Solid State Communications Vol. 3, pp. 71-73, 1965. Pergamon Press Ltd. Printed in Great Britain.

PARAMAGNETIC RELAXATION IN SMALL CRYSTALS

A. M. Stoneham

Theoretical Physics Division, Atomic Energy Research Establishment, Harwell, Didcot
Berkshire, England

(Received 28 February 1965 by W. M. Lomer)

Continuum models of phonon spectra of small crystals fail for wavelengths of the order of the crystal dimensions. Spin lattice relaxation rates, calculated here, may differ considerably from infinite crystal values, and are strongly field dependent. Advantages of using small crystals for the system MgO:Co^{2+} are discussed.

THE phonons involved in the direct process of spin lattice relaxation typically have frequencies of the order of 10^{10} cps. The separation of phonon frequencies in small crystals may be of this order. For example, when magnesium is burnt in oxygen small cubes of MgO of side, a, less than $1/7\mu$ are formed;[1] treating these as elastic cubes with a free surface boundary condition the lowest frequency is $2.36 \cdot 10^{10}$ cps, corresponding to a wavelength 2a. In this note the direct process relaxation time of Co^{2+} in small crystals of this type is calculated as a function of frequency, magnetic field and the parameters of the cubes. An important conclusion is that the relaxation time should be very long if the Larmor frequency is much less than the lowest crystal vibration frequency. Honig[2] may have observed this for a finely ground powder of phosphorous doped silicon.

The spin phonon interaction has a line shape $\gamma_s(\omega - \omega_s)$ where

$$\omega_s = g\beta H/\hbar \tag{1}$$

γ_s may be inhomogeneous from strain broadening which is larger near the surface; this will be neglected. In any one crystal the phonons in the lowest modes will have a frequency distribution $\gamma_p(\omega - \omega_p)$, where ω_p is related to the crystal mass M_c, density ρ and velocity of sound for transverse waves v_t by

$$\omega_p = v_t \pi \left(\frac{\rho}{M_c}\right)^{1/3} \tag{2}$$

There is a distribution of cube dimensions, so the ω_p have a distribution $\gamma_c(\omega - \omega_c)$. The transition probability for spins of mean Larmor frequency ω_s is proportional to

$$I = \int\int\int dx\,dy\,d\omega_p\,\gamma_c(\omega_p - \omega_c)\,\gamma_s(x - \omega_s)\,\delta(x - y)\,\gamma_p(y - \omega_p)$$

Assuming that the γ_i are all Lorentian with widths Δ_i

$$I = \frac{2}{\pi\Delta}\left\{1 + \left(\frac{\omega_s - \omega_c}{\Delta/2}\right)^2\right\}^{-1}$$

where

$$\Delta = \Delta_s + \Delta_p + \Delta_c$$

Co^{2+} has an effective spin $\frac{1}{2}$, so for a given crystal γ_s and the electron spin resonance line shape are identical.[3] The E.S.R. line shape for the assembly of crystals will be

$$I'(\omega) = \frac{2}{\pi\Delta_s}\left\{1 + \left(\frac{\omega - \omega_c}{\Delta_s/2}\right)^2\right\}^{-1} = \gamma_s(\omega).$$

The spin phonon interaction is linear in the normal coordinates Q_α of the environment of the magnetic ions, where

$$\frac{Q_\alpha}{R} = \sum_{\underset{\sim}{f}\,s} \sqrt{\frac{\hbar\omega_{\underset{\sim}{f}\,s}}{2M_c v_s^{\,2}}}\;\psi_\alpha(\underset{\sim}{f}, s)\,[a_{\underset{\sim}{f}s} + a^{+}_{\underset{\sim}{f}\,s}]\sin\varphi_{\underset{\sim}{f}\,s}$$

in the notation of reference 4. For an infinite homogeneous sample the average over the phases φ is made because not every vibration has an antinode at the magnetic ion in question. Here the phases are fixed by the position of the spin with respect to the crystal and by the boundary conditions at the surface. The average over phases proceeds as before, but it gives an average of the different relaxation times of ions distributed over the crystal. The result is the same because of the geometry of the lattice vibrations responsible for relaxation. The spins with a given phase for a mode with wave vector parallel to one cube axis lie in the plane containing the other two cube axes, and if the spins are randomly distributed through the cube the number of spins with a given phase is independent of the phase. We assume the transverse modes of lowest frequency are solely responsible for relaxation, and label them (i, j) when the wave and polarization vectors are parallel to the i, j cube axes respectively. The non-zero $\psi_\alpha(i, j)$ are

$$\psi_4(z,y) = \psi_4(y,z) = \psi_5(x,z) = \psi_5(z,x) = \psi_6(x,y) = \psi_6(y,x) = 1$$

