

Acoustic Behavior of the Jahn-Teller Ion Ni^{3+} in Al_2O_3

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(Received 26 September 1966)

We have measured the attenuation of 100- and 260-Mc/sec longitudinal acoustic waves in $\alpha\text{-Al}_2\text{O}_3$ (corundum) containing a few ppm of Ni^{3+} , and have compared our data with previous measurements at 2 Mc/sec. The attenuation as a function of temperature shows a relaxation-type behavior with a peak at 12°K for 100-Mc/sec waves and 14°K for 260-Mc/sec waves. From our data we can deduce a temperature-dependent relaxation time τ which is in reasonably good agreement with the relaxation time for the dynamic Jahn-Teller effect as observed in spin resonance. Above 12°K, we find $\tau = 5 \times 10^{-14} e^{-130/T}$ sec, the form expected for a thermal-activation process. At low temperatures, τ varies approximately linearly with temperature, as expected for phonon-assisted tunneling. Unexplained deviations from theory are observed below about 6°K at 2 Mc/sec, but we find no evidence for resonant absorption of acoustic phonons.

I. INTRODUCTION

BY studying the resonant acoustic modes of α aluminum oxide (corundum) spheres, we have previously shown that the acoustic loss at low temperatures increases rapidly with Ni^{3+} content.¹ We have interpreted these results in terms of the Jahn-Teller distortion of the octahedral sites occupied by Ni^{3+} .² In this earlier work the frequency was about 2 Mc/sec. At this frequency the acoustic loss rises rapidly with decreasing temperature but never passes over a peak. In the absence of a peak the relaxation time τ can only be obtained if we assume the measured loss and frequency shift arise from the same relaxation process.

We have now extended this work by studying the acoustic loss at 260 and 100 Mc/sec. At these frequencies loss peaks are observed at 14 and 12°K, respectively. With these new experimental results we have obtained more reliable values for the relaxation time as a function of temperature which make a more detailed comparison between theory and experiment possible.

The new relaxation times indicate that the assumptions used previously to obtain τ from the 2-Mc/sec data are not completely justified. Furthermore, at the higher frequencies the relation between the acoustic propagation direction and the crystal symmetry can be investigated and thereby yield information concerning the symmetry of the crystal defect involved.

II. EXPERIMENTAL PROCEDURE

The single crystal of $\text{Al}_2\text{O}_3:\text{Ni}^{3+}$ was prepared by the Verneuil or flame-fusion process and contained 30 ppm Ni of which optical absorption and spin resonance indicated about 1/10 was Ni^{3+} . The sample, approximately a 1-cm cube, was polished on six sides to an accuracy of $\frac{1}{4}$ wavelength of sodium light with opposite

faces parallel to within 5 sec of arc. Crystallographic directions normal to the faces were $\langle 11\bar{2}0 \rangle$, $\langle 0001 \rangle$, and $\langle 10\bar{1}0 \rangle$.

Measurement of the acoustic attenuation at 260 Mc/sec was done using the pulse-echo technique³ in which one transducer functions as both transmitter and detector of pulses. The experimental procedure for evaluating the change in loss versus temperature was to measure the difference in loss level between the 1st and 100th reflections by means of a calibrated attenuator as the temperature was slowly varied over the range 1.4 to 77°K. The transducer, a 20-Mc/sec longitudinal tourmaline plate, was bonded to the crystal with Dow-Corning 200 silicone oil, viscosity 12 500 centistokes.

Absolute loss values are difficult to obtain for low-loss materials such as corundum since relatively large errors are introduced by beam spreading, diffraction effects, and bonding losses. Combined these can equal or exceed the intrinsic loss of the sample. Diffraction effects are exhibited as undulations in the otherwise exponential decay of the echo train. Such effects were evident for all three crystallographic directions of the alumina crystal and particularly bad for propagation parallel to the $[10\bar{1}0]$ direction. Thus, as is seen in Fig. 1, the over-all loss level for this direction is greater than for the other two.

To determine the background loss we extrapolate the high-temperature part of the curve using the same temperature dependence observed for propagation parallel to the c axis. Since, as will be shown later, propagation parallel to the c axis ($[0001]$) has no Jahn-Teller loss, this correction for the background allows us to obtain the loss attributable only to the Jahn-Teller ions.

III. THEORY

A. Semiphenomenological Theory

We consider a model consisting of the Ni^{3+} ion and the octahedron of nearest-neighbor oxygen ions; we neglect the trigonal distortion of the octahedron, which

¹ E. M. Gyorgy, M. D. Sturge, D. B. Fraser, and R. C. LeCraw, *Phys. Rev. Letters* **15**, 19 (1965); E. M. Gyorgy, R. C. LeCraw, and M. D. Sturge, *J. Appl. Phys.* **37**, 1303 (1966).

