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Quadrupolar Nuclear Relaxation in the III-V Compounds*†

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The results of nuclear quadrupolar spin-lattice relaxation time T_1 measurements in most of the III–V compounds and germanium are presented and discussed. It is shown that the T_1's may be correlated with the quadrupole interaction for a free atom and appear to be relatively insensitive to different properties of the materials except for the Debye temperature. A theoretical derivation of the transition probabilities for a point charge zincblende lattice is given. This derivation follows Van Kranendonk's treatment for the NaCl lattice. An attempt is made to relate the point-charge model to the III–V compounds with the aid of experimental multiplication factors. A theoretical derivation, which is based on the spin-temperature concept, and an experimental verification of the dependence of the quadrupolar relaxation time on the nuclear spin are given. The spin dependence, $1/T_1 \propto f(I) = (2I+3)/I^2(2I-1)$, is important in the interpretation of other experimental data. A theoretical derivation is given of a relaxation time that is isotropic as the orientation of the static field is varied with respect to the crystalline axes. This apparently accounts for the absence of an experimental observation of any systematic variations of the relaxation time with crystal orientation in this and other investigations. An experimental investigation of the temperature dependence of quadrupolar relaxation is reported. The observed temperature dependence verifies Van Kranendonk's predictions for a Raman "two-phonon" process. Debye temperatures of several III–V compounds are obtained from the temperature dependence of the relaxation times.

I. INTRODUCTION

THIS paper presents a discussion of the results of nuclear spin-lattice relaxation time measurements on most of the III–V compounds and germanium. A theoretical derivation and an experimental verification of the dependence of the quadrupolar relaxation on the nuclear spin are given.[1] The spin dependence is important in the interpretation of other experimental data. A theoretical derivation is given of a relaxation time that is isotropic for all spin values as the orientation of the magnetic field is varied with respect to the crystalline axes.[1] This apparently accounts for the absence of an experimental observation of any systematic variations of the relaxation time with crystal orientation in this and other investigations.[2,3,3a] An experimental investigation of the temperature dependence of quadrupolar relaxation is also reported. The observed temperature dependence agrees with the predictions of Van Kranendonk.[4] It is shown that the spin-lattice relaxation times in the III–V compounds and germanium may be correlated with the quadrupole interaction for a free atom and appear to be relatively insensitive to different properties of the materials except for the Debye θ.

In many solids the nuclear spins interact more strongly with one another than they do with the lattice. These nuclei may then be considered to form a thermodynamic system—the spin system—and it is possible to speak of the "spin temperature." If the spin temperature is unequal to the lattice temperature and if equilibrium is to be achieved, there must be a thermal contact between the spin system and the lattice. The process whereby the spins achieve thermal equilibrium with the lattice is called spin-lattice relaxation. In many nonmetals the thermal contact is provided by the interaction of the nuclear quadrupole moment with the electric field gradients that vary in time because of the thermal vibrations of the lattice. In such cases one speaks of quadrupolar relaxation. Because the quadrupolar transition probabilities for $\Delta m = \pm 1$, ± 2 are functions of I and m, it is necessary to consider the effects of the nuclear dipole-dipole interactions in order to obtain a unique relaxation time. If the dipole-dipole interactions are ignored, the population distribution of the Zeeman levels does not remain a Boltzmann distribution. The spin temperature concept correctly accounts for the effects of the strong dipole-dipole interactions. A single, unique relaxation time is then obtained without the necessity of a detailed consideration of all of the possible dipole-dipole transitions.

The importance of the nuclear quadrupole moment in determining the spin-lattice relaxation time was first discussed and demonstrated by Pound.[5] He pointed out that one would obtain relaxation times of the correct order of magnitude if one used the quadrupole interaction with the lattice vibrations in a theory like Waller's[6] treatment of electron relaxation times. Waller considered the effects of the modulation of the electron dipole-dipole interaction by the lattice vibrations. Applying this method to the nuclear dipole-dipole interaction, Heitler and Teller[7] had found that the predicted relaxation times were greater than 10^4 sec. Therefore, Pound concluded that the relaxation of

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[1] R. L. Mieher, Phys. Rev. Letters **4**, 57 (1960).

[2] N. Bloembergen and P. P. Sorokin, Phys. Rev. **110**, 865 (1958).

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

[3a] E. R. Andrew, K. M. Swanson, and B. R. Williams, Proc. Phys. Soc. (London) **77**, 36 (1961).

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

[5] R. V. Pound, Phys. Rev. **79**, 685 (1950).

[6] I. Waller, Z. Physik **79**, 370 (1932).

[7] W. Heitler and E. Teller, Proc. Roy. Soc. (London) **A155**, 699 (1936).

nuclei with quadrupole moments was a quadrupole effect if the crystal was free of paramagnetic impurities. Pound also described some saturation experiments that could only be explained by quadrupolar relaxation effects.

The first detailed theory was developed by Van Kranendonk.[4] Using the approximations that the lattice vibrations could be described by a Debye spectrum and that the lattice could be described by an array of point charges located at the lattice sites, he derived expressions for the quadrupolar transition probabilities. The dominant mechanism for this model was the Raman process in which one quantum of lattice vibration is absorbed, another quantum is emitted, and a nucleus makes a $\Delta m=\pm 1$ or ± 2 transition. The difference in energy of the two quanta is equal to the energy exchanged in the process with the nuclear spin system. The effects of the Sternheimer[8] polarization of the electrons surrounding the nucleus and any other field gradient contributions, such as changes in the covalent character of the electron wave functions, were described by a multiplication factor for the point charges. Van Kranendonk also derived the temperature dependence of the relaxation time, which varied from a T^{-7} dependence at temperatures less than 0.02 of the Debye temperature to T^{-2} dependence for temperatures greater than the Debye temperature. The angular dependence of the transition probabilities was also obtained, and it was shown that for this model the $\Delta m=1$ transitions could vary by 50% with changes in crystal orientation in the magnetic field.

Other theoretical calculations[9–11] have been made on relaxation mechanisms in the alkali halides and rather complete data have been taken on these materials.[3]

The equipment and samples used in this work are discussed in Sec. II. The theoretical work is discussed in Sec. III. An order of magnitude calculation is given in Sec. III(A) for the benefit of those who are mainly interested in the experimental results. The detailed calculations require considerable notation and the order of magnitude calculations present a clearer picture of some of the physics involved in the relaxation time calculation. The experimental results are presented and discussed in Sec. IV.

II. EXPERIMENTAL

Pulse techniques[12,13] were used in making all of the T_1 measurements reported in this paper. The equipment consisted of a continuous-wave (cw) crystal oscillator, a gated amplifier, four stages of class C power amplification, a symmetric twin-tee bridge, a fast recovery amplifier with phase sensitive rf detection, and associated pulse generating equipment. This equipment and its performance have been discussed elsewhere.[14,15]

The special merits of this equipment include the rf phase sensitive detection that is achieved by introducing a high-level cw signal between the last stage of rf amplification and the detector. The signal from the detector depends on the phase angle between the amplified nuclear signal and the cw signal, hence the name "phase-sensitive detection." Since the nuclei are rotated by the strong rf pulse, which has as a signal source the same cw oscillator from which the reference signal is obtained, there is a definite phase relation between the nuclear signal and the reference signal. The video signal obtained when these two signals are mixed in the detector is a beat signal of frequency $\gamma H-\omega_{\mathrm{cw}}$. The envelope of the beat signal is the Bloch decay. Since the rf circuitry is tuned to a given frequency, the magnetic field is adjusted to resonance or zero beat frequency. The relative phase of the nuclear signal and the reference is adjusted by means of a lumped constant phase shifter that is followed by a limiter-amplifier in the reference circuit.

The rf phase-sensitive detection permits operation in the large-signal, linear portion of the diode characteristic. Furthermore, the Bloch decay for a negative-spin-temperature magnetization has the opposite sign to the decay signal for a positive spin temperature. This is very convenient when making a multiple exposure of several Bloch decays of equilibrium recovery from a negative spin temperature.

The equipment was tuned to operate at 7.5 Mc/sec. This choice was dictated by the gyromagnetic moment of As which is 0.73 kc/sec-gauss. The maximum field available for most of this work was 10 500 gauss. The data on Sb^{123} were also taken with the 7.5-Mc/sec equipment in a field of 13 600 gauss. This field was obtained in a 12-in. Varian magnet with the aid of tapered pole pieces. Low-frequency pulse equipment was constructed for making the T_1 measurements of Ge^{73} at 1.5 Mc/sec and of Rb^{85} at 3.5 Mc/sec.

The basic timing for the T_1 measurements was determined by an audio oscillator. The oscillator drove a trigger circuit that was the first stage of the pulse circuitry. Changing the frequency of the oscillator changed the time between the 180° and 90° pulses. For the longer T_1 measurements the oscillator frequency was divided by a scalar which then triggered the pulse equipment. In this way it was possible to obtain pulses several minutes apart. The audio oscillator was calibrated several times during the course of the work; both the audio-frequency signals of WWV and a Hewlett-Packard model 524B cycle counter were used to make the calibrations. The long time and short time stabilities were both about ±1%; this was also about

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[9] T. P. Das, D. K. Roy, and S. K. Ghosh, Roy. Phys. Rev. **104**, 1568 (1956).

[10] K. Yosida and T. Moriya, J. Phys. Soc. Japan **11**, 33 (1956).

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[12] E. L. Hahn, Phys. Rev. **80**, 580 (1950).

[13] H. Y. Carr and E. M. Purcell, Phys. Rev. **94**, 630 (1954).

[14] J. J. Spokas, thesis, University of Illinois, Urbana, Illinois, 1958 (unpublished).

[15] J. J. Spokas and C. P. Slichter, Phys. Rev. **113**, 1462 (1959).

the accuracy with which the oscillator frequency dial could be set.

