can be illustrated from the correlation functions calculated by Carboni and Richards.[2] These authors have performed numerical calculations in the case of linear exchange chains. Indeed, the spin motion is only due to the exchange Hamiltonian E. But for the present purpose, in the high-frequency range ($\omega > \omega_x$), their results may be regarded as being still valid because D^0 only affects the low-frequency range. Figure 2 shows the sum $\sum f(i, 0; \omega)$ restored from the frequency Fourier transform of the first four cross-correlation functions ($i = -4 \cdots +4$) (Fig. 4 of Ref. 2) and the self-correlation function $f(0, 0; \omega)$ (Fig. 5 of Ref. 2). Their contributions are equal and opposite. Therefore, the other cross-correlation functions must have a negligible influence.

In liquids, the motion Hamiltonian M of the atoms or molecules is defined by coordinates which are different from those of the spins. Thus, in the case of an individual spin, a commutation rule equivalent to (2) is still valid:

$$[s_i^\alpha, M] = 0 \ .$$

Therefore, the self-correlation spectrum $f(0, 0; \omega)$ is narrowed in the same way as $F(\omega)$, and in the case of an extreme narrowing the contribution of the cross correlation becomes quite negligible.

In conclusion, the macroscopically identical behavior of the paramagnetic resonance line, under the influence of either exchange or motion, masks two quite distinct phenomena. In solids with exchange interactions the line shape is due to the correlations of one spin with all the others. On the contrary, in liquids the line shape comes from the self-correlation of one spin: The motion completely "decorrelates" the spins amongst themselves.

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Paramagnetic Spin-Lattice Relaxation via the Anharmonic Raman Process*

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The anharmonic Raman process, which was shown by Van Kranendonk and Walker to be important in the case of nuclear quadrupolar relaxation, is shown here to be of sufficient magnitude to explain the Raman relaxation rates of the paramagnetic ions Cr^{3+} and Ni^{2+} in MgO. This new relaxation process involves the anharmonic three-phonon interaction.

The theory of the spin-lattice relaxation of paramagnetic ions in insulating crystals has recently been reviewed by Stevens[1] and by Abragam and Bleaney.[2] Many of the more important original papers on the subject are contained in the book edited by Manenkov and Orbach.[3] It is evident from these articles that a major assumption of previous theories which has not been seriously questioned up to the present is that the phonons can be treated in the harmonic approximation. Recently, however, Van Kranendonk and Walker[4] showed that a new relaxation process, which they called the anharmonic Raman process, and which depends for its existence on the anharmonic three-phonon coupling, is important in the theory of nuclear quadrupolar relaxation. More recently still, two papers[5,6] concerned with the derivation of the rate equations describing spin-lattice relaxation in anharmonic crystals have confirmed the existence of the anharmonic Raman process described by Van Kranendonk and Walker. There are as yet, however, no estimates of the magnitudes of the relaxation rates predicted by this process for paramagnetic ions. The purpose of this paper is to show that the anharmonic Raman process predicts relaxation rates having magnitudes comparable to those observed in the cases of MgO : Ni^{2+} and MgO : Cr^{3+}. The main conclusion is thus that the anharmonic Raman process deserves serious consideration as a possible relaxation mechanism for paramagnetic ions in crystals.

The Feynman diagram corresponding to the anharmonic Raman process is shown in Fig. 1(a), and a somewhat different pictorial view of the same process is shown in Fig. 2. An explicit mathematical description of the anharmonic Raman process will be given below.

In their analysis of nuclear quadrupolar relaxation, Van Kranendonk and Walker showed that the

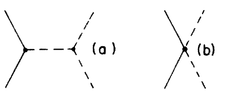

FIG. 1. Feynman diagrams describing (a) the anharmonic Raman process, and (b) the first-order Raman process. The solid lines represent spin states and the dashed lines represent phonons.

anharmonic Raman process gives relaxation rates having the same temperature and magnetic field dependence as the well-known first-order Raman process [Fig. 1(b)], but is faster by approximately two orders of magnitude. Whereas the relaxation rates calculated previously on the basis of the first-order Raman process were far too slow to explain the observed experimental results in the case of the alkali halides, the anharmonic Raman process was shown to give excellent agreement with experiment. More recent work on Cu_2O and on R_2MX_6 compounds by Armstrong and Jeffrey[7] has given further evidence of the importance of the anharmonic Raman process in nuclear quadrupolar relaxation.