² Similar effects have been observed in other crystals containing the Jahn-Teller ions Ni^{3+} and Mn^{3+} ; see Ref. 1 and D. B. Fraser, E. M. Gyorgy, R. C. LeCraw, J. P. Remeika, F. J. Schnetter, and L. G. Van Uitert, *J. Appl. Phys.* **36**, 1016 (1965).

³ H. J. McSkimin and P. Andreatch, Jr., *J. Acoust. Soc. Am.* **34**, 609 (1962).

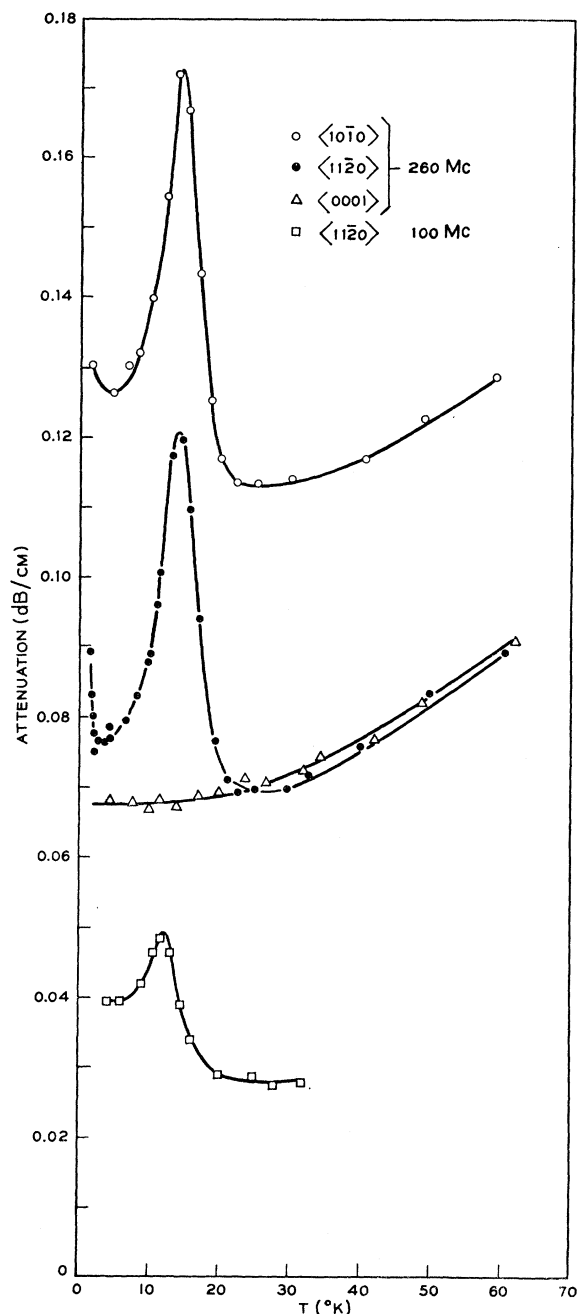


FIG. 1. Temperature dependence of attenuation of longitudinal acoustic waves for different frequencies and directions of propagation.

does not split the 2E ground state of Ni^{3+} . It is important to remember that, whereas those properties of our model which depend on the point symmetry will carry over the real system, those which depend on specific assumptions about it will not. For instance, our model has discrete vibrational energy levels, while we know that those of the real system are continuous.

Distortions of the octahedron can be described in

terms of collective coordinates, which would be normal coordinates in the case of an octahedral XY_6 molecule. The only coordinates we need worry about are the E_g pair⁴ Q_2, Q_3 ; these transform as $(x^2 - y^2)$ and $(3z^2 - r^2)$, respectively. Only an E_g distortion can split the 2E state in first order, and thus produce a Jahn-Teller effect. The potential surface on which the nuclei move in (Q_2, Q_3) space is the well-known "Mexican hat" illustrated in Fig. 2.^{5,6} There are weak potential minima along the three directions indicated, which correspond to tetragonal distortion (usually extension) along the x , y , or z axes of the octahedron. The nature of this distortion is illustrated in Fig. 3. The minima are separated by rather low potential barriers, which in fact vanish if nonlinear effects are neglected.⁵ While the height of these barriers, typically of the order 10^{-2} eV, is small on the scale of Fig. 2, it is large compared to kT at the temperature of interest in the present work (i.e., $T \lesssim 20^\circ\text{K}$). To a first approximation, therefore, the system can be considered to be localized in one of the potential wells (the "static Jahn-Teller effect"). If we consider an ensemble of such systems, each well will on the average be equally occupied.