To obtain the best signal-to-noise ratio most of the data was taken at 77.4°K. The liquid nitrogen was contained in a brass pot placed in a Dewar. A brass tube served as the ground conductor of a coaxial cable and ran through the brass pot down into the neck of the Dewar. The rf coil was contained in a shielding can at the end of the brass tube. Since the nitrogen was contained in the pot and did not get into the neck of the Dewar, it was possible to vary the sample temperature with a heater wound around the tube between the shielding can and the brass pot. A temperature of 71°K was obtained by passing He gas through liquid nitrogen for one T_1 measurement on InP. The temperatures were measured with a copper-constantan thermocouple. One end of the thermocouple was in contact with the sample and the reference junction was in an ice bath. The thermocouple was calibrated against a standard platinum resistor.

Most of the relaxation time measurements were made with a 180°–90° pulse sequence. When the oscilloscope was triggered by the 90° pulse, the Bloch decay of the partially recovered magnetization was recorded by a Polaroid scope camera. After a wait of about 10 relaxation times the sequence was repeated with a different time spacing between the 180°–90° pulses. If the relaxation time was not too long, several exposures were made for the same pulse spacing in order to obtain photographic integration. Several Bloch decays were recorded on the same photograph without moving the camera. Thus by reading the amplitudes along any vertical line, the readings were normalized to the amplitude of the fully recovered magnetization of that line. Several readings could be made at different positions on the same set of Bloch decays so that an additional integration of the data was obtained.

For the very long relaxation times a saturation recovery type of measurement was used. First a picture of the equilibrium magnetization was taken. Then a rapid sequence of pulses saturated the resonance. At some later time a picture of the partially recovered magnetization was taken. After a wait of about 10 relaxation times the sequence was repeated and recorded on another photograph. Since the T_1 of germanium was about 6 min, the time required to take one saturation recovery photograph was about 1 hr and, therefore, many hours were required to make the T_1 measurement. By taking a picture of the equilibrium magnetization before each saturation, it was possible to eliminate errors due to any changes in gain of the equipment.

Most of the samples used in this experiment were polycrystalline. Although the impurity content was not known for most of the samples, it was possible to show in most cases that the T_1 contributions of paramagnetic impurities were negligible. Also, it was determined that there was very little quadrupolar broadening of the resonance lines by charged impurities and lattice strains.

Since the phosphorus nucleus has spin of $\frac{1}{2}$ its relaxation is determined by paramagnetic impurities. The T_1 of P in InP at 77.4°K was about 175 sec. Therefore, the expected paramagnetic contribution to the 2.93-sec relaxation time of the In^{115} is negligible since the uncertainties in all of the data are between ±5% and ±10%. The ratio of the T_1's of the Ga^{69} and Ga^{71} nuclei in GaAs agree within 10% with the ratio predicted by their quadrupole moments; this indicates that paramagnetic effects were small in this compound. The relaxation time of Al^{27} in AlSb is 400 sec at 77.4°K and might be expected to have appreciable paramagnetic contribution. Nevertheless, the Debye θ given by the temperature dependence of T_1 agrees with the Debye θ determined by specific heat measurements (see Sec. IV). The other long relaxation time was that of 375 sec for the Ge^{73} nuclei. Since only this one measurement was made on germanium, it is not possible to say with certainty that there was no paramagnetic contribution. Nevertheless, the sample used was a high-quality single crystal of 20 ohm-cm, *p*-type conductivity at room temperature and would have about 10^{14} impurities per cc. Since this is a higher purity than even optical quality alkali halides, which have much longer nuclear relaxation times due to paramagnetic impurities, it is likely that the relaxation time of the Ge^{73} was entirely a quadrupolar effect. Also, an independent T_1 measurement using fast passage techniques agrees within the experimental errors with the value obtained in this experiment.[16] The only material in which paramagnetic impurities prevented a measurement of the quadrupolar T_1 was GaP. The T_1's were about 3 sec at 77°K, and the T_1 of P was shorter than the T_1 of Ga. No change with temperature was observed.

At room temperatures some of the samples had to be crushed because of a small skin depth, but most measurements were taken at liquid nitrogen temperature, and it was not necessary to use powdered samples. The possibility of quadrupolar broadening, which might affect the use of the spin-temperature concept, was checked by looking for quadrupole echo effects[17] following a 90°–45° pulse sequence. This effect is quite apparent in some of the alkali halides such as I^{127} in KI. The only quadrupole echoes were found in germanium and in one In^{115} resonance in a powdered sample of InSb that was taken from the impurity end of a zone refined bar. The germanium quadrupolar broadening was observable only because of the very narrow dipole-dipole root second moment of 0.15 gauss. Order of magnitude calculations indicated that about 10^5 dislocations per cm^2 could cause the observed broadening. Another indication of the lack of quadrupolar broadening was the In resonances in InAs and

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[16] R. G. Shulman (private communication).

[17] I. Solomon, Phys. Rev. **110**, 61 (1958).

InP. Indium has two isotopes, In^{115} (96%) and In^{113} (4%), whose resonances are separated by only 15 gauss in a field of 8000 gauss. In these two compounds the In^{113} resonance was clearly resolved in the wings of the In^{115} resonance, which was taken with a Pound-Knight-Watkins spectrometer. The In^{113} was also visible on the Bloch decays of In^{115} as a small, superimposed beat signal. The absence of quadrupolar broadening in the III–V compounds has been discussed by Shulman *et al.*[18]

III. THEORETICAL

In this section the theoretical expressions for the transition probabilities for the zincblende lattice are derived using the point-charge lattice approximation. Van Kranendonk's notation is used. The point-charge lattice is not a good approximation for the strongly covalent III–V compounds, although there might be an ionic contribution to the relaxation time. Nevertheless, the derived transition probabilities can be used in connection with the spin temperature assumption to give the spin dependence and angular dependence of the relaxation time. Also, an attempt is made to relate the theoretical results to the experimental T_1's using multiplication factors that have been obtained from quadrupolar broadening experiments.

A. Order of Magnitude Calculation

If the displacements of the nuclei from their equilibrium positions are small compared to the interatomic distance, the quadrupolar Hamiltonian may be expanded in a power series of the displacements. The total displacement of a nucleus by a given mode of lattice vibration is given by the amplitude of vibration of that mode; however, it is the relative displacements of two lattice sites that determines the local distortion of the lattice. This relative displacement, r, is given by $r\sim(2\pi R/\lambda)q$, where q is the amplitude of vibration of a normal mode, λ is the wavelength of the mode, and R is the interatomic distance. The amplitude of vibration at high temperatures may be approximated by considering a classical oscillator whose energy is

$$\tfrac{1}{2}M\omega^2q^2=\tfrac{1}{2}kT, \tag{1}$$

where M is now taken as the mass of the crystal. [The crystal mass, M, appears in the final expression, Eq. (7), as the mass density, $m=M/V$, because the volume of the crystal, V, appears in the density of states expression, Eq. (6).] The relative displacement is now given by

$$r\sim\frac{2\pi R}{\lambda}\left(\frac{kT}{M\omega^2}\right)^{\frac{1}{2}}=\frac{R}{v}\left(\frac{kT}{M}\right)^{\frac{1}{2}}, \tag{2}$$

where v is taken to be the velocity of sound in the crystal.

The quadrupolar Hamiltonian may be written

$$\begin{gathered}\mathcal{H}_Q=\mathcal{H}_Q{}^{(0)}+\mathcal{H}_Q{}^{(1)}+\mathcal{H}_Q{}^{(2)}+\cdots,\\ \mathcal{H}_Q\sim(\partial\mathcal{H}_Q/\partial r)r+(\partial^2\mathcal{H}_Q/\partial r^2)r^2,\end{gathered} \tag{3}$$

where $\mathcal{H}_Q{}^{(0)}$ is the static interaction and is taken to be zero, and the effects of terms of higher order than $\mathcal{H}_Q{}^{(2)}$ are assumed to be negligible. For the order-of-magnitude calculations these terms are approximated as follows:

$$\begin{gathered}\mathcal{H}_Q\sim e^2\gamma Q/R^3,\quad \partial\mathcal{H}_Q/\partial r\sim e^2\gamma Q/R^4,\\ \partial^2\mathcal{H}_Q/\partial r^2\sim e^2\gamma Q/R^5.\end{gathered} \tag{4}$$

The term γ is the multiplication factor that is introduced to account for the contributions to the field gradient due to the Sternheimer[8] effect, covalent effects, etc.

The important mechanism is the Raman process that results from a first-order perturbation treatment of the second-order term of the Hamiltonian $\mathcal{H}_Q{}^{(2)}$. The transition probability W for this Raman process is

$$\frac{1}{T_1}\sim W=\frac{2\pi}{\hbar^2}\int_0^{\omega_m}\int\rho(\omega_i)\rho(\omega_j)\times\delta(\omega_i-\omega_j\pm\omega_L)|\mathcal{H}|^2d\omega_id\omega_j. \tag{5}$$

The integral counts all of the possible ways in which a phonon of lattice mode i can be absorbed and a phonon of the mode j can be emitted. The integral is over all lattice frequencies up to ω_m, the maximum allowed frequency for a Debye distribution. The δ function requires that the energy difference of the initial and final lattice states is just the energy exchanged with the spin system. $\rho(\omega)$ is the density of lattice modes per unit frequency interval. Since the Larmor frequency, ω_L, is very small compared to most of the lattice frequencies, it may be assumed that $\rho(\omega_i)=\rho(\omega_j)$. For a Debye distribution,

$$\rho(\omega)=3V\omega^2/2\pi^2v^3, \tag{6}$$

where V is the volume of the crystal.

The integration of Eq. (5) gives

$$\frac{1}{T_1}\sim\frac{9}{8\pi^3}\frac{1}{\hbar^3}\left(\frac{e^2\gamma Q}{R^3}\right)^2\left(\frac{kT}{mv^5}\right)^2\omega_m{}^5. \tag{7}$$

This order of magnitude term gives the T^2 dependence of the high temperature transition probabilities and shows the dependence on the square of the quadrupole moment. Using the values $Q=10^{-24}$ cm², $m=3$ gm/cc, $v=2.5\times10^5$ cm/sec, $\omega_m=10^{13}$ sec⁻¹, $R=2.5\times10^{-8}$ cm, $T=300$°K, and $\gamma=100$ in Eq. (7) gives a relaxation time of 1.0 sec. Because of the high powers of several factors in Eq. (7), a different choice of constants would vary the predicted T_1 by an order of magnitude. However, the experimental values at room temperature are in the range of 0.1 to 1.0 sec. The value of γ is chosen to give a reasonable T_1. This multiplication

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[18] R. G. Shulman, B. J. Wyluda, and H. J. Hrostowski, Phys. Rev. **109**, 808 (1958).

factor is one of the most difficult points of a quantitative comparison between theory and experiment [see Sec. III(F)].