The calculation of the magnitude of the anharmonic Raman process requires a knowledge of the magnitude of the first-order spin-phonon coupling and of the anharmonic three-phonon coupling. The three-phonon interaction can be obtained approximately if the Grüneisen constant is known. The Grüneisen constant for MgO has been measured experimentally,[8] as have the magnitudes of the spin-phonon coupling coefficients[9,10] of the ions Ni^{2+} and Cr^{3+} in MgO. The spin-lattice relaxation times of these ions in the Raman region are also known experimentally.[11,12] The fact that this experimental information is available is the reason we have chose the systems MgO : Cr^{3+} and MgO : Ni^{2+} for our comparison of theory and experiment.

We begin our detailed analysis by describing the Hamiltonian for the system, which is

$$H = H_s + H_{\text{ph}} + V_3 + V^{(1)}_{\text{s-ph}} + V^{(2)}_{\text{s-ph}} . \tag{1}$$

H_s is the spin Hamiltonian describing the energy levels of the paramagnetic ion in the presence of the static crystal field and external magnetic field; it has eigenstates $|m\rangle$ and energy levels ϵ_m. H_{ph} describes the phonons in the harmonic approximation and has eigenstates $|a\rangle$ and energy levels E_a. The three-phonon anharmonic interaction is written

$$V_3 = \frac{1}{3!} \sum_{pp'p''} V(pp'p'') A_p A_{p'} A_{p''} \tag{2}$$

and the first- and second-order spin-phonon interactions are written

$$V^{(1)}_{\text{s-ph}} = \sum_p \hat{f}_p A_p \tag{3}$$

and

$$V^{(2)}_{\text{s-ph}} = \sum_{pp'} \hat{f}_{pp'} A_p A_{p'} , \tag{4}$$

where $A_p = a_p^\dagger + a_{\bar{p}}^-$, $a_p^\dagger$ and a_p being the creation and annihilation operators for phonons in mode p; p stands for both the quasimomentum and the polarization of the phonon, and $\bar{p}$ indicates a phonon of opposite momentum to that of mode p. The quantities $\hat{f}_p$ and $\hat{f}_{pp'}$ are operators in spin space with matrix elements

$$\langle m | \hat{f}_p | m' \rangle \equiv f_{mm'}(p) \tag{5}$$

and

$$\langle m | \hat{f}_{pp'} | m' \rangle \equiv f_{mm'}(p, p') . \tag{6}$$

The important quantity to know for a study of spin-lattice relaxation is the probability per unit time that a spin makes a transition from state m to state m'. This is given by the formula

$$w_{mm'} = \frac{2\pi}{\hbar} \sum_{a,a'} P_a |\langle m'a' | T_{ma} | ma \rangle|^2 \times \delta(E_a + \epsilon_m - E_{a'} - \epsilon_{m'}) , \tag{7}$$

where P_a is the probability that a system of harmonic phonons in thermal equilibrium has energy E_a. (In writing this expression, the zero-order Hamiltonian is taken to be $H_s + H_{\text{ph}}$ and the perturbation causing the transitions is assumed to be $V_3 + V^{(1)}_{\text{s-ph}} + V^{(2)}_{\text{s-ph}}$; another possible separation into zero order and perturbing parts is discussed by Van Kranendonk and Walker and the method of separation is shown not to affect the final result.) The T matrix corresponding to the Feynman diagram of Fig. 1(a) for the anharmonic Raman process is the second-order perturbation-theory expression

$$T_{ma} = V^{(1)}_{\text{s-ph}} \frac{P}{E_a + \epsilon_m - H_{\text{ph}} - H_s} V_3 + V_3 \frac{P}{E_a + \epsilon_m - H_{\text{ph}} - H_s} V^{(1)}_{\text{s-ph}} , \tag{8}$$

where P indicates that a principal value should be taken. Hence the expression for the anharmonic Raman-process transition probability can be written in the form

$$w_{mm'} = \frac{2\pi}{\hbar} \sum_{pp'} n_p (n_{p'} + 1) |g_{m'm}(p', p)|^2 \times \delta(\epsilon_m + \epsilon_p - \epsilon_{m'} - \epsilon_{p'}) , \tag{9}$$

where the effective matrix element for phonon scat-

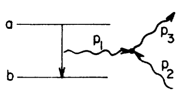

FIG. 2. Pictorial view of the anharmonic Raman process. The spin makes a transition from state a to state b emitting the virtual phonon p_1; this virtual phonon then collides with the incoming phonon p_2 with which it combines to form the emitted phonon p_3.

tering is given by

$$g_{m'm}(p',p)=2P\sum_{p''}\frac{\epsilon_{p''}}{\epsilon_{p''}^2-(\epsilon_m-\epsilon_{m'})^2}\times V(pp'p'')f_{m'm}(\bar{p}'') \,. \quad (10)$$

Thus it can be seen that the expression for the transition probability for the anharmonic Raman process can be obtained from that for the well-known first-order Raman process [see Fig. 1(b)] by replacing the matrix element $f_{m'm}(p',p)$ by $g_{m'm}(p',p)$. If these two quantities are of comparable magnitude, their sum $f_{m'm}(p',p)+g_{m'm}(p',p)$ should be substituted into the expression for the transition probability.