If a strain is applied to the crystal, it will in general make the three wells inequivalent. For instance, compression parallel to a cube axis, or shear parallel to a (111) plane, will lower (or raise) the energy of one well relative to the other two. On the other hand compressive strain parallel to $\langle 111 \rangle$ will not make the wells inequivalent. All these crystallographic directions are referred to the axes of the octahedron. If these axes are

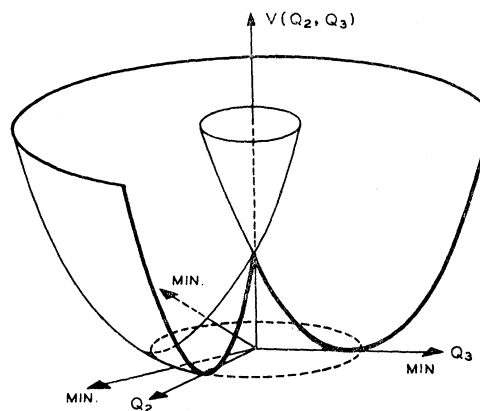


FIG. 2. Potential surface in (Q_2, Q_3) space for a doubly degenerate electronic state (after Ref. 6). If we write $Q_2 = \rho \sin\theta$, $Q_3 = \rho \cos\theta$, the three directions marked "min" have $\theta = 2\pi/3, 4\pi/3, 0$, and correspond to tetragonal distortion along x , y , and z axes, respectively.

⁴ J. H. Van Vleck, *J. Chem. Phys.* **7**, 72 (1939).

⁵ U. Opik and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A238**, 425 (1957); W. Moffitt and W. Thorson, *Phys. Rev.* **108**, 1251 (1957); A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (N. Y.)* **3**, 304 (1958).

⁶ W. Moffitt and W. Thorson, in *Calcul des fonctions d'onde Moléculaire*, edited by R. Daudel (*Rec. Mém. Centre Nat. Rech. Sci., Paris*, 1958), p. 141.

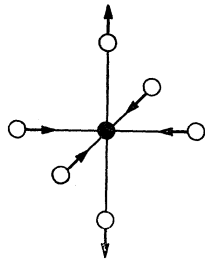


FIG. 3. Distortion of a perfect octahedron corresponding to $Q_3 > 0, Q_2 = 0$.

canted relative to the crystal axes, we have to make an appropriate angular transformation. For instance, in Al_2O_3 , the crystallographic $[0001]$ axis (c axis) is the $[111]$ axis of the octahedron. The fact that compressive strain parallel to the c axis does not affect the Jahn-Teller ion (except to displace all levels equally) is an important result which we will use later.

When strain has made the wells inequivalent, the ensemble will tend to relax and to populate preferentially the lowest well. If this relaxation is instantaneous, there is an effect on the elastic constants but not on the loss. This effect has been calculated¹ by considering the contribution of a single Jahn-Teller ion to the strain derivative of the free energy. We find⁷

$$\Delta c = -2n_0\alpha^2/kT, \quad (1)$$

where Δc is the change in the appropriate elastic constant ($c = c_{11} - c_{12}$ in the case of a cubic crystal whose axes coincide with those of the octahedron); n_0 the number of Jahn-Teller ions and 3α the splitting between the potential minima produced by unit strain.

If we use an alternating strain (acoustic wave) and relaxation is not instantaneous, there will be acoustic loss and dispersion. We will assume the existence of a single relaxation time τ (methods of calculating τ will be discussed later). The response to an acoustic wave can then be calculated; a simple physical way of doing this by analogy with a lossy resonant circuit is given in Ref. 1. We find for the loss factor Q^{-1} of a crystal, acoustically resonant at a frequency ω ,

$$Q^{-1} = -\frac{\Delta c}{c} \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (2a)$$

$$= -2\tau\Delta\omega. \quad (2b)$$

Here $\Delta\omega$ is the (negative) shift of resonant frequency from its value in the pure crystal. The acoustic loss can be equivalently expressed as an attenuation coefficient for a running wave⁸:

$$\begin{aligned} A &= 4.343\omega/sQ \text{ dB/cm} \\ &= 4.343 \times \frac{2n_0\alpha^2}{\rho s^3 kT} \frac{\omega^2\tau}{1 + \omega^2\tau^2}, \end{aligned} \quad (3)$$

⁷ The numerical coefficient was erroneously given as 12 in Ref. 1.
⁸ M. Pomerantz, Proc. IEEE 53, 1438 (1965); W. P. Mason and T. B. Bateman, J. Acoust. Soc. Am. 36, 644 (1964).

where s is the velocity of sound and ρ the density of the crystal.

B. Origin of the Relaxation Time

At temperatures such that kT approaches V_0 , the height of the potential barrier, the relaxation mechanism is simply thermal activation across the barrier, leading to the equation⁹

$$\tau^{-1} = 2\nu_0 e^{-V_0/kT}. \quad (4)$$

When $kT \ll V_0$, on the other hand, this mechanism no longer contributes, and in order to explain the observation of a finite τ we have to consider other mechanisms. The only mechanisms that can contribute in this region are those involving quantum-mechanical tunneling.