Similar order of magnitude calculations show that the direct process is negligible at high temperatures by a factor of 10^{-8}. The Raman process is more effective because all of the lattice modes can contribute to relaxation and only modes at the Larmor frequency can contribute to the direct process. Also, the Larmor frequency is low on the lattice frequency scale and, therefore, the density of states is small at this frequency. Another Raman process results from the second-order perturbation treatment of the first-order term $\mathcal{H}_Q^{(1)}$ in the Hamiltonian. This process is also negligible by a factor of 10^{-10} because it involves the ratio of the quadrupolar Hamiltonian to the much larger energy of a lattice phonon.

B. Derivation of the Quadrupolar Transition Probabilities for the ZnS Lattice

The first detailed calculation of the transition probabilities due to the interaction of the nuclear quadrupole moment with the lattice vibrations was done by Van Kranendonk[4] for the NaCl-type lattice. In his work the ions are approximated by point charges located at the lattice sites and the lattice modes of vibration are approximated by a Debye distribution. An exact calculation of the transition probabilities can be made for this model. Although this model is not completely successful in predicting the absolute spin lattice relaxation for the alkali halides,[3] it does give correctly many of the features of the quadrupolar relaxation.

Although it will be shown that the relaxation probably occurs via a covalent interaction in the III–V compounds, the following derivation of the transition probabilities for the zinc-blende lattice will use the point-charge model, will parallel the work of Van Kranendonk, and will use his notation. Since it would be extremely complicated to express the field gradients in terms of the variations with the lattice vibrations of the actual wave functions, an attempt will be made to relate the ionic model to the true physical picture with the aid of empirical multiplication factors.

Yosida and Moriya[10] have considered covalent effects for the alkali halides. Their treatment is for the case of a small admixture of covalent character into the alkali halide wave functions, but the III–V compounds are strongly covalent. Therefore, no attempt has been made to apply their results to this work.

The quadrupolar Hamiltonian is discussed by Cohen and Reif[19] and may be written

$$\mathcal{H}_Q=\sum\nolimits_\mu Q_\mu V_{-\mu}, \tag{8}$$

where

$$\begin{aligned} Q_0&=A(3I_z^2-I^2), & V_0&=V_{zz},\\ Q_{+1}&=A(I_\pm I_z+I_zI_\pm), & V_{\pm1}&=V_{xz}\pm iV_{yz},\\ Q_{\pm2}&=AI_\pm^2, & V_{\pm2}&=\tfrac{1}{2}(V_{xx}-V_{yy})\pm iV_{xy}, \end{aligned} \tag{9}$$

in which $A=eQ/4I(2I-1)$, $I_\pm=I_x\pm iI_y$, and the terms, V_{xx}, V_{xy}, etc., are the electric field gradients at the nucleus. The Q_μ are the quadrupole operators. Q is the nuclear quadrupole moment and I is the nuclear spin.

The V_μ's may be expanded in a power series of the relative displacements of the point charges about their equilibrium positions as follows:

$$V_\mu=A_\mu+\sum_i \mathbf{A}_{\mu i}\cdot\mathbf{r}_i+\sum_{ij} A_{\mu ij}:\mathbf{r}_i\mathbf{r}_j+\cdots. \tag{10}$$

In general the summations of i, j are over all lattice sites, but in the following treatment they will be restricted to the nearest neighbors. This restriction simplifies the calculations and is a reasonable one since the final expression for the relaxation time contains the lattice constant to the -13th power. Also, the ionic model is admittedly only a crude approximation of the zinc-blende lattice, which is strongly covalent.

The first term in the expansion A_μ is the static field gradient and it is zero for a lattice of cubic symmetry. The other terms couple the nuclear spin system to the lattice vibrations. The dominant interaction is a Raman process due to the first-order perturbation treatment of the quadratic term $A_{\mu ij}$. The direct process and the Raman process due to the linear term $\mathbf{A}_{\mu i}$ are negligible and were discussed above. The effects of the displacements involving orders higher than the quadratic would involve three or more phonons and are also negligible.

The relative displacements must now be expressed in terms of the lattice vibrations. If it is assumed that all lattice sites are equivalent, then the total displacement of site i is

$$\mathbf{s}_i=\sum_{\mathbf{k},p} a_{\mathbf{k},p}\hat{e}_{\mathbf{k},p}\exp(i\mathbf{k}\cdot\mathbf{R}_i), \tag{11}$$

where the summation is over all lattice modes; the p sum is over the three directions of polarization, $\hat{e}_{,\mathbf{k}}$, and the $\mathbf{k}$ sum is over all allowed wave numbers. The relative displacement of two lattice sites is

$$\mathbf{r}_i=\mathbf{s}_i-\mathbf{s}_0=\sum_{\mathbf{k},p} a_{\mathbf{k},p}\hat{e}_{\mathbf{k},p}[\exp(i\mathbf{k}\cdot\mathbf{R}_i)-\exp(i\mathbf{k}\cdot\mathbf{R}_0)]. \tag{12}$$

This may be rewritten by grouping together terms involving $+k$ and $-k$ to give

$$\mathbf{r}_i=\sum\nolimits_\lambda{}' q_\lambda B_i(\mathbf{k},s)\hat{e}_\lambda, \tag{13}$$

where $\lambda=(\mathbf{k},p,s)$ and the prime indicates that the summation is only over $+k$. The functions q_λ and

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

$B_i(\mathbf{k},s)$ are

$$\begin{aligned} q_\lambda &= \delta(s,1)(a_{\mathbf{k},p}+a_{-\mathbf{k},p})+i\delta(s,2)(a_{\mathbf{k},p}-a_{-\mathbf{k},p}), \\ B_i(\mathbf{k},s) &= \delta(s,1)[\cos(\mathbf{k}\cdot\mathbf{a}_i)-1]+\delta(s,2)\sin(\mathbf{k}\cdot\mathbf{a}_i), \end{aligned} \tag{14}$$

where $\mathbf{a}_i=\mathbf{R}_i-\mathbf{R}_0$, δ is the Kronecker delta function, and s takes only the values 1 and 2. The term $B_i(\mathbf{k},s)$ gives the relative displacement of the ith lattice site from its equilibrium position and corresponds to the $2\pi R/\lambda$ which was used in the order of magnitude calculations. The matrix elements of the q_λ give the amplitude of vibration of the λ lattice mode. They are

$$\begin{aligned} \langle n_\lambda+1\,|q_\lambda|n_\lambda\rangle &= \langle n_\lambda|q_\lambda|\,n_\lambda+1\rangle \\ &= (\hbar/M\omega_\lambda)^{\frac{1}{2}}(n_\lambda+1)^{\frac{1}{2}}, \end{aligned} \tag{15}$$

where $|n_\lambda\rangle$ is the wave function of the lattice with n quanta in the λ mode. M is the mass of the crystal and ω_λ is the frequency of the λ mode. The average number of quanta of the λ mode is given by the Boltzmann factor,

$$\bar{n}_\lambda=[\exp(\hbar\omega_\lambda/kT)-1]^{-1}. \tag{16}$$

The Hamiltonian is now

$$\begin{aligned} \mathcal{H}_Q &= \sum_\mu Q_\mu \sum_{ij} A_{\mu ij}\colon \sum_{\lambda,\lambda'} B_iB_j' q_\lambda q_\lambda' \hat{e}_\lambda\hat{e}_{\lambda'}, \\ &= \sum_\mu Q_\mu \sum_{\lambda,\lambda'} w_\mu(\lambda,\lambda') q_\lambda q_{\lambda'}, \end{aligned} \tag{17}$$

where

$$w_\mu(\lambda,\lambda')=\textstyle\sum_{ij} B_iB_j' A_{\mu ij}\colon \hat{e}_\lambda\hat{e}_{\lambda'}.$$

The probability of a nucleus making a transition from a state m to a state $m+\mu$ is

$$W(m,\,m+\mu)=\frac{2\pi}{\hbar^2}\int_0^{\omega_m}\int_0^{\omega_m}\rho(\omega)\rho(\omega')\delta(\omega-\omega'+\omega_\mu) \sum\{|\mathcal{H}_{Q\mu}(\lambda,\lambda')|\}^2 d\omega d\omega'. \tag{18}$$

The integration counts all of the possible ways in which a phonon of lattice mode λ' is absorbed and a phonon of lattice mode λ is emitted. The δ function requires that the energy change of the lattice $\hbar(\omega-\omega')$ is the energy $\hbar\omega_\mu$ exchanged with the spin system when a nucleus makes a $\Delta m=\mu$ transition. The Σ sign stands for the summation over p and s. The curly brackets, { }, represent the average of the Hamiltonian over all directions of $\mathbf{k}$. Since the nuclear frequency is very small compared to a typical lattice frequency, the density of states, $\rho(\omega)$, for the emitted and absorbed phonons may be taken as equal. For a Debye distribution of lattice modes, the density of states for mode λ is

$$\rho(\omega)=(V/4\pi^2v)k^2, \tag{19}$$

where V is the volume of the crystal and v is the velocity of sound waves, which is assumed to be a constant for all λ.

