

Theoretical Investigations on the Anisotropy of the Spin-Lattice Relaxation in Paramagnetic Crystals

D. K. Ray, T. Ray, and S. K. Gupta

Citation: [Journal of Applied Physics](#) **39**, 832 (1968); doi: 10.1063/1.2163634

View online: <http://dx.doi.org/10.1063/1.2163634>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/39/2?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Paramagnetic to antiferromagnetic transition in AMnCl₃ \(A=Rb and Cs\) single crystals as observed by 87 Rb and 133 Cs spin-lattice relaxation](#)

J. Appl. Phys. **91**, 3095 (2002); 10.1063/1.1445275

[Temperature dependence of spin-spin and spin-lattice relaxation times of paramagnetic nitrogen defects in diamond](#)

J. Chem. Phys. **109**, 8471 (1998); 10.1063/1.477511

[Theory of spin-lattice relaxation for paramagnetic ions](#)

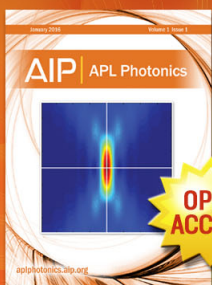
AIP Conf. Proc. **24**, 524 (1975); 10.1063/1.29993

[Proton Spin-Lattice Relaxation in Paramagnetic Crystals in High Fields and Low Temperatures](#)

J. Appl. Phys. **39**, 499 (1968); 10.1063/1.2163502

[Effect of Paramagnetic Impurities on Proton Spin—Lattice Relaxation Time in Methane](#)

J. Chem. Phys. **44**, 2320 (1966); 10.1063/1.1727042



Launching in 2016!
The future of applied photonics research is here

AIP | APL
Photonics

Theoretical Investigations on the Anisotropy of the Spin-Lattice Relaxation in Paramagnetic Crystals

D. K. RAY, T. RAY, AND S. K. GUPTA

Saha Institute of Nuclear Physics, Calcutta, India

Theoretical expressions for the spin-lattice relaxation have been used to study the anisotropies of these parameters in crystals of cubic symmetry. In the case of ions with $S = \frac{1}{2}$, the anisotropy is only present at very low temperature where the single-phonon term is dominant and is shown to be independent of the phonon distribution and determined by the nature of the paramagnetic ion and ligand charge distribution. For the case of ions with $S > \frac{1}{2}$, where also the anisotropy is independent of phonon distribution at low temperature, parameters of the dynamical spin Hamiltonian obtained from static strain measurements for a number of ions in MgO have been used to predict the anisotropies expected. Ions are shown to be more anisotropic if contributions from either Γ_{3g} or Γ_{5g} mode dominate. Anisotropies at high temperature where the two-phonon process is important have been shown to be dependent on the phonon distribution as well, and have been estimated for a number of ions in MgO. The effects of dipolar flip-flop process, the covalency in the charge distribution of magnetic ion and ligands and the modified phonon distribution due to spin-phonon interaction on the anisotropy factors have been discussed. The importance of these studies has been stressed.

In this paper, we present the results of our theoretical investigations on the anisotropy of the spin-lattice relaxation time for Co^{2+} , Ni^{2+} , and Cr^{3+} in MgO crystal with respect to the Zeeman-field orientation about the crystal axes. The anisotropy factor in dilute paramagnetic systems depends on: (i) the phonon distribution in the crystal, (ii) the angular averages of the coefficients, $a(\Gamma_{ag}^i, kp)$, connecting the symmetry modes of the complex, $Q(\Gamma_{ag}^i)$, formed by the nearest ligands around the paramagnetic site and the phonons for any \mathbf{k} vector, and (iii) the overlap and the covalency of the charge distribution of the metal and the ligand ions. In the present calculations, we have assumed the Debye distribution of the phonons without making the long wavelength approximation,¹ and the effective ionic model that has been used takes partial account of the overlap and covalency effects.

The method of calculation followed is to first write down the effective spin-phonon interaction Hamiltonian in a symmetric form. This \mathcal{H}_{dyn} is then used to derive expressions for the transition probabilities between any two spin levels. For $S = \frac{1}{2}$ systems, the transition probability gives us directly the anisotropy factor for the relaxation time. For $S > \frac{1}{2}$ cases, this is obtained from the appropriate linear combinations of the transition probabilities for $\Delta M_s = \pm 1$ and ± 2 .