While there are no direct measurements of the magnitude of $f_{mm'}(p,p')$, it is possible to obtain an estimate of the magnitude of $g_{mm'}(p,p')$ from experimental data. What we shall do, therefore, is to compute the spin-lattice relaxation time by substituting the experimentally determined $g_{mm'}(p,p')$ into (9); this calculated value of the spin-lattice relaxation time agrees roughly with the experimentally measured value, showing that the anharmonic Raman process should be seriously considered as an effective relaxation mechanism.

Another possible approach, which would give the magnitudes of both the first-order and anharmonic Raman processes, is to calculate the spin-phonon coupling constants using a point-charge model similar to that used by Van Kranendonk and Walker[4] in their study of nuclear quadrupolar relaxation. It is not clear to us, however, how accurately a point-charge model would describe the spin-phonon coupling in the case of paramagnetic ions, and we therefore prefer to base our discussion on experimentally determined quantities. It should be mentioned here that Ray *et al.*[13] have estimated the magnitude of the first-order Raman process for the Cr^{3+} and Ni^{2+} ions in MgO using a point-charge model to compute the spin-phonon coupling coefficients, and have achieved good agreement with experiment.

The conventional way of writing $V_{\text{s-ph}}^{(1)}$ for the iron-group ions which we will be discussing is

$$V_{\text{s-ph}}^{(1)}=\sum_{i,j}\hat{\gamma}_i G_{ij} e_j\,, \quad (11)$$

where Voigt notation is used (i.e., $i,j=1,2,\ldots,6$), e_j is the strain tensor, and the $\hat{\gamma}_i$'s are spin operators defined by

$$\hat{\gamma}_{\alpha\beta}=S_\alpha S_\beta+S_\beta S_\alpha,\ \alpha\neq\beta;\quad \hat{\gamma}_{\alpha\alpha}=S_\alpha^2\,. \quad (12)$$

In Eq. (12), $\alpha,\beta=x,y,z$. The G_{ij}'s are called the spin-phonon coupling coefficients. A detailed discussion of Eq. (11) and of the method of measuring the spin-phonon coupling coefficients has been given in the review of Tucker.[14]

A comparison of Eqs. (3) and (11) allows us to express the quantity $\hat{f}_p$ in terms of the spin-phonon coupling coefficients G_{ij}; the result is

$$\hat{f}_p=\sum_{i,j}\hat{\gamma}_i G_{ij}\xi_{pj}\,, \quad (13)$$

where

$$\xi_{p;\alpha\beta}=i(\hbar/2NM\omega_p)^{1/2}(k_\alpha e_{p\beta}+k_\beta e_{p\alpha})(1-\tfrac{1}{2}\delta_{\alpha\beta}) \quad (14)$$

and $\vec{e}_p$ is the polarization vector associated with phonons in mode p. For the case of cubic symmetry, which is the case in MgO : Ni^{2+} and MgO : Cr^{3+}, there are only two independent spin-phonon coupling coefficients and these can be taken to be G_{11} and G_{44}.

The approximate expression (see Van Kranendonk and Walker[4])

$$V(pp'p'')=2\sqrt{3}\,\gamma_G M v^2 \xi_p \xi_{p'} \xi_{p''} N\Delta(k_1+k_2+k_3) \quad (15)$$

will be used for $V(pp'p'')$. [Note carefully our definition (2) of $V(pp'p'')$.] Here γ_G is the Grüneisen constant and $\xi_p=(\hbar\omega_p/2NMv^2)^{1/2}$.