The matrix elements of the Hamiltonian that cause relaxation are now

$$\begin{aligned} \langle|\mathcal{H}_{Q_\mu}(\lambda,\lambda')|\rangle \\ &= (2\hbar Q_{\mu m}/M\omega_\lambda)[(n_\lambda+1)n_\lambda']^{\frac{1}{2}} w_\mu(\lambda,\lambda'), \end{aligned} \tag{20}$$

where

$$Q_{\mu m}=\langle m+\mu|Q_\mu|m\rangle.$$

The factor of 2 comes from the fact that $w_\mu(\lambda,\lambda')=w_\mu(\lambda',\lambda)$. Using Van Kranendonk's notation, the Hamiltonian is now written as follows

$$|\mathcal{H}_Q(\lambda,\lambda')|^2=\frac{4\hbar^2Q_{\mu m}^2}{M^2\omega_\lambda^2}\frac{e^x}{(e^x-1)^2}M_\mu(ka), \tag{21}$$

where $x=\hbar\omega/kT$. The functions $M_\mu(ka)$ are

$$\begin{aligned} M_\mu(ka) &= \sum_{s,s'} w_\mu^*(\lambda,\lambda')w_\mu(\lambda,\lambda') \\ &= \sum_{s,s'}\sum_{ijlm} N_{\mu ijlm}L_{sil,s'jm}, \end{aligned} \tag{22}$$

where

$$N_{\mu ijlm}=A_{\mu ij}\colon A_{\mu lm}^*,$$

and

$$L_{sil,sjm}=\{B_i(\mathbf{k},s)B_l(k,s)\}\{B_j(\mathbf{k}',s')B_m(\mathbf{k}',s')\}.$$

The curly brackets still indicate an average over all directions of $\mathbf{k}$.

For the NaCl- and CsCl-type lattice there is no mixing between sine- and cosine-like vibrations because the lattices have inversion symmetry. The lattice site for the zinc-blende lattice does not have inversion symmetry and there is a mixing of the two types of vibrations.

The only $L(ka)$ functions which are not zero and which are multiplied by nonzero N functions are as follows:

$$\begin{aligned} &(s=s'=1),\quad L_{1il,1il} \\ &\quad=\tfrac{1}{4}[1-f(\sqrt{3}ak/2)]^2=L_1,\quad (i=l) \\ &\quad=\tfrac{1}{4}[f(ak/\sqrt{2})-f(ak/2)]^2=L_2;\quad (i\neq l) \\ &(s=s'=2),\quad L_{2il,2il} \\ &\quad=\tfrac{1}{4}[3+f(\sqrt{3}ak/2)-4f(\sqrt{3}ak/4)]^2=L_3,\quad (i=l) \\ &\quad=\tfrac{1}{4}[2+f(ak/\sqrt{2})+f(ak/2) \\ &\qquad\qquad -4f(\sqrt{3}ak/4)]^2=L_4;\quad (i\neq l) \\ &(s=1,\quad s'=2;\quad s=2,\quad s'=1),\quad L_{1il,2il} \\ &\quad=\tfrac{1}{2}[1-f(\sqrt{3}ak/2)][3+f(\sqrt{3}ak/2) \\ &\qquad\qquad -4f(\sqrt{3}ak/4)]=L_5,\quad (i=l) \\ &\quad=\tfrac{1}{2}[f(ak/\sqrt{2})-f(ak/2)][2+f(ak/\sqrt{2}) \\ &\qquad\qquad +f(ak/2)-4f(\sqrt{3}ak/4)]=L_6;\quad (i\neq l) \end{aligned} \tag{23}$$

where $f(x)=(\sin x)/x$.

For the point-charge approximation the $A_{\mu ij}\neq 0$ only for $i=j$. They may be obtained by expanding the expressions for V_μ in terms of small deviations about an equilibrium position and keeping the coefficients of the quadratic terms of the deviations. The V_μ's for a point charge, γe, are

$$\begin{aligned} V_0&=\gamma e[(3Z^2-R^2)/R^5],\\ V_{\pm1}&=\gamma e[3Z(X\pm iY)/R^5],\\ V_{\pm2}&=\gamma e[3(X\pm iY)^2/2R^5], \end{aligned} \tag{24}$$

where γ is the same multiplying factor used in the order of magnitude calculations. It represents the effects of any contributions to the field gradients by the Sternheimer polarization, covalent effects, etc. The V_μ's are rewritten with $R=[(X_0+x)^2+(Y_0+y)^2+(Z_0+z)^2]^{\frac{1}{2}}$, where X_0, Y_0, Z_0 is the equilibrium position of the charge and x, y, z is the deviation from equilibrium, which is small compared to R_0. Expanding in powers of x, y, z and retaining the coefficients of the quadratic terms of x, y, z gives the components of the tensor $A_{\mu ij}$.

The $A_{\mu ij}$ may be written

$$A_{\mu ij}=(\gamma e c_\mu/R^5)\begin{vmatrix}(xx)_\mu & (xy)_\mu & (xz)_\mu\\ (yx)_\mu & (yy)_\mu & (yz)_\mu\\ (zx)_\mu & (zy)_\mu & (zz)_\mu\end{vmatrix},\quad \begin{aligned} c_0&=1\\ c_{\pm1}&=3\\ c_{\pm2}&=\tfrac{3}{2}\end{aligned} \tag{25}$$

where $(xx)_\mu$ represents the coefficient of the xx term in the expansion for V_μ. For example, the $(xx)_\mu$ terms are

$$\begin{aligned} (xx)_0&=(3Z^2-R^2)\left(-\frac{5}{2R^2}+\frac{35X^2}{2R^4}\right)+\frac{10X^2}{R^2}-1,\\ (xx)_{\pm1}&=Z(X\pm iY)\left(-\frac{5}{2R^2}+\frac{35X^2}{2R^4}\right)-\frac{5XZ}{R^2},\\ (xx)_{\pm2}&=(X\pm iY)^2\left(-\frac{5}{2R^2}+\frac{35X^2}{2R^4}\right)-\frac{10(X^2\pm iXY)}{R^2}+1, \end{aligned} \tag{26}$$

where R, X, Y, Z refer to the equilibrium position of the point charge and the 0 subscripts have been omitted to avoid confusion with the μ subscripts.

Using the general $A_{\mu ii}$ expressions, the $N_{\mu ijlm}$ may be added as follows

$$\begin{aligned} N_{\mu1}&=N_{\mu3}=N_{\mu5}=\textstyle\sum_i N_{\mu ii,ii}=\sum_i A_{\mu ii}:A_{\mu ii}^*,\\ N_{\mu2}&=N_{\mu4}=N_{\mu6}=\displaystyle\sum_{i,j} N_{\mu ii,jj}=\sum_{i,j} A_{\mu ii}:A_{\mu jj}^*. \end{aligned} \tag{27}$$

The subscripts 1, 2, $\cdots$, are the same as the subscripts on the L's. The function $M_\mu(ka)$ is now

$$M_\mu(ka)=\sum_{n=1}^{6} N_{\mu n}L_n. \tag{28}$$

The transition probabilities may be written

$$W(m,m+\mu)=C|Q_{\mu m}|^2T^{*2}\sum_{n=1}^{6} N_{\mu n}D_n(T^*), \tag{29}$$

where

$$D_n(T^*)=T^*\int_0^{1/T^*}\frac{x^2e^x}{(e^x-1)^2}L_n(cT^*x)dx, \tag{30}$$

$C=24/\pi d^2v^3a^3$, $T^*=T/\theta_D$, $c=k_ma=2(6\pi^2)^{\frac{1}{3}}$, $d=M/V$, $a=$lattice constant, and θ_D is the Debye temperature. The term c is determined by the fact that the total number of lattice modes must equal $3N$, where N is the number of lattice sites in the crystal.

Van Kranendonk evaluated the temperature dependence of the relaxation time for the NaCl lattice. The following calculations will be for the high-temperature approximation and the temperature dependence will be assumed to be given by Van Kranendonk's general function $E(T^*)$, which is given in Fig. 3. This general function is experimentally verified and discussed in Sec. IV.

The functions $D_n(T^*)$ may be evaluated numerically for any given temperature. Van Kranendonk does this for several temperatures for the $D_n(T^*)$'s pertinent to the NaCl-type lattice. He also expands the $D_n(T^*)$ for high temperatures as follows:

$$D_n(T^*)=L_{n0}-\tfrac{1}{12}L_{n2}(cT^*)^2+\cdots, \tag{31}$$

where

$$L_{np}=\frac{1}{c}\int_0^c x^pL_n(x)dx.$$

If the transition probability is written

$$W(m,m+\mu)=C|Q_{\mu m}|^2T^{*2}E_\mu(T^*), \tag{32}$$

where

$$E_\mu(T^*)=N_{\mu1}(D_1+D_3+D_5)+N_{\mu2}(D_2+D_4+D_6),$$

then the quantities $E_\mu(T^*)$ are approximately proportional to each other and may be written as $E_\mu(T^*)=E(T^*)E_\mu(\infty)$. The temperature dependence of the transition probability is now expressed as $T^{*2}E(T^*)$. The functions $E_\mu(\infty)$ are obtained from the above expression for $E_\mu(T^*)$ if the D_n's are replaced by the L_{n0}'s.