Several different ways of treating the acoustic loss due to tunneling have appeared in the literature. One approach¹⁰ treats the acoustic loss as a resonant process involving transitions between the lowest vibronic levels of the Jahn-Teller distorted complex. The splitting between these levels is due to tunneling.

The attenuation is given by

$$A = (C\omega^2/kT)g(\omega), \quad (5)$$

where C is a constant (containing n_0, α , etc.) and $g(\omega)$ is the shape function for the resonance. If the upper level (3Γ above the ground state) is lifetime broadened by an amount \hbar/τ , we have

$$g(\omega) = \frac{\tau}{1 + (\omega - 3\Gamma/\hbar)^2\tau^2}, \quad (6)$$

where Γ is the tunneling matrix element. Note that if $\Gamma\tau/\hbar \ll 1$, Eqs. (5) and (6) become

$$A = \frac{C}{kT} \frac{\omega^2\tau}{1 + \omega^2\tau^2}, \quad (7)$$

which is formally equivalent to (3).¹¹ Bersuker estimates τ and finds $\Gamma\tau/\hbar \gg 1$; however, his calculation does not agree with other estimates (see below). This is apparently because he does not take the inevitable random strain in the crystal into account. Such strain tends to localize the system in one or other potential well, broadening the resonance, and drastically reducing the probability of a resonant transition. Since we apparently observe a relaxation rather than a resonant process we will not consider the resonant process further.

Another approach, conceptually very simple, was used by the present authors in discussing earlier work.¹ We implicitly assumed the system to be initially localized in one of the potential wells and considered

⁹ J. L. Snoek, Physica 8, 711 (1941).

¹⁰ I. B. Bersuker, Zh. Eksperim. i Teor. Fiz. 44, 1577 (1963) [English transl.: Soviet Phys.—JETP 17, 1060 (1963)].

¹¹ For a more rigorous justification in an analogous situation see P. Kwok, Phys. Rev. 149, 666 (1966).

the rate of transition between wells. We assumed that there are two mechanisms acting in series; tunneling through the barrier (in itself a lossless process which cannot lead to relaxation) followed by relatively rapid relaxation within the potential well.¹² The tunneling process was assumed to be rate limiting. Our treatment, which we may call a "fast-relaxation" theory, was logically incomplete, in that we made no attempt to justify theoretically our assumption that the second process really is fast. However, this assumption is consistent with the fact that one does not normally see acoustic loss associated with point defects having only a single potential well; this implies that relaxation within the well is either very fast or very slow. Our theory gave a temperature-independent relaxation time at low temperatures. In the one-dimensional WKB approximation¹³

$$\begin{aligned} \tau^{-1} &= \Gamma/\hbar \\ &= 2\nu_0 \exp\left(-\hbar \int_{V>\frac{1}{2}h\nu_0} [\mu(V(x)-\frac{1}{2}h\nu_0)]^{1/2} dx\right). \end{aligned} \quad (8)$$

Here Γ is the tunneling matrix element, $V(x)$ is the potential along the lowest path between the potential minima, ν_0 is the vibrational frequency in the well, and μ is the effective mass (the oxygen mass in the case of the octahedral molecule). To fit (8) to the limiting value of τ at low temperatures (knowing the maximum value of V , V_0 from the activation energy at higher temperatures) we had to assume either a rather wide barrier (corresponding to at least 30% Jahn-Teller distortion) or a value of μ of several oxygen masses. The latter assumption did not seem unreasonable, since more than the nearest neighbor octahedron is involved in the Jahn-Teller distortion.

Having fitted the limiting value of τ at 0°K by Eq. (8), and the high-temperature data by Eq. (4), we could fit the data in the intermediate range of temperatures by taking thermal average of (8) over the continuous vibrational energy levels of our complex. To do this we arbitrarily assumed an analytic form for $V(x)$ and replaced $h\nu_0$ by the energy of the vibrational level. There was, of course, some doubt as to the exact density of states function to use; we assumed it (by analogy with a two-dimensional harmonic oscillator) to be proportional to energy.