There are no contributions from $\alpha = 2, 3$; the relaxation rate does not depend on the normal coordinates of E symmetry. In most respects the theory of Foglio and Pryce[5] may be used. Any experiment is likely to use a large number of randomly oriented cubes, so an average over magnetic field direction is necessary. The reciprocal of the relaxation time, simplified using (1) and (2) is:

$$\frac{1}{\tau} = kT \frac{3}{\pi^3} \left(\frac{g-2}{g}\right)^2 \left(\frac{G_{T_2}}{\delta}\right)^2 \frac{\omega_c^4}{\rho v_t^5} \frac{\omega_s^2}{\omega_c \Delta} \left\{1 + \left(\frac{\omega_s - \omega_c}{\Delta/2}\right)^2\right\}^{-1} \tag{3}$$

where G_{T_2} is a coupling coefficient and δ the energy of the first excited state. The corresponding result for an infinite crystal with the magnetic field parallel to a cubic axis is

$$\frac{1}{\tau_0} = kT \frac{1}{3\pi} \left(\frac{g-2}{g}\right)^2 \left(\frac{G_{T_2}}{\delta}\right)^2 \frac{\omega_s^4}{\rho v_t^5} \left\{\frac{3}{5} + \frac{2}{5}\left(\frac{v_t}{v_\ell}\right)^5\right\}.$$

When $\omega_s = \omega_c$, i.e. when $1/\tau$ is a maximum,

$$(1/\tau) = (1/\tau_0) \frac{9}{\pi^2} \frac{\omega_c}{\Delta} \left\{\frac{3}{5} + \frac{2}{5}\left(\frac{v_t}{v_\ell}\right)^5\right\}^{-1} = 1.34 \frac{\omega_c}{\Delta} (1/\tau_0).$$

This result resembles the reduction in lifetime for a similar transition for a spin placed in a resonant cavity.[6] As ω_s is altered τ/τ_0 varies from approximately Δ/ω_c to ω_c/Δ. Δ may be found directly from (3) and $1/\tau$ as a function of the magnetic field. Alterations necessary when Δ is of the order of the Co^{2+} hyperfine splitting are straightforward but tedious.

The main features of an experiment of this type are:

(a) Relaxation times are very sensitive to magnetic impurities. This influence will be reduced by the fast direct process relaxation when $\omega_s = \omega_c$. Further, crystals produced by burning Mg may be purer than those grown from a melt of MgO.

(b) If $(\omega_s - \omega_c)/\Delta$ is large the direct process will be very slow, and two phonon processes should dominate the relaxation. In large crystals the two phonon processes become important only at higher temperatures. The Orbach process is never much faster than the Raman process[7] and, apart from the technical difficulty of measurement, interference between the two processes will be important when their relaxation rates are nearly equal.

Extrapolating experimentally estimated relaxation times to 1.4°:[7]

Raman Process: about 1 month

Orbach Process: 190 seconds,

so it should be possible to measure the Orbach relaxation rate reliably in small crystals at liquid helium temperatures. These estimates do not include the field dependent contribution to the Raman rate; rough calculations indicate that it is unimportant.

(c) Δ_p is a measure of the interactions of the phonons involved in relaxation with the crystal environment, the spins and with other phonons. As, in principle, $I(\omega)$, $I'(\omega)$ and γ_c yield $\gamma_p(\omega)$, some light may be shed on these interactions.

(d) Spin lattice relaxation sometimes confuses cross relaxation experiments, and may be reduced to an acceptable level by making $(\omega_s - \omega_c)/\Delta$ large and ω_s small.

Acknowledgements - The author is greatly indebted to Dr. J. C. Gill for stimulating discussions. The work on which this note is based was performed at the University of Bristol whilst the author was in receipt of a D.S.I.R.

Research Studentship.

References

1. BASSETT G. A., private communication.
2. HONIG A., Proceedings of the Jerusalem Conference on Paramagnetic Relaxation (Edited by LOW W.) p. 439 (1963).
3. STONEHAM A. M., Phys. Letters to be published.
4. STONEHAM A. M., Proc. Phys. Soc. **85**, 107 (1965).
5. FOGLIO M. E. and PRYCE M. H. L., Proc. Phys. Soc. to be published.
6. ABRAGAM A., The Principles of Nuclear Magnetism p. 264. Oxford University Press (1961).
7. WHITTLESTONE P. R. M., Ph. D. Thesis, University of Bristol (1964).

Les modèles continus de spectres de phonon des petits cristaux ne sont pas valables pour longeurs d'ondes de l'ordre des dimensions des cristaux. En général les temps de relaxation spin-réseau, ici calculés, ne sont pas d'accord avec les valeurs pour les cristaux infinis, et ils dépendent fortement du champ magnetique. Les avantages d'employer des petits cristaux pour le système MgO:Co^{2+} sont décris.