The functions L_{n0} have been numerically evaluated for the zinc-blende lattice.

$$\begin{aligned} L_1&=0.200, & L_2&=0.013,\\ L_3&=0.558, & L_4&=0.162,\\ L_5&=0.548, & L_6&=-0.046. \end{aligned}$$

The orientational dependence of the transition probabilities is contained in the functions $N_{\mu n}$ and may be obtained by making a general transformation of the $A_{\mu ij}$'s. The desired transformation matrix is the matrix $D_{m',m}{}^2$ for the transformation of normalized second order spherical harmonics. However, a similarity transformation must be made because the functions V_μ are not normalized. More details of the calculations are given in the Appendix. This calculation is long but straightforward and the results are

$$\begin{aligned} N_{11}&=[(\gamma e)^2/r^{10}](576-360\alpha^2),\\ N_{12}&=[(\gamma e)^2/r^{10}](-227.55+1231.1\alpha^2),\\ N_{21}&=[(\gamma e)^2/r^{10}](486+90\alpha^2),\\ N_{22}&=[(\gamma e)^2/r^{10}](80.22-307.78\alpha^2), \end{aligned} \tag{33}$$

where $\alpha^2=\alpha_1^2\alpha_2^2+\alpha_1^2\alpha_3^2+\alpha_2^2\alpha_3^2$, and α_1, α_2, α_3 are the direction cosines between the magnetic field and the [100], [010], [001] crystal directions. The $E_\mu(\infty)$'s are now

$$\begin{aligned} E_{\pm1}(\infty)&=[(\gamma e)^2/r^{10}](723.4-312\alpha^2),\\ E_{\pm2}(\infty)&=[(\gamma e)^2/r^{10}](645.4+78\alpha^2). \end{aligned} \tag{34}$$

The final form of the transition probability for the zinc-blende lattice is

$$W(m,\, m+\mu)=C|Q_{\mu m}|^2T^{*2}E(T^*)E_\mu(\infty). \tag{35}$$

C. Relation between T_1 and the Transition Probabilities

In a recent paper Hebel and Slichter[20] derive a general relation between T_1 and the transition probabilities which is similar to a relation previously obtained by Gorter.[21] The derivation is based on a spin temperature description of the spin system. Casimir and Du Pré[22] first used the spin temperature concept in connection with paramagnetic relaxation. Van Vleck[23] also made early use of the spin temperature concept to get an expression for the paramagnetic relaxation in Ti and Cr alums in the form of a diagonal sum in order to avoid solving a complicated spin Hamiltonian involving combined crystalline and Zeeman splittings. The final expression is

$$1/T_1=\tfrac{1}{2}[\sum_{n,m}(E_n-E_m)^2W_{nm}]/[\sum_n E_n^2]. \tag{36}$$

The energy values E_n are chosen such that the trace of the energy matrix is zero. For the problem treated in this work, $E(m)=-\gamma\hbar Hm$.

The validity of the spin temperature has been examined by Abragam and Proctor.[24] For the pure Zeeman case of equally spaced energy levels the spin temperature describes the system in a time of the order of magnitude of the spin-spin relaxation time T_2 after the perturbation causing a nonequilibrium situation is removed. Therefore, the spin temperature will correctly describe the spin systems in the III–V compounds if (1) quadrupolar effects which would destroy the equal level spacings are negligible, and (2) the transition probabilities that cause spin-lattice relaxation and, therefore, tend to create a non-Boltzmann population distribution are much less than the transition probabilities that bring about a Boltzmann distribution. A more straightforward statement of (2) is that of $T_2\ll T_1$.

In Sec. II a discussion was given of the reasons for believing that there was negligible quadrupolar broadening of the resonance lines in the III–V compounds. The T_2's are of the order of 10^{-4} sec and the T_1's range from about 10^{-1} to 10^3 sec. Therefore, the spin temperature should be a valid description of the spin systems that are investigated here.

D. Spin Dependence of T_1

In order to compare the relaxation times of nuclei that have different nuclear spins (the III–V nuclei have spin values of $\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$, and $\frac{9}{2}$) it is necessary to have an explicit expression for the spin dependence. Equation (36) may be used to obtain an expression for T_1 for any value of the nuclear spin I. It is important to note that, as a consequence of the spin temperature assumption, Eq. (36) will predict a single relaxation time for any value of nuclear spin. When the transition probabilities given by Eq. (35) are substituted in Eq. (36), the expression for T_1 is

$$\frac{1}{T_1}=\tfrac{1}{2}[\sum_{m,\mu}(\mu)^2|Q_{\mu m}|^2CT^*\,E(T^*)E_\mu(\infty)]/[\textstyle\sum_m m^2], \tag{37}$$

where the quadrupole matrix elements are given by

$$\begin{aligned} Q_{\pm1,m}&=A(2m\pm1)[(I\mp m)(I\pm m+1)]^{\frac{1}{2}},\\ Q_{\pm2,m}&=A[(I\mp m)(I\mp m-1)\\ &\qquad\times(I\pm m+1)(I\pm m+2)]^{\frac{1}{2}}. \end{aligned} \tag{38}$$

Equation (37) becomes

$$\begin{aligned} 1/T_1=[(2I+3)/40I^2(2I-1)](eQ)^2CT^{*2}E(T^*)&\\ \times[E_1(\infty)+4E_2(\infty)].& \end{aligned} \tag{39}$$

The term $f(I)=(2I+3)/I^2(2I-1)$ contains the entire dependence of T_1 on the nuclear spin. Since the sum involves the quadrupole operators, $f(I)$ is general for any lattice and the details of the lattice are contained in the terms $CE_\mu(\infty)$. The same spin function appears in the theory of relaxation in liquids for the case of extreme motional narrowing.[25,26]

E. Angular Depencence of T_1

Van Kranendonk's work predicted that the probability of a $\Delta m=1$ transition would vary by 50% as the field was changed from a [100] to a [111] direction. Nevertheless, experimental measurements on the alkali halides[2,3] and on InSb (this work) have failed to show any systematic orientational dependence of the relaxation time.

In Sec. III(B) the angular dependence of the transition probabilities was derived. If these transition probabilities are substituted in the T_1 expression, it becomes

$$1/T_1=(1/40)f(I)[(e^2\gamma Q)^2/r^{10}]CT^{*2}E(T^*)(3305). \tag{40}$$

Therefore, the point charge model and spin temperature assumption predict an isotropic relaxation time

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[26] R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1953).

for the zinc-blende lattice because the angular dependences of the transition probabilities exactly cancel in the final T_1 expression. This isotropy holds also if one uses Van Kranendonk's[4] transition probabilities for the NaCl lattice or Yosida and Moriya's[10] transition probabilities for the NaCl and CsCl lattices. [Because of a different choice of quadrupole Hamiltonian their coefficients of α^2 in $E_2(\infty)$ are $\frac{1}{16}$ those of α^2 in $E_1(\infty)$. This is balanced by a factor of 2 difference in the $Q_{\mu m}$'s so that the predicted relaxation is still isotropic.] An isotropic T_1 for the case of a spin of $\frac{3}{2}$ has also been derived[3,3a] by explicitly introducing the T_2 energy-conserving spin flips into a differential equation for the (equally spaced) level populations. This yields an isotropic T_1 when $T_2 \ll T_1$ which is also the condition for the spin-temperature assumption.

F. Comparison of the Van Kranendonk Model with the III-V Compounds

The multiplying factor γ for the point charges has been introduced to account for the difference between the point charge model and the actual physical situation. For both the angular dependence and the absolute theoretical calculation of the relaxation times there is a question of whether or not the multiplying factor correctly connects the model and physical reality. Also, if it is correct to use such a factor, how is it determined what its value should be?

It is shown in Sec. IV that the experimental T_1's are apparently related to the values of the $\langle r^{-3}\rangle_{\text{av}}$ for a p-valence electron of the free atoms. Townes and Dailey[27] have shown that the static quadrupolar effects in microwave spectroscopy are mainly accounted for by the covalent parts of the wave functions and that the ionic effects are relatively small.

It has been shown in Sec. III(E) that an isotropic T_1 is predicted by the point charge model for the NaCl and ZnS lattices and by the covalent effects considered by Yosida and Moriya for the NaCl and CsCl lattices. However, the angular effects are contained in the tensors $A_{\mu ij}$ and these tensors will be different for a completely covalent effect. The general displacement of a point charge might be replaced by a general extension (compression) and rotation of a covalent bond. In any case, for the point charge model $A_{\mu ij}\neq 0$ only if $i=j$, but for the strongly covalent case a distortion of one bond might affect the field gradients produced by a given distortion of the other bonds so that $A_{\mu ij}\neq 0$ for $i\neq j$. Since the tensors appear as a sum of self products and a sum of cross products in the final transition probability expression, it is difficult to make any general statements about the effects of a different method of obtaining the tensors. Since no angular dependence of quadrupolar relaxation times has been observed experimentally, it is possible that the process is isotropic in crystals of cubic symmetry for any type of quadrupole-moment interaction with lattice vibrations.

Shulman *et al.*[28] have measured the broadening of the In resonance line while applying a reversible strain to a single crystal of InSb. From the second moment of the broadened line the field gradients at the nuclei were determined. If these experimental field gradients are compared with those calculated for a point charge model for the same lattice strain an empirical γ is obtained. The line broadening is due to the first order effects of the lattice strains. The relation between the field gradients and the applied stress is expressed by Shulman in terms of a field gradient-stress four-tensor. The number of independent components of this tensor is much less than the 81 possible components of a four-tensor. For a crystal of cubic symmetry there are only two independent components. The same multiplying factor relates both of these components to the point-charge model. Therefore, for this case, the multiplication factor is a scalar. The empirical γ is 63 ± 13 if only nearest neighbors are considered.

Roderick[29] has made line shape measurements on impurity-doped InSb. For charged Te impurities in InSb a multiplication factor of 350 is required to account for the observed broadening of the In^{115} line.

These two multiplication factors refer to different types of interactions. The case of $\gamma=63$ is for strain effects and the case of $\gamma=350$ is for electric field effects. Since the γ is squared in Eq. (40), the predicted T_1's for the γ's differ by a factor of 30. Equation (40) gives $T_1=24$ sec for $\gamma=63$ and $T_1=0.8$ sec for $\gamma=350$ when the following values are used: $Q=1.16\times 10^{-24}$ cm², $d=5.8$ g/cc, $v=2.26\times 10^5$ cm/sec, $a=6.48$ A, $\theta_D=205°\text{K}$, $T=77.4°\text{K}$. The experimental relaxation time is 0.80 ± 0.05 sec. The apparent agreement is accidental, nevertheless, the closer agreement for the electrical γ may be significant. The effects of the long-wavelength acoustical modes should be similar to the effects of the static displacements of Shulman's experiment, but the effects of the optical modes may not be properly accounted for by the static strain multiplication factor.

Measurements[30] on doped GaSb give $\gamma(\text{Ga})\cong 250$ and $\gamma(\text{Sb})\cong 50$. The experimental T_1's give $\gamma(\text{Ga})=0.65\gamma(\text{Sb})$. Since the ratio of the γ's in the same material should be more significant than a single γ, it does not appear that other experiments on the III–V compounds give a very reliable γ to insert in the T_1 equation for the point charge model.