The results (13) and (15) allow the transition probabilities to be evaluated in terms of the known parameters G_{11}, G_{44}, and γ_G. The relaxation rate can then be evaluated in terms of the transition probabilities using one of two methods. If the impurity concentration is sufficiently high that the spin-spin relaxation time is much shorter than the spin-lattice relaxation time, and if the energy levels of the ion in a magnetic field are roughly equidistant, the logical way of proceeding is to assume the existence of a spin temperature; as is well known, the spin-lattice relaxation time T_1 is given in this case by the Hebel-Slichter formula[15]

$$\frac{1}{T_1}=\frac{1}{2}\left[\sum_{mm'} w_{mm'}(\epsilon_m-\epsilon_{m'})^2\Big/\sum_m \epsilon_m^2\right], \quad (16)$$

where the spin levels are assumed to satisfy $\sum_m \epsilon_m = 0$. The other method of proceeding applies in the case where the concentration of impurities is sufficiently dilute that spin-spin interaction can be neglected; one should then use the rate equations to analyze the time evolution of the populations of the spin energy levels; for the case of more than two energy levels per ion, more than one relaxation

TABLE I. Values of the spin-phonon coupling coefficients G_{11} and G_{44} for Ni^{2+} and Cr^{3+} in MgO as measured by ultrasonic (Ref. 10) and uniaxial stress (Ref. 9) methods.

Method	Ion	G_{11} (cm^{-1})	G_{44} (cm^{-1})
Uniaxial stress	Ni^{2+}	57	36
	Cr^{3+}	0.6	4.2
Ultrasonic	Ni^{2+}	57	50
	Cr^{3+}	<1.3	6.5

TABLE II. Theoretically computed values A occurring in the relation $T_1^{-1}=AT^7$ are compared with the experimentally measured values. The results in the Theory 1 and Theory 2 columns are obtained using the uniaxial stress and the ultrasonic values of the G_{ij}'s, respectively. The numbers are A in units of $\sec^{-1}\,{}^\circ\mathrm{K}^{-7}$.

	Theory 1	Theory 2	Experiment
A for Ni^{2+}	5.6×10^{-7}	8.3×10^{-7}	8×10^{-7} (Ref. 11)
A for Cr^{3+}	94×10^{-10}	220×10^{-10}	8×10^{-10}(Ref. 12)

time results. In spite of the profound differences in principle involved in the above two methods, the relaxation rates obtained in the two cases do not, in general, differ greatly in magnitude. We shall use the former method as it gives a single relaxation time and is thus simpler to compare with the experimental results, which are expressed in terms of a single measured relaxation time.

Finally, making use of the results (9), (10), and (13)-(16), evaluating the sums over phonon momenta using the Debye approximation, and assuming that kT is much less than the Debye energy, one finds for the anharmonic Raman process

$$1/T_1=AT^7\,, \tag{17}$$

where

$$A=1.34\times10^6(2S+3)(2S-1)\frac{(G_{44}{}^2+\frac{3}{8}G_{11}{}^2)\,k}{(Mv^2)^2\quad\hbar\Theta_D^6}\,\gamma_G^2 \tag{18}$$

and Θ_D is the Debye temperature. In evaluating (18), the following data were used: $\Theta_D=948\,{}^\circ\mathrm{K}$; $M=\rho a^3$, where $\rho=3.6\ \mathrm{g\ cm^{-3}}$ and $a=2.1\times10^{-8}$ cm ; also $v=(6\pi^2)^{-1/3}\hbar^{-1}k\Theta_D a$. The values of G_{11} and G_{44} as measured by both the ultrasonic attenuation method[10] and the uniaxial stress method[9] are shown in Table I. Finally, in Table II, the theoretically calculated value of A is compared with the experimentally determined value.

It can be seen from Table II that in the case of Ni^{2+} in MgO, the theoretically calculated anharmonic Raman relaxation rate is in excellent agreement with experiment. The predicted relaxation rate for Cr^{3+} in MgO, on the other hand, is too fast by an order of magnitude. In attempting to assess the significance of these results it is necessary to note the following: (i) Equation (11) is a good approximation at long wavelengths, but gives only a rough estimate of the coupling of the spin to short-wavelength phonons; unfortunately, the interaction between the spin and short-wavelength phonons enters the calculation in an important way [see Eq. (10)]. (ii) Equation (15) is also a long-wavelength approximation, and even at long wavelengths it is not exact (see Van Kranendonk and Walker[4]). (iii) The use of the Debye approximation with an average velocity of sound will also introduce some error. (iv) The interpretation of the experimental results for Cr^{3+} is difficult because the relaxation rate varies as T^7 over only a very narrow range of temperature; above 50 °K there is an anomalously large increase in the rate as the temperature is increased; one possible explanation of this is that the fact that Cr^{3+} is a lattice defect may affect the phonon modes.[12] Thus, there are several sources of numerical uncertainty in our calculation. We feel, however, that our calculation demonstrates that the anharmonic Raman process has at least the right order of magnitude to explain experimentally observed relaxation rates, and should be considered together with the first-order Raman process when attempting to account for observed relaxation rates varying as T^7.

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