The objectives of this study are primarily: First, the measurement of the anisotropy of the relaxation time at any particular temperature may throw some light on the phonon processes operative at that temperature. Second, we know that from the solutions of rate equations one obtains $2S$ -number of independent relaxation times for any system with spin $S > \frac{1}{2}$. The fact that anisotropy factor is different for each of these relaxation times can possibly be utilized in ascertaining which of the relaxation times is being observed.

Co^{2+}

(i) Single-phonon process: In the case of Kramer's doublets the single phonon is effective only in the presence of the Zeeman field and in the XV_6 -complex. The \mathcal{H}_{dyn} can be written as²

$$\begin{aligned} \mathcal{H}_{\text{dyn}} = & C_{11}\beta(S_1H_1)_0(\Gamma_{1g})Q(\Gamma_{1g}) \\ & + C_{33}\beta\sum_i(S_1H_1)_2(\Gamma_{3g}^i)Q(\Gamma_{3g}^i) \\ & + C_{55}\beta\sum_i(S_1H_1)_2(\Gamma_{5g}^i)Q(\Gamma_{5g}^i), \end{aligned} \quad (1)$$

where β is the Bohr magneton. Using the long wavelength approximation, we finally obtain for the relaxation time, assuming $g\beta H \ll kT$,

$$\begin{aligned} 1/T_1 T = & 1.7[1 - f(\theta, \phi)]; \\ f(\theta, \phi) = & l^4 + m^4 + n^4, \end{aligned} \quad (2)$$

where l, m, n are the direction cosines of the Zeeman field with respect to the crystal axes. At any temperature, therefore, T_1 attains a minimum value of $0.87/T$ sec when the Zeeman field is along one of the body diagonals. The maximum value of T_1 will be determined by the C_{55}^2 -proportional term and this is found to be $\sim 14.5/T$ sec.

(ii) Two-phonon process: The effective dynamical Hamiltonian in this case is³

$$\begin{aligned} \mathcal{H}_{\text{dyn}} = & C_{435}\sum_{ijl}\langle\Gamma_4^i|\Gamma_3^j,\Gamma_5^l\rangle S_1(\Gamma_4^i)[P(\Gamma_3^j)Q(\Gamma_5^l) \\ & - Q(\Gamma_3^j)P(\Gamma_5^l)] + C_{455}\sum_{ijl}\langle\Gamma_4^i|\Gamma_5^j,\Gamma_5^l\rangle \\ & \times S_1(\Gamma_4^i)[P(\Gamma_5^j)Q(\Gamma_5^l) - Q(\Gamma_5^j)P(\Gamma_5^l)]. \end{aligned} \quad (3)$$

¹ J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

² S. Kumar and D. K. Ray (to be published in Phys. Rev.).

³ T. Ray and D. K. Ray (to be published in Phys. Rev.).

The constants are evaluated by a third-order perturbation calculation on the Co^{2+} spin-orbit states by \mathcal{H}_{0-L} and $\mathcal{H}_{\text{lattice}}$. Operating \mathcal{H}_{dyn} on the spin states we obtain

$$W_{|1/2\rangle \rightarrow |1/2\rangle} = (2R^4/p^2\pi^3) \int_0^{\omega_{\max}} \frac{\exp(\hbar\omega_{kp}/kT)}{[\exp(\hbar\omega_{kp}/kT) - 1]^2} \times [C_{455}^2 G(3, 5, \omega_{kp}v_p) + C_{455}^2 G(5, 5, \omega_{kp}v_p)] \times (\omega_{kp}^8/v_p^{10}) d\omega_{kp}, \quad (4)$$

where the G functions are defined as

$$G(\alpha, \beta, \omega_{kp}v_p) = \langle [a(\Gamma_\alpha, kp)/kR]^2 \rangle_{\alpha} \times \langle [a(\Gamma_\beta, kp)/kR]^2 \rangle_{\beta}. \quad (5)$$

These are computed as a function of ω and the results are considerably off from that expected from the long wavelength approximation. The two-phonon relaxation time for Co^{2+} is isotropic, but absolute magnitude calculations show that from about 20°K the predicted T^7 law is violated. So one should be able to demarcate the temperature region where the two-phonon process takes over from the study of the anisotropy of the relaxation time vs temperature alone.