A logically more complete treatment of the problem of relaxation by tunneling has been given by Sussman.¹⁴ He was primarily interested in the reorientation rate of the O₂⁻ center in alkali halides, but his calculation is also applicable to the Jahn-Teller case.¹⁵ Sussman

considers the relaxation mechanism to be tunneling accompanied by the simultaneous emission or absorption of a phonon. Apart from the tunneling aspect, the process is analogous to the "direct process" in spin-lattice relaxation.¹⁶ Sussman's calculation predicts a large dependence of relaxation rate on local strain, i.e., the random strain which is always present in any real crystal. If this strain produces a splitting between potential minima of u_0 , Sussman gives

$$\tau^{-1} = \gamma^2 \frac{u_0^3 \coth(u_0/2kT)}{8\pi\rho\hbar^4 s^5}, \quad (9)$$

where γ is the ratio of the off-diagonal matrix element to the strain ($\gamma \sim \alpha\Gamma/h\nu_0$), ρ is the density and s the (appropriately averaged) velocity of sound. We can put an upper limit of 2 cm⁻¹ on u_0 , since no "freeze-out" effects are seen down to 3°K, such as would be expected when $u_0 \sim kT$.^{17,18}

Sussman's treatment is only valid when $\Gamma/h\nu_0 \lesssim 10^{-2}$, i.e., $\gamma \lesssim 10^{-2}\alpha$. We will see that $\alpha \sim 10^4$ cm⁻¹, so the largest reasonable value of γ is 100 cm⁻¹. Substituting in Eq. (9) we find $\tau^{-1} \lesssim 10^4$ sec⁻¹ at 4°K. This is too slow by more than three orders of magnitude.

Sussman's calculation has been repeated by Pirc, Zeks, and Gosar.¹⁹ These authors take into account terms in the coupling neglected in Ref. 14.²⁰ While these terms only operate in second order, they turn out to be dominant for small u_0 . Like Sussman's, these calculations are only valid when there are strains sufficiently large to localize the system in one or other potential well; i.e., $u_0 \gtrsim \Gamma$. However, for $\Gamma < u_0 < kT$, these authors differ from Sussman in finding a relaxation time independent of strain. They find, for $kT \gg \hbar\omega$, u_0 ,

$$\tau^{-1} = BT, \quad (10)$$

where

$$B = 18\Gamma^2\alpha^2k/\pi\rho\hbar^4s^5,$$

which is larger by a factor of order $(h\nu_0/u_0)^2$ than Sussman's result. When kT is not large compared to u_0 , we must replace Eq. (10) by the more general expression

$$\tau^{-1} = BTf(u_0/kT), \quad (11)$$

where

$$f(x) = x(2+e^{-x})/3(1-e^{-x}).$$

At 0°K Eq. (11) becomes

$$\tau^{-1}(0) = 2Bu_0/3k. \quad (12)$$

¹⁶ R. de L. Krönig, *Physica* **6**, 33 (1939); J. H. Van Vleck, *Phys. Rev.* **57**, 426 (1940).

¹⁷ This is consistent with optical linewidths in Al₂O₃ crystals grown by similar techniques. These indicate strains of order 10⁻⁴ or less (see Ref. 18), implying $u_0 \lesssim 1$ cm⁻¹, since $\alpha \sim 10^4$ cm⁻¹ (see below).

¹⁸ A. L. Schawlow, in *Quantum Electronics II*, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 50.

¹⁹ R. Pirc, B. Zeks, and P. Gosar, *J. Phys. Chem. Solids* **27**, 1219 (1966).

²⁰ J. A. Sussman (private communication) has independently pointed out the importance of these terms.

¹² This implies that the vibronic level widths are large compared with their separations.

¹³ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955), p. 302.

¹⁴ J. A. Sussman, *Physik Kondensierten Materie* **2**, 146 (1964).

¹⁵ J. A. Sussman (private communication).

Besides the "direct" process, there is a "Raman" process^{14,19} in which a phonon is scattered by the impurity, taking up or losing a small amount of energy. Using a Debye model, Pirc, Zeks, and Gosar find for the sum of the direct and Raman processes¹⁹

$$\tau^{-1} = BT[1 + (T/T_0)^2],$$

where

$$kT_0 = (2\hbar^3 \rho s^5)^{1/2} / \alpha. \quad (13)$$

In Al_2O_3 , T_0 is 100°K (within a factor of 2) so the Raman process can be neglected in our case.

C. Application to Experiment

The first and most general prediction of any of the above theories is that a longitudinal wave propagating parallel to the c axis of Al_2O_3 cannot couple to the Jahn-Teller ions. As we see from Fig. 1, this prediction is well borne out in practice. The next prediction is that the change in elastic constants should vary as $1/T$. It was not possible to measure this at 260 Mc/sec, but at 2 Mc/sec this relation is well obeyed. Substituting the observed change in Eq. (1) we find $\alpha = 15\,000 \pm 6000 \text{ cm}^{-1}$, where the uncertainty is primarily due to the uncertainty in n_0 . This value of α is in good agreement with other measurements of the splitting of e orbitals by tetragonal strain.²¹