The strain-broadening is due to the first-order displacement effects of the lattice strains. The charge-broadening is due to field gradients produced by charged centers (with possibly some strain effects present). The relaxation time is due to the second-order

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effects of displacements caused by thermal vibrations. Perhaps these phenomena really do have different γ's.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

In this section the nuclear quadrupolar relaxation times for most of the III–V compounds and germanium are discussed. The theoretical temperature dependence given by Van Kranendonk is verified experimentally by results obtained in KI and InP. The isotropic relaxation time and the spin function, $f(I)$, are also experimentally verified.

A. Temperature Dependence of T_1

The temperature dependence of the Raman process (two phonons) has been given by Van Kranendonk[4] as $1/T_1 \propto T^{*2}E(T^*)$, where $T^*=T/\theta$ and $E(T^*)$ is a numerical function (see Fig. 3). This function, $E(T^*)$, connects the high-temperature region of $T^*>1$ in which $1/T_1 \propto T^2$ to the low-temperature region of $T^*<0.02$ in which $1/T_1 \propto T^7$. Another temperature dependence for the quadrupolar relaxation process has been proposed by Khutsishvili.[31] He suggests a process that involves four phonons and predicts $1/T_1 \propto T^4$ in the high-temperature region.

Temperature dependence measurements were made of I^{127} in a single crystal of KI between 77°K and 800°K. The results of these measurements are plotted in Fig. 1 and two lines are drawn through the 300°K point. One line corresponds to a T^2 dependence and the other line to a T^4 dependence. It is clear that the data is very close to a T^2 dependence and that a T^4 dependence is definitely ruled out. Other observations[3,32] of the Raman square-law temperature dependence in alkali halides have been reported.

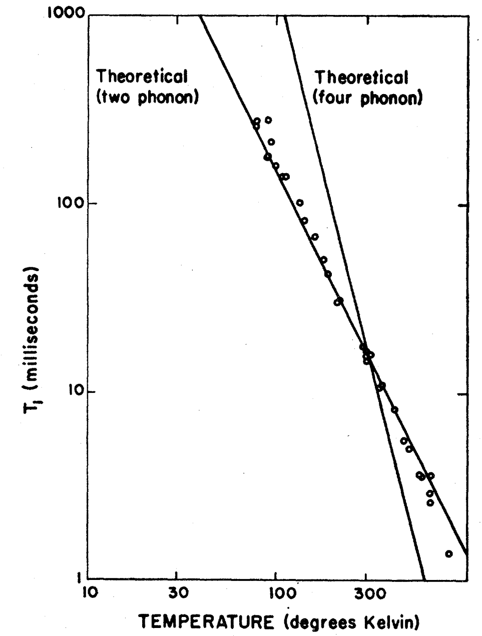

FIG. 1. Relaxation times of I^{127} in KI. The "two-phonon" process predicts $T_1 \propto T^{-2}$ and the "four-phonon" process predicts $T_1 \propto T^{-4}$.

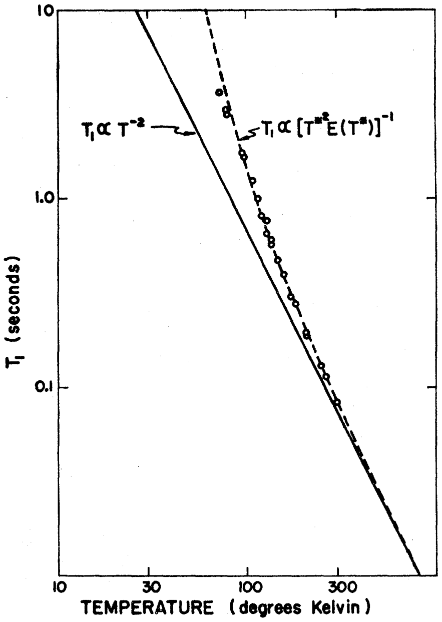

FIG. 2. Relaxation times of In^{115} in InP. Because $T<\theta$, the data deviate from the straight lines, $T_1 \propto T^{-2}$; the dashed line is calculated using Van Kranendonk's function $E(T^*)$.

In order to verify the function $E(T^*)$ temperature dependence measurements were made of the In^{115} resonance in InP. The deviation from a square-law dependence can be seen in Fig. 2. The data are compared to $E(T^*)$ by assuming a Debye temperature, since a calorimetric value has not been reported, and plotting $E(T^*)=T_R{}^2E(T_R{}^*)T_1(T_R)/T^2T_1(T)$ vs T and fitting the room temperature (T_R) point to the $E(T^*)$ curve. This plot is Fig. 3. A Debye θ of 400±25°K gives the best fit to the predicted curve. The ±25°K indicates the range of Debye temperatures for which some of the data points will lie on the curve. Less extensive temperature dependence data were taken on InAs, InSb, and AlSb. The best fit for the In^{115}As was for a Debye θ of 240±30°K. The best fit for the In^{115}Sb data was for a Debye θ of 200±20°K and this agrees with the calorimetric value of 200±5°K and the value of 208°K that is predicted by the elastic constant data.[33] T_1 measurements on AlSb were made only at 77.4 and 300°K and give $\theta=340$°K, which agrees within the expected errors with $\theta=350$°K from specific-heat data.[34]

The Debye temperature of a material can be obtained by fitting the experimental relaxation time data to the

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curve of $E(T^*)$ or by fitting the experimental specific heat data to the general Debye specific-heat curve. It is well known that the density of states of the lattice vibrations for an actual solid is not a Debye distribution. This raises a question whether or not the two methods give the same Debye temperature. In terms of the actual density of states, $\rho(x)$, the relaxation time prediction would involve integrals of the form

$$\int_0^\infty \frac{\rho(x)e^x}{(e^x-1)^2}\left(\frac{\rho(x)}{x^2}L_n(cT^*x)\right)dx, \tag{41}$$

while the specific heat would involve the integral

$$\int_0^\infty \frac{\rho(x)e^x}{(e^x-1)^2}(x^2)dx. \tag{42}$$

Since the L_n functions are complicated and the $\rho(x)$ would in general be represented numerically, further comparison of the two integrals would involve numerical integrations. As discussed above, the two methods give the same Debye temperature for InSb and AlSb within the experimental errors. These are the only compounds for which the methods can be compared at present because calorimetric specific heats are not available for InP and InAs.

It is known that the Debye θ determined by specific heat measurements show a temperature dependence and it might be that the θ values determined by quadrupolar relaxation would also show a temperature dependence. The scatter in Fig. 3 appears larger than in Fig. 2 because the data have been divided by T^2. This scatter is too large to permit a definite statement but the data around $T=0.2$ appear to lie somewhat above the theoretical curve. It would probably be of interest to make careful measurements on a material in which the temperature dependence of the specific heat Debye θ is known.

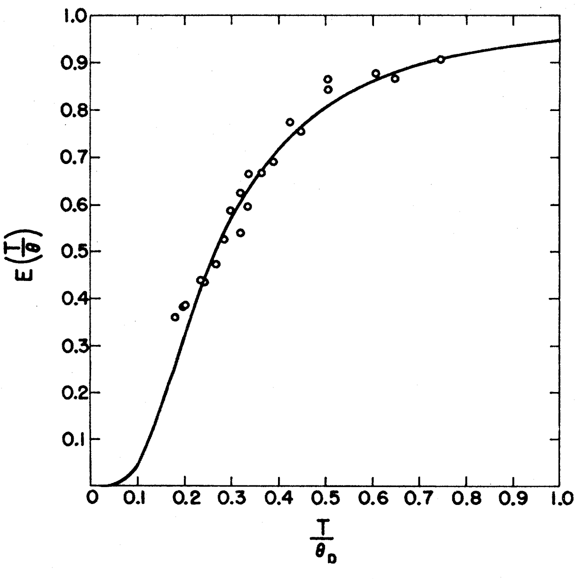

FIG. 3. Van Kranendonk's function $E(T^*)$. The experimental data is plotted as $E(T^*)=T_R^2E(T_R^*)T_1(T_R)/T^2T_1(T)$.

The predicted temperature dependence of the relaxation time goes as T^{-7} for temperatures less than 0.02 of the Debye temperature. It is probably not possible to verify this for nuclear relaxation because the relaxation times in this temperature region are too long. Due to its large quadrupole moment, In^{115} has a relatively short nuclear relaxation time. For InP the T^{-7} region would occur for temperatures less than 8°K. But at 8°K the In^{115} relaxation time, as predicted by the theoretical temperature dependence and the high-temperature experimental relaxation times, would be about 10^6 sec. Even if very pure material were obtained by zone refining, it would be very difficult to make measurements of such long relaxation times. Electron relaxation times are much shorter and both the linear temperature dependence of the direct processes and the seventh-power temperature dependence of the Raman processes have been observed by Feher.[35]

B. Spin Dependence of the Relaxation Times

It is important to verify the theoretical spin dependence because this factor must be considered when the relaxation times in the different compounds are discussed. A direct measurement that verifies the spin-dependence function $f(I)=(2I+3)/I^2(2I-1)$ is possible in those materials that contain isotopes of different spin values. One such material is AlSb, because antimony has two isotopes of spins $\frac{5}{2}$ and $\frac{7}{2}$. Unfortunately, the Ga^{69} and the Sb^{121} resonances overlap in GaSb and the Bloch decay consists of a mixture of the two signals. Also, the resonance line of Sb in InSb is very broad and the Sb^{123} resonance was unobservable. Rubidium is another element that has two isotopes of different spin values, $\frac{3}{2}$ and $\frac{5}{2}$. Since a good single crystal of RbCl was available, T_1 measurements were made in this material on both Rb isotopes at 77.4°K.