Ni^{2+} AND Cr^{3+}

(i) Single-phonon process: For $2 > S > \frac{1}{2}$, we have

$$\mathcal{H}_{\text{dyn}} = C_{33} \sum_i (S)_2(\Gamma_{3g}^i) Q(\Gamma_{3g}^i) + C_{55} \sum_i (S)_2(\Gamma_{5g}^i) Q(\Gamma_{5g}^i). \quad (6)$$

The constants are estimated using the experimental data for the uniaxial stress measurements⁴ in MgO crystal doped with Ni^{2+} and Cr^{3+} ions. For Ni^{2+} ($S=1$), the two relaxation times are found to be

$$1/T_1 T = (34.2 + 2.2f); \quad (7.6 - 2.2f) \text{ sec}^{-1} \text{ } ^\circ\text{K}^{-1}, \quad (7)$$

where f stands for $f(\theta, \varphi)$ defined earlier. Hence for Ni^{2+} there is no appreciable anisotropy in the relaxation time due to single phonon process. For Cr^{3+} ($S=\frac{3}{2}$), the three relaxation times predicted from the solutions of the rate equations are

$$1/T_1 T = (0.003 + 0.29f); \quad (0.88 - 0.29f); \quad 0.883 \text{ sec}^{-1} \text{ } ^\circ\text{K}^{-1}. \quad (8)$$

This shows that one of the relaxation times has con-

siderable anisotropy with a possibility of change in the magnitude by a factor of three.

(ii) Two-phonon process: The \mathcal{H}_{dyn} in this case is

$$\mathcal{H}_{\text{dyn}} = \sum_{\alpha\beta\gamma} C_{\alpha\beta\gamma} \sum_{ijl} \langle \Gamma_\alpha^i | \Gamma_\beta^j, \Gamma_\gamma^l \rangle \times S_2(\Gamma_\alpha^i) Q(\Gamma_\beta^j) Q(\Gamma_\gamma^l). \quad (9)$$

The nonvanishing terms are got only for C_{313} , C_{333} , C_{355} , C_{515} , C_{535} , and C_{555} . In evaluating these constants, one has to do a fourth-order-perturbation calculation on the ground orbital singlet Γ_{2g} state by \mathcal{H}_{0-L} and $\mathcal{H}_{S=0}$ each operating twice. Using Eq. (9) we calculate the transition probabilities for $\Delta M_s = \pm 1$ and ± 2 which we denote by W_1 and W_2 and hence the relaxation times. For Ni^{2+} , we get the following anisotropies: $T_1 = (W_1 + 2W_2)^{-1}$ is isotropic and has the values 150 and 80 μsec , at 40° and 100°K, respectively. But $T_1 = (3W_1)^{-1}$ has maximum values of 341 and 192 μsec , and minimum values of 176 and 92 μsec at these temperatures. For Cr^{3+} , we find: $T_1 = (2W_1)^{-1}$ has maximum values of 102 and 2.0 msec, and minimum values of 50 and 0.7 msec, at 100° and 300°K, respectively. For $T_1 = (2W_2)^{-1}$, the corresponding values are 81, 1.1 and 67, 0.9 msec, and for $T_1 = (2W_1 + 2W_2)^{-1}$, the corresponding values are 45, 0.7 and 29, 0.4 msec.

Thus, for Ni^{2+} , both the relaxation times are more or less isotropic for the single-phonon process, but one of these would show considerable anisotropy above 40°K where the two-phonon process is dominant. For Cr^{3+} at low temperature, only one of the relaxation times shows considerable anisotropy, whereas at high temperature (above 100°K) all the relaxation times indicate anisotropy by a factor of two. The deviations from the predicted T^7 law are considerable for both Ni^{2+} and Cr^{3+} . For the latter, the calculated value is less by two orders of magnitude at 300°K.

In conclusion, we note that for the single-phonon process, where the long-wave approximation is valid, the anisotropy does not depend on the phonon distribution and the angular averages of a coefficients. For Co^{2+} , the contribution from Γ_{3g} mode is dominant at low temperature and shows considerable anisotropy, whereas for Ni^{2+} and Cr^{3+} , contributions from both the Γ_{3g} and Γ_{5g} modes are of the same order of magnitudes and show less anisotropy. For the two-phonon process, where contribution from high-frequency phonons is important, relative contributions from various modes depend on the phonon distribution as well as on the angular averages of a coefficients. Our results in this case show considerable deviation in the T_1 vs T relationship from the predicted T^7 and T^9 laws, but the anisotropy of T_1 does not change perceptibly with temperature. However, for real phonons, the anisotropy factor might show some dependence on temperature. For semidilute crystals, the dipolar interaction will play an important role on the anisotropy. The flip-flop

⁴N. S. Shiren, *Proceedings of XIth Colloque Ampere, Eindhoven, 1962* (North-Holland Publishing Company, Amsterdam, 1963), p. 114.

process gives a single relaxation time for any ion with $S > \frac{1}{2}$. For the two-phonon process, this relaxation time is totally isotropic but not for the single-phonon process. The covalency and overlap will also affect the magnitude rather than the anisotropy of the relaxation time, particularly for those ions, where σ and π contributions

are nearly of the same order. The presence of the paramagnetic ion affects the phonon distribution in two ways: changing the local force constants and modifying the phonon distribution through δC_{0-L} . We intend to incorporate all these effects in details in a future publication.