At 260 Mc/sec we find a peak in the attenuation at 14°K. At 100 Mc/sec the peak is at 12°K. If we assume a relaxation process, so that Eq. (3) holds, the peak occurs at the temperature T_m at which $\omega\tau = 1$. Remembering that Δc varies as T^{-1} , we may write (3) as

$$A(T) = \frac{2T_m A(T_m) \omega \tau}{T(1 + \omega^2 \tau^2)}. \quad (14a)$$

Here $A(T)$ is the attenuation at temperature T , corrected for the background loss of the crystal and apparatus, and

$$A(T_m) = 4.343(n_0 \alpha^2 \omega / \rho s^3 k T_m). \quad (14b)$$

We determine the background loss by extrapolating the high-temperature curve, using the same temperature dependence as is observed for propagation parallel to the c axis (for which there is no Jahn-Teller loss). The measured maximum loss $A(T_m)$ is less by a factor of about 30 than that calculated from Eq. (14b), using parameters deduced from $\Delta c/c$ observed at 2 Mc/sec. This discrepancy arises in part from differences in concentration and polarization but most of it must be due to the fact that only a small fraction (about 10%) of the Ni^{3+} ions contribute to the loss. This view is supported by the observation of more than one type of Ni^{3+} ion in spin resonance.²²

²¹ A. L. Schawlow, A. H. Piksis, and S. Sugano, *Phys. Rev.* **122**, 1469 (1961); M. D. Sturge, *ibid.* **131**, 1456 (1963); **140**, A880 (1965).

²² F. R. Merritt and M. D. Sturge, *Bull. Am. Phys. Soc.* **11**, 202 (1966).

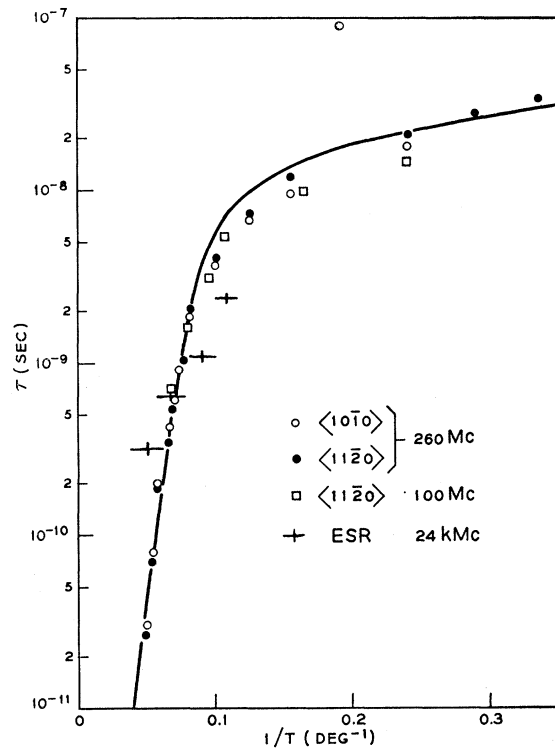


FIG. 4. Relaxation time τ deduced from the attenuation of longitudinal waves using Eq. (14a). Filled circles: 260 Mc/sec, $\langle 11\bar{2}0 \rangle$ propagation; open circles: 260 Mc/sec, $\langle 10\bar{1}0 \rangle$ propagation; squares: 100 Mc/sec, $\langle 11\bar{2}0 \rangle$ propagation. Crosses represent approximate values of relaxation time deduced from spin-resonance measurements (Ref. 22). The full line is the theoretical curve arrived at by combining Eqs. (4) and (10), using the parameters given in the text.

In Ref. 1 we substituted our 2-Mc/sec data on the loss and frequency shift of resonant spheres of Al_2O_3 into Eq. (2b) to find τ as a function of temperature. This procedure assumes that all the ions which contribute to the frequency shift also contribute to the loss. We now know that this is probably not correct and gives relaxation times probably a factor of 10 too low. If this correction (which only affects the absolute value of τ , not its temperature dependence) is made, the relaxation times of Ref. 1 at all but the lowest temperature are in reasonable agreement with the present data, which are more reliable.

The relaxation time τ , deduced from Eq. (14), is plotted as a function of temperature in Figs. 4 and 5. Also in Fig. 4 are some relaxation times²² deduced from the temperature dependence of spin resonance in the same crystals of $\text{Al}_2\text{O}_3:\text{Ni}^{3+}$. These were deduced by fitting the spin-resonance data to motional narrowing theory²³; the fit was not very good and the values of τ are correspondingly uncertain. Within this uncertainty they agree with the present data. Having found τ at a

²³ H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.* **21**, 279 (1953); C. P. Slichter, *Principles of Magnetic Resonance* (Harper & Row, Inc., New York, 1963), p. 154.

given temperature from the 260-Mc/sec data, we can calculate the attenuation at all frequencies from Eq. (14). The results for three temperatures, 14, 8, and 4.2°K, are given by the full curves in Fig. 6. The points in Fig. 6 are experimental results for longitudinal waves propagating parallel to $\langle 11\bar{2}0 \rangle$. In the case of the 2-Mc/sec data, the Q values of Ref. 1 were converted to dB/cm using Eq. (3), and corrected for the different polarization through Bersuker's¹⁰ Eq. (8). These 2-Mc/sec data were obtained on different crystals from those used in the present experiments, and the concentrations of Ni^{3+} are doubtful (relative to the present data) within a factor of 2 or 3. Allowing for this uncertainty, agreement with Eq. (14) is good over the entire frequency range above 8°K; but below this temperature agreement is not so good. In particular there is excess loss at 2 Mc/sec. We are unable to account for this discrepancy, which is in the wrong direction for a resonant process [Eq. (6)].