The theoretical prediction for Sb is

$$\frac{T_1(\mathrm{Sb}^{121})}{T_1(\mathrm{Sb}^{123})}=\left[\frac{Q(\mathrm{Sb}^{123})}{Q(\mathrm{Sb}^{121})}\right]^2\frac{f(\frac{7}{2})}{f(\frac{5}{2})}=(1.63)(0.425)=0.69.$$

For AlSb the experimental ratio is 0.75 ± 0.10. The theoretical prediction for Rb is

$$\frac{T_1(\mathrm{Rb}^{87})}{T_1(\mathrm{Rb}^{85})}=\left[\frac{Q(\mathrm{Rb}^{85})}{Q(\mathrm{Rb}^{87})}\right]^2\frac{f(\frac{5}{2})}{f(\frac{3}{2})}=(4.28)(0.24)=1.027.$$

For RbCl the experimental ratio is 1.23 ± 0.40. The larger experimental error for the rubidium results is due to the small signal-to-noise ratio of the Rb^{85} resonance.

There are two isotopes of gallium, Ga^{69} and Ga^{71}, with the same spin, $\frac{3}{2}$, and their relaxation times should

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[35] G. Feher, Phys. Rev. **114**, 1245 (1959).

TABLE I. Experimental T_1's measured at 77.4°K.

Nucleus and compound	Experimental T_1 in seconds	Nucleus and compound	Experimental T_1 i seconds
$In^{115}Sb$	0.80± 0.05	$Ga^{69}As$	14.5 ± 1.0
$InSb^{121}$	0.51± 0.10	$Ga^{71}As$	33.0 ± 3.0
$In^{115}As$	1.35± 0.05	$GaAs^{75}$	5.0 ± 0.3
$InAs^{75}$	1.45± 0.10	$Al^{27}Sb$	400.0 ±20.0
$In^{115}P$	2.93± 0.05	$AlSb^{121}$	2.0 ± 0.1
InP^{31}	165.0 ±15.0	$AlSb^{123}$	2.65± 0.15
$Ga^{71}Sb$	12.0 ± 0.5	Ge^{73}	375.0 ±40.0
$GaSb^{123}$	1.55± 0.1	$Rb^{87}Cl$	4.0 ± 0.3
		$Rb^{85}Cl$	3.25± 0.75

be inversely proportional to the square of the ratio of their quadrupole moments. For GaAs the experimental T_1 ratio is $T_1(\mathrm{Ga}^{71})/T_1(\mathrm{Ga}^{69})=2.3\pm0.4$ and the square of the ratio of the quadrupole moments is

$$[Q(\mathrm{Ga}^{69})/Q(\mathrm{Ga}^{71})]^2=2.52.$$

C. Angular Dependence Measurements

The experimental confirmation of the isotropy of the relaxation time in the III–V compounds was of interest in this work because most of the measurements were made on polycrystalline materials. Relaxation times of the In^{115} resonance in a single crystal of InSb were measured for several different crystal orientations in the magnetic field. The measured relaxation time at 77.4°K was 0.80±0.05 sec; the ±0.05 sec represents the random experimental variations. It was shown in Sec. III(E) that the point-charge model predicts an isotropic T_1. Since the III–V compounds are not accurately represented by a point-charge model, it is possible that the isotropic quadrupolar relaxation times are characteristic of any type of quadrupole moment-lattice vibration coupling in crystals of cubic symmetry.

D. Discussion of T_1 Relations

The experimental T_1 values measured at 77.4°K in this experiment are listed in Table I. In Sec. III an expression for the relaxation times of the point charge model was derived. Many properties of the material, such as the density, velocity of sound, lattice constant, and Debye temperature appear in this equation. Since these factors will be different for each compound, and since all of the properties, especially the lattice constant, may not be properly included in the relaxation by the point charge approximation, it is convenient to discuss the ratios of the relaxation times of the two types of nuclei in the same compound. Perhaps these ratios also depend on the properties of the materials, but the dependence should be less than that of the individual relaxation times.

If the time-varying field gradients at the III and the V nuclei were the same, then the ratio of the relaxation times would be given by

$$\frac{T_1(\mathrm{III})}{T_1(\mathrm{V})}=\left[\frac{Q(\mathrm{V})}{Q(\mathrm{III})}\right]^2\frac{f[I(\mathrm{V})]}{f[I(\mathrm{III})]},\tag{43}$$

where $Q(\mathrm{V})$ is the quadrupole moment of the V nucleus and $f[I(\mathrm{V})]$ is the spin function for the V nucleus.

The interactions that cause relaxation are the field gradients at the nuclei due to the second order effects of displacements caused by thermal vibrations of the lattice. If it is assumed that the ratios of these field gradients at the III and the V nuclei are equal to ratios of the static-field gradients, $q(\mathrm{V})/q(\mathrm{III})$, due to one covalent bond, then the ratios of the relaxation times are given by

$$\frac{T_1(\mathrm{III})}{T_1(\mathrm{V})}=\left[\frac{Q(\mathrm{V})q(\mathrm{V})}{Q(\mathrm{III})q(\mathrm{III})}\right]^2\frac{f[I(\mathrm{V})]}{f[I(\mathrm{III})]}.\tag{44}$$

This assumption for the III–V compounds has as yet no theoretical basis other than simplicity and an intuitive appeal.

In Table II the relation given by Eq. (43) is investigated. The last column gives the ratios of the T_1 ratio given by Eq. (43) to the experimental T_1 ratio. If the field gradients at both nuclei were the same, then the numbers in the last column would equal one.

In Table III the covalent situation is investigated. Since a prediction of the field gradient at the nucleus depends on a knowledge of $\langle r^{-3}\rangle_{\mathrm{av}}$ for the electrons, and this factor is not known for the various III–V compounds, the field gradient due to a p-valence electron of the free atom of the element in question is used.

The product Qq is measured in atomic beam experiments. It is known accurately for the III elements but not for the V elements. The values of Q and q which are used in the above tables are listed in Table IV. The

TABLE II. T_1 relations for nuclei in the same compound.

Nuclei and compound	$T_1(\mathrm{III})/T_1(\mathrm{V})$	$[Q(\mathrm{V})/Q(\mathrm{III})]^2$	$f[I(\mathrm{V})]/f[I(\mathrm{III})]$	$[Q/Q]^2[f/f]$	$[Q/Q]^2[f/f][T_1(\mathrm{V})/T_1(\mathrm{III})]$
$Ga^{69}As^{75}$	2.9	2.50	1.0	2.50	0.86
$Ga^{71}As^{75}$	6.6	6.25	1.0	6.25	0.95
$Ga^{71}Sb^{123}$	7.75	32.2	0.102	3.28	0.42
$In^{115}Sb^{121}$	1.57	0.21	4.32	0.91	0.58
$In^{115}As^{75}$	0.93	0.067	18.0	1.21	1.30
$Al^{27}Sb^{121}$	200.0	12.5	1.0	12.5	0.062
Ge^{73}–$GaAs^{75}$	75.0	2.25	18.0	40.5	0.54

TABLE III. T_1 relations with covalent assumption.

Nuclei and compound	$T_1(\text{III})/T_1(\text{V})$	$[Q(\text{V})q(\text{V})/Q(\text{III})q(\text{III})]^2$	$[Qq/Qq]^2[f/f]$	$[Qq/Qq]^2[f/f]T_1(\text{V})/T_1(\text{III})$
$Ga^{69}As^{75}$	2.9	11.65	11.65	4.0
$Ga^{71}As^{75}$	6.6	29.1	29.1	4.4
$Ga^{71}Sb^{123}$	7.75	445.0	45.4	5.8
$In^{115}Sb^{121}$	1.57	2.09	9.03	5.8
$In^{115}As^{75}$	0.93	0.224	4.04	4.3
$Al^{27}Sb^{121}$	200.0	1180.0	1180.0	5.9
Ge^{73}–$GaAs^{75}$	75.0	3.87	69.6	0.93

values of Q were taken from Townes.[36] The q values were chosen to give the measured Qq values for the III elements and were determined from atomic spectroscopy data[37,38] to give $\langle r^{-3}\rangle_{\text{av}}$ for bonding states of neutral atoms for the V elements and germanium.

With the exception of AlSb, the quadrupole moments and spin factors in Table II correlate with the experimental ratios within a factor of 2. (Note that the first two rows consider GaAs so that the difference in the numbers in the last column represents the error of the experimental ratios.) Since all of the experimental ratios have less than ±20% uncertainty, and the quadrupole moments of Al and Sb are known with reasonable accuracy, the AlSb data cannot be ignored. Of course, there is no reason to expect the field gradients to be the same at both nuclear sites; even if the point charge model were a good approximation, the effects of factors such as Sternheimer polarization would give different multiplication factors for the different elements.

The numbers in the last column of Table III are about 4.3 for the arsenic compounds and 5.8 for the antimony compounds. Because of the ±20% uncertainty in the experimental ratios, perhaps these numbers should be considered as 5±1. Nevertheless, since the numbers do not vary with III elements, it is difficult to see why they should vary with the V elements. Perhaps the difference is due to an incorrect Qq value for As or Sb. In any case, the AlSb data now agree with the data on the other compounds when the Qq ratios are considered. This number, 5±1, represents the difference in the ratios of the square of the field gradients due to the second order effects of the lattice displacements and the ratios of the square of the field gradients of the p-valence electrons of the free atoms which are listed in Table IV. At the present there is no explanation for the magnitude of this number or for its approximate uniformity for all of the compounds.

TABLE IV. Quadrupole moments Q and atomic field gradients q.

Nucleus	% Abundance	Spin	Q (10^{-24} cm^2)	q (10^{24} cm^{-3})
Al^{27}	100.0	$\frac{5}{2}$	0.15±0.01	7.23
P^{31}	100.0	$\frac{1}{2}$	0.00 ···	···
Ga^{69}	60.2	$\frac{3}{2}$	0.19±0.01	18.9
Ga^{71}	39.8	$\frac{3}{2}$	0.12±0.01	18.9
Ge^{73}	7.6	$\frac{9}{2}$	0.20±0.10	31.2
As^{75}	100.0	$\frac{3}{2}$	0.30±0.20	40.8
In^{115}	95.8	$\frac{9}{2}$	1.16±0.05	22.3
Sb^{121}	57.2	$\frac{5}{2}$	0.53±0.10	70.4
Sb^{123}	42.8	$\frac{7}{2}$	0.68±0.10	70.4

The relaxation times of a given nucleus in different compounds may also be compared if the various properties of the materials and their influence on the relaxation times are known. Table V makes a comparison in which only the effect of the Debye temperature is considered. The relaxation time is multiplied by $(T/\theta)^2E(T/\theta)$ to eliminate the temperature dependence. The Debye temperatures of GaAs and GaSb were calculated using their elastic constants.[39] The Debye temperatures of InP, InAs, InSb, AlSb, and GaP (the GaP numbers are taken from Weber *et al.*[40]) were determined by the temperature dependence of the relaxation times.