On Spin-Spin Relaxation Effects

C. J. GORTER AND J. C. VERSTELLE

Kamerlingh Onnes Laboratory, Leiden, Netherlands

Results of different series of observations recently carried out in Leiden on spin-spin relaxation effects in paramagnetic salts of the iron group are reported and discussed. The character of the frequency-zero band and the resonance bands in parallel fields have been studied in different Tutton salts, and is found to be in agreement with the present theory. The behavior of the Kronig-Bouwkamp band in high parallel fields is the same salts is also reasonably well understood; this is not so for $\text{Cu}(\text{NH}_4)_2\text{Br}_4 \cdot 2\text{H}_2\text{O}$. The complicated behavior in salts where there is a known tendency to chain formation is also not yet clear.

De Vrijer's low-field third relaxation has been studied in different salts and is confirmed to be a cross-relaxation phenomenon.

I. INTRODUCTION

Waller¹ predicted in 1932 that interactions between the magnetic moments of neighboring ions in a paramagnetic substance would in some circumstances determine the rapidity of the response of the magnetization upon variations of an external magnetic field. This response is called spin-spin relaxation in contrast with spin-lattice relaxation due to the interaction between the magnetic moments and heat waves in the substance.² Low temperatures and oscillating fields of quite high frequency are usually required to eliminate the mentioned spin-lattice relaxation. In paramagnetic substances which very well obey Curie's law $\chi_0 = C/T$, the ratio between the complex susceptibility $\chi' - i\chi''$ and the static susceptibility χ_0 is independent of the temperature T and of the amplitude of the oscillating magnetic field.³

Most of the data collected in the Kamerlingh Onnes Laboratory concern the magnetic absorption χ'' at frequencies between 10^3 and 5×10^9 Hz.

II. RELAXATION AND RESONANCE

The simplest results are those on a system of equal magnetic ions with one basic Kramers doublet ($S = \frac{1}{2}$). The spin-spin relaxation then essentially depends on the magnetic dipole and exchange interactions between neighboring ions and, of course, on the magnitude and

direction of the constant external field H_c . If the exchange interaction is negligible in comparison with the dipole-dipole interaction, χ''/ν has at $H_c = 0$ a Gaussian shape with the center at $\nu = 0$. If, however, exchange interaction is preponderant, the zero-field band is narrowed down to a *Debye* shape.⁴ This has some analogy to paramagnetic resonance (ESR) in a relatively larger perpendicular constant field. As was predicted by Caspers,⁵ among others, and confirmed by Locher,⁴ Verbeek, and Van Noort for the Tutton salts $\text{CuCs}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ which have a very weak and a relatively strong exchange interaction, respectively, the situation is rather different if the constant field is parallel to the high-frequency field. One then finds weak absorption lines of approximately equal intensities $\int (\chi''/\nu) d\nu$ at the Larmor frequency and twice the Larmor frequency, in the absence of exchange, and still weaker and broadened lines at the same two frequencies in the case of strong exchange interaction (Fig. 1).

Kronig-Bouwkamp Band

Kronig and Bouwkamp⁶ predicted in 1938 that in a relatively large parallel field, the low-frequency band would narrow down exponentially, the width of χ''/ν and thus also the frequency of the χ'' maximum decreasing proportionally to $\exp(-\alpha H_c^2/H_i^2)$ where the

¹ I. Waller, Z. Phys. **79**, 370 (1932).

² C. J. Gorter, *Paramagnetic Relaxation*, (Elsevier Publishing Co., Amsterdam, 1947).

³ C. J. Gorter, Physica **3**, 503 (1936); Leiden Comm. 241e.

⁴ P. R. Locher and C. J. Gorter, Physica **27**, 997 (1961); Leiden Comm. 329a.

⁵ W. J. Caspers, Physica **26**, 798 (1960); Leiden Comm. Suppl. 118b; J. H. Van Vleck, Nuovo Cimento, Suppl. VI, 993 (1957).

⁶ R. de L. Kronig and C. J. Bouwkamp, Physica **5**, 521 (1938).