear relaxation rate in InSb by Bridges and Clark[9] gave agreement with the predicted spin dependence and orientation independence but disagreed with the predicted temperature dependence at low and medium temperatures ($T < 0.5\theta_D$).

On the basis of the above-mentioned investigations, the motivation for a better calculation of the temperature dependence of the nuclear quadrupolar spin-lattice relaxation rate is three-fold:

(a) Nuclear quadrupolar relaxation is dependent on the phonon spectrum and thus is a probe for gross

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