Evidently the "strength of coupling" to the lattice is about the same for a given nucleus in the compounds GaP, GaAs, GaSb, InAs, and InSb. Apparently InP and AlSb require consideration of other factors in addition to the Debye temperature. This may result from InP and AlSb being composed of the elements

TABLE V. Comparison of T_1's for a given nucleus in different compounds.

Nucleus and compound	$T_1(T/\theta)^2E(T/\theta)$	θ(°K)
$InSb^{121}$	0.054	200
$GaSb^{121}$	0.050	265
$AlSb^{121}$	0.041	340
$Ga^{71}Sb$	0.56	265
$Ga^{71}As$	0.58	355
$Ga^{71}P$[a]	0.58	400
$In^{115}P$	0.032	400
$In^{115}As$	0.086	240
$In^{115}Sb$	0.084	200
$InAs^{75}$	0.092	240
$GaAs^{75}$	0.088	355

[a] Taken from reference 40.

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[36] C. H. Townes, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 38/1.

[37] T. P. Das and E. L. Hahn, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Suppl. 1.

[38] R. G. Barnes and W. V. Smith, Phys. Rev. **93**, 95 (1954).

[39] T. B. Bateman, H. J. McSkimin, and J. M. Whelan, J. Appl. Phys. **30**, 544 (1959).

[40] M. J. Weber, L. Rimai, and L. Neuringer, Bull. Am. Phys. Soc. **6**, 225 (1961).

TABLE VI. Comparison of all relaxation times.

Nucleus and compounds	$T_1(T/\theta)^2E(T/\theta)Q^2f(I)$	$T_1(T/\theta)^2E(T/\theta)(Qq)^2f(I)$
Al(Sb)	5.9	3.0
Ga(P,As,Sb)	1.1	4.0
In(As,Sb)	0.85	4.2
(Ga,In)As	1.1	18.0
(Ga,In)Sb	4.7	23.1
Ge	1.8(0.5 → 4.0)	17.5

with larger separations in the periodic table than the elements of the other compounds.

Since the above product of T_1 and the temperature factor for a given nucleus is almost independent of the compound in which it appears, the values in Table V have multiplied by $Q^2f(I)$ and by $(Qq)^2f(I)$ for each element. These results are given in Table VI.

The first column of numbers in Table VI shows that the field gradients due to the lattice vibrations for the Ge nucleus are about as strong as for the III–V nuclei even when the uncertainties (as given in the brackets) due to the uncertainties in the value of Q for Ge are taken into consideration. Since the Ge relaxation time must be a pure covalent effect, the covalent effect should also be important in the III–V compounds even if the ionic effect is also important. The last column shows that when the Qq values are considered the III elements give a constant and the V elements and Ge give another constant. The ratio of the numbers is, of course, the factor of 5 ± 1 that appeared in Table IV. The value for Al is available only from the AlSb data; values from AlAs and AlP (which were not available) would probably be closer to 4 for the last column.

Table IV shows that the T_1 ratios of the nuclei in the same compound may be correlated with their Qq ratios. Table V shows that the strength of coupling to the lattice for a given nucleus is the same in the different compounds with the exceptions of AlSb and InP. Table VI shows that consideration of the temperature factor, Qq values, and $f(I)$ gives a very good correlation of all of the experimental data. Therefore, it appears that, except for the Debye θ, the coupling to the lattice is relatively insensitive to changes in the properties of the materials from one compound to another.

The results given in Tables V and VI should be considered only a correlation of the experimental data. The factor $C=24/\pi d^2v^3a^3$ that appears in Eq. (40) has not been used in the above correlation. It is surprising that the T_1's in different compounds may be correlated so simply. Even if the point charge model is replaced by another coupling mechanism, the theoretical T_1 expression based on a Debye model for the lattice vibration should contain a term involving the mass density, velocity of sound, and the lattice constant. Attempts to correlate the data with properties of the materials other than the Debye θ have not been successful.

It would certainly be of interest if a relaxation time calculation based on covalent effects could explain the correlations of Tables III, V, and VI, the slightly different behavior in AlSb and InP and, of course, the absolute values of the relaxation times.

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APPENDIX. CALCULATION OF THE ANGULAR DEPENDENCE OF $A_{\mu ij}$

To investigate the angular dependence of the transition probabilities it is necessary to carry through the calculations with the components of the $A_{\mu ij}$ tensors expressed in terms of the angles between the magnetic field and the crystal axes. One way to do this would be to express the positions of the charges, X, Y, Z, R, in terms of the angles. It is more convenient, however, to evaluate the tensors for the case of the magnetic field along one of the crystal axes and apply a general transformation to the $A_{\mu ij}$ tensors. The correct transformation matrix is the matrix $D_{m,m}(\alpha,\beta,\gamma)$ for the transformation of normalized second-order spherical harmonics. A similarity transformation must be made because the potentials V_μ from the $A_{\mu ij}$ were obtained are not normalized.

The transformation matrix is (following Rose[41])

$$D_{m,m'}{}^{j}(\alpha,\beta,\gamma)=e^{-im'\alpha}d_{m'm}{}^{j}(\beta)e^{-im\gamma}, \tag{A1}$$

where α, β, and γ are the Euler angles. For $j=2$ the

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[41] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

expression for d^2 is

$$d^2=\begin{vmatrix} c^4 & -2c^3s & 6^{\frac{1}{2}}c^2s^2 & -2cs^3 & s^4 \\ 2c^3s & c^4-3c^2s^2 & 6^{\frac{1}{2}}(cs^3-c^3s) & 3c^2s^2-s^4 & -2cs^3 \\ 6^{\frac{1}{2}}c^2s^2 & 6^{\frac{1}{2}}(c^3s-cs^3) & c^4+s^4-4c^2s^2 & 6^{\frac{1}{2}}(cs^3-c^3s) & 6^{\frac{1}{2}}c^2s^2 \\ 2cs^3 & 3c^2s^2-s^4 & 6^{\frac{1}{2}}(c^3s-cs^3) & c^4-3c^2s^2 & -2c^3s \\ s^4 & 2cs^3 & 6^{\frac{1}{2}}c^2s^2 & 2c^3s & c^4 \end{vmatrix}, \tag{A2}$$

where $c=\cos(\beta/2)$ and $s=\sin(\beta/2)$. Since the angle α corresponds to a rotation about an axis parallel to the magnetic field, the term $e^{-im'\alpha}$ may be dropped. $D^2(\beta\gamma)$ is then

$$D^2(\beta\gamma)=\begin{vmatrix} a^{-2} \\ a^{-1} \\ 1 \\ a^1 \\ a^2 \end{vmatrix}\, |d^2|, \tag{A3}$$

where $a=e^{i\gamma}$.

The normalized spherical harmonics of second order are

$$Y_2=\left(\frac{15}{2\pi}\right)^{\frac{1}{2}}\left(\frac{1}{4r^2}\right)\begin{vmatrix} (x+iy)^2 \\ -2z(x+iy) \\ (\frac{2}{3})^{\frac{1}{2}}(3z^2-r^2) \\ 2z(x-iy) \\ (x-iy)^2 \end{vmatrix}, \tag{A4}$$

whereas the potentials for a point charge, which were used to obtain $A_{\mu ij}$, are given by

$$V=\left(\frac{3}{2}\right)\left(\frac{1}{r^5}\right)\begin{vmatrix} (x+iy)^2 \\ 2z(x+iy) \\ \frac{2}{3}(3z^2-r^2) \\ 2z(x-iy) \\ (x-iy)^2 \end{vmatrix}. \tag{A5}$$

Since $V=MY$ requires the matrix

$$M=\text{const}\begin{vmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & (\frac{2}{3})^{\frac{1}{2}} & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{vmatrix}, \tag{A6}$$

the matrix d^2 becomes

$$d^2=\begin{vmatrix} c^4 & 2c^3s & 3c^2s^2 & -2cs^3 & s^4 \\ -2c^3s & c^4-3c^2s^2 & 3(c^3s-cs^3) & s^4-3c^2s^2 & 2cs^3 \\ 2c^2s^2 & 2(cs^3-c^3s) & c^4+s^4-4c^2s^2 & 2(cs^3-c^3s) & 2c^2s^2 \\ 2cs^3 & s^4-3c^2s^2 & 3(c^3s-cs^3) & c^4-3c^2s^2 & -2c^3s \\ s^4 & -2cs^3 & 3c^2s^2 & 2c^3s & c^4 \end{vmatrix}. \tag{A7}$$

For the particular case of the zinc-blende lattice, if the x, y, z axes are taken to be the [100], [010], [001] crystalline directions, then the nearest neighbors are at the positions (111), $(1\bar{1}\bar{1})$, $(\bar{1}1\bar{1})$, $(\bar{1}\bar{1}1)$. If the $A_{\mu ii}$ are calculated for these positions, then the above transformation may be used to express them in terms of the Euler angles.

$$A'=D^2(\beta\gamma)A=D^2(\beta\gamma)\begin{vmatrix} A_2 \\ A_1 \\ A_0 \\ A_{-1} \\ A_{-2} \end{vmatrix}, \tag{A8}$$

which gives, for example,

$$A_2'=D_{22}A_2+D_{21}A_1+D_{20}A_0+D_{2-1}A_{-1}+D_{2-2}A_{-2}. \tag{9A}$$

The transition probability calculations are carried out as described in Sec. III. In the final expression the Euler angles may be expressed in terms of the direction cosines between the magnetic field and the crystalline directions.