Figure 5 shows that at low temperatures τ^{-1} varies approximately as T . This supports the "direct process" theory¹⁹ rather than the "fast-relaxation" theory¹ of tunneling. However, there is some evidence that below 2°K the relaxation time is leveling off, since the loss rises roughly as T^{-1} in this region (see Fig. 1). This leveling off is probably due to breakdown of the condition $u_0 \ll kT$, so that Eq. (10) no longer holds. We cannot fit Eq. (11) to the data because u_0 is a random variable, but if we simply substitute the minimum value of τ^{-1} ($2 \times 10^7 \text{ sec}^{-1}$) in Eq. (12) we find $u_0 \doteq 2 \text{ cm}^{-1}$, in accord with previous estimates.¹⁷

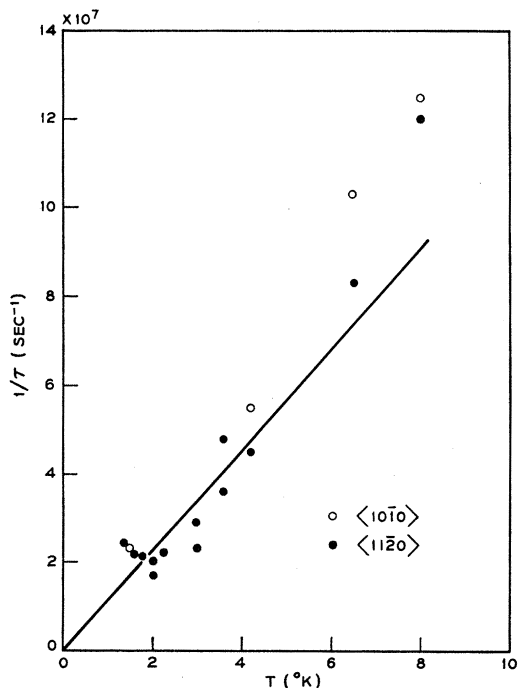


FIG. 5. Inverse relaxation time τ^{-1} at low temperatures, plotted to illustrate the linear dependence on T predicted by Eq. (10).

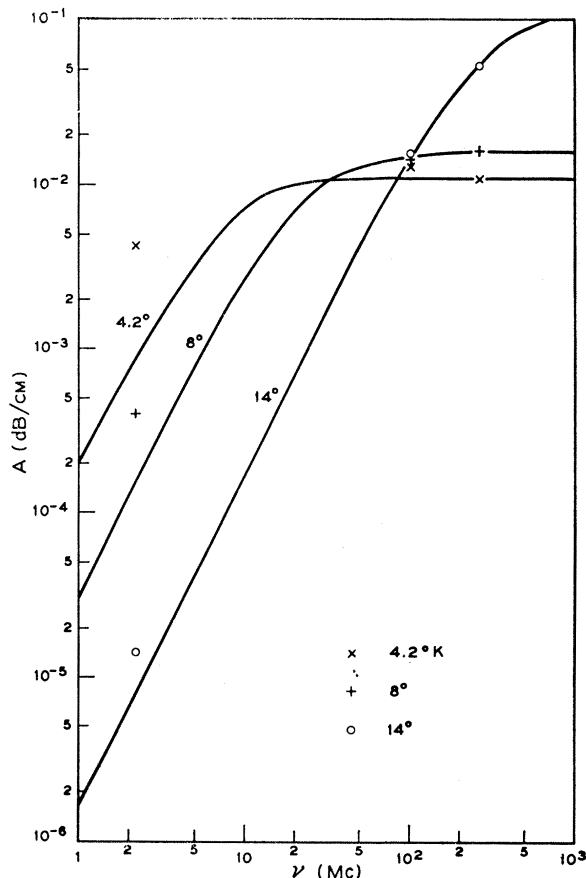


FIG. 6. Frequency dependence of acoustic attenuation at different temperatures (propagation parallel to $\langle 11\bar{2}0 \rangle$). The 2-Mc/sec points are deduced from the data of Ref. 1. They have been corrected for polarization but not for concentration.

At higher temperatures (above 12°K) we can get a good fit with Eq. (4). The full curve in Fig. 4 is the combination of Eqs. (4) and (10), with the following parameters: $B = 1.1 \times 10^7 \text{ sec}^{-1} \text{ deg}^{-1}$, $\nu_0 = 10^{13} \text{ sec}^{-1}$, $V_0 = 0.011 \text{ eV}$. The values of ν_0 and V_0 are in accord with previous experimental^{1,24} and theoretical⁵ estimates. The value of B implies $\Gamma = 0.2 \text{ cm}^{-1}$.

If we substitute Γ and ν_0 in Eq. (8) we find

$$\hbar^{-1} \int [2\mu(V - \frac{1}{2}h\nu_0)]^{1/2} dx = 6.$$

Taking μ to be one oxygen mass we find an effective width of the barrier of about 0.5 Å, which implies a Jahn-Teller distortion of about 15%. This is a reasonable figure.

IV. CONCLUSIONS

We have shown that the low temperature acoustic loss which arises when Ni^{3+} is introduced into Al_2O_3 is

²⁴ S. Geschwind and J. P. Remeika, J. Appl. Phys. 33, 370 (1962).

due to the Jahn-Teller effect. The frequency dependence of the loss shows that it is a relaxation rather than a resonant process. While there is some deviation from the theoretical dependence at the lowest frequencies it is not in the direction expected for a resonant process. This result is consistent with the presence of small random strains in the crystal, which broaden the resonance and localize the wave functions sufficiently that a relaxation calculation is valid.

From our data we have deduced a temperature dependent relaxation time which is in good agreement with the relaxation time deduced from the transition from the static to dynamic Jahn-Teller effect observed in

spin resonance. At relatively high temperatures the relaxation time shows the usual thermal activation type of behavior, but at low temperatures effects of tunneling are seen. We conclude from the temperature dependence below 6°K that tunneling accompanied by one-phonon emission is the primary relaxation process.

ACKNOWLEDGMENTS

We are grateful to Dr. P. Gosar and Dr. J. A. Sussman for preprints and for helpful and stimulating correspondence, and to M. B. Graifman for help with the spin-resonance experiment.

Magnetic Relaxation in Nickel above the Curie Temperature*

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(Received 8 August 1966; revised manuscript received 9 November 1966)

Magnetic relaxation in nickel above the Curie temperature (354°C) has been studied up to a temperature of 450°C. The spin-relaxation rate $1/\tau_r$, which is equal to the magnetic resonance half-width $\Delta\omega = \gamma\Delta H$, is determined from the field dependence of the microwave Kerr rotation. We fit the relaxation to an expression: $1/\tau_r = 3(C/T)(H/M)\omega_d^2\tau_c$, where C is the Curie constant, T the absolute temperature, M/H the transverse static susceptibility, ω_d the pseudodipolar coupling frequency, and τ_c the spin correlation time. At high temperatures, τ_c is constant and is set equal to $1/\omega_e$, the reciprocal exchange frequency, by a suitable choice of ω_d . As the temperature is dropped below 420°C, τ_c begins to increase as $(T - T_c)^{-2/3}$. This increase in τ_c is compatible with critical-neutron-scattering studies of nickel and with measurements of the static susceptibility. Below 385°K, τ_c remains constant at a value 1.8 times the high-temperature value. It is believed that the development of spin-wave excitations in this temperature range prevents a further increase in the spin correlation time. A shift in the spectroscopic splitting factor from $g = 2.22$ below T_c to $g = 2.29$ above T_c is observed. Well above T_c , a small amount of Kerr rotation, which is associated with the Hall effect, is observed. The magnitude of this rotation is consistent with the results of dc studies.

I. INTRODUCTION

RECENTLY, the magnetic critical point has been the subject of considerable theoretical and experimental investigation. Approximate solutions for the Ising and Heisenberg models have given accurate expressions for the transition temperature¹ and the initial susceptibility in the critical region. For a face-centered cubic lattice and spin $\frac{1}{2}$ the initial susceptibility is found for both models to be of the form

$$\chi_0 \propto (T - T_c)^{-\gamma}. \quad (1)$$

The exponent γ is 5/4 for the Ising model² and 4/3

for the Heisenberg model³ for all three-dimensional lattices. The deviation from the Curie-Weiss value $\gamma = 1$ is the result of short-range correlations which are neglected in a molecular-field calculation but which have been examined in more recent work.

Kouvel and Fisher⁴ have re-examined the magnetization data of Weiss and Forrer⁵ for nickel and find that, near T_c ,

$$\gamma_{Ni} = 1.35 \pm 0.02. \quad (2)$$

Recent measurements by Arajs⁶ confirm this result. Similarly, the value of γ for iron^{6,7} has been found to be 1.33 ± 0.04 . These results indicate that correlation effects play an important role in these metals and that the Heisenberg model appears to give an adequate description of their behavior.

* Supported by the U. S. Atomic Energy Commission through Contract No. AT(11-1)-34, Project 47. Report Code No. UCB-34P47-3.

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