Nuclear Magnetic Relaxation in Ionic Crystals

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We present results of a calculation of the nuclear magnetic relaxation time in ionic crystals. Two mechanisms of relaxation are considered: relaxation due to quadrupole effects, and relaxation produced by paramagnetic impurities. The results obtained are in qualitative agreement with the experimental data.

1. Experimental and theoretical investigation of nuclear magnetic resonance and relaxation phenomena are of considerable interest. A theoretical treatment of nuclear magnetic relaxation in ionic crystals was first given by Waller[1], who calculated the relaxation time resulting from modulation of the spin-spin interaction of the nuclear magnetic moments by the thermal vibrations of the lattice. However, this mechanism gives nuclear magnetic relaxation times far exceeding the experimental values. Another possible mechanism of nuclear magnetic relaxation in ionic crystals was considered in a paper of the author[2], but this mechanism also gives large values for the relaxation time.

The present paper gives results of calculations of the nuclear magnetic relaxation time in ionic crystals for two other mechanisms (for a more detailed presentation, cf. Refs. 3 and 4).

2. Pound[5] showed experimentally that, in sufficiently pure ionic crystals, the relaxation of nuclei with spin greater than ½ is often produced by quadrupole effects. The most convincing experiments were done with single crystals of $NaNO_3$ at room temperature (where the relaxation of Na nuclei was studied).

A nucleus with spin greater than ½ possesses a quadrupole moment. Because of the thermal vibrations of the lattice, the quadrupole energy of the nucleus in the crystalline field will be a function of the time. This varying energy is the perturbation which causes spin transitions of the nuclei. Both pure quadrupole transitions and transitions due to interference of the nuclear quadrupole energy (V_q) with the elastic energy (V_e) are possible. We expand the quadrupole and elastic energy of the nucleus in powers of the deformation tensor w. (The expansion is justified because of the smallness of the thermal vibrations of the lattice.) It is well known that the components of the deformation tensor have nonzero matrix elements for the emission or absorption of one phonon.

Next we calculate the probability of a spin transition for processes involving various numbers of phonons. The calculation is done by the standard scheme of perturbation theory, where we limit ourselves to determining orders of magnitude (i.e., we disregard numerical coefficients of order unity).

The results of the calculation show that for $T < \Theta$ (the Debye temperature), the most important process is the pure quadrupole, two-phonon process which is caused by the term quadratic in w, in V_q, in the first approximation of perturbation theory; for $T > \Theta$, the most important process is the four-phonon interference process (which is caused by the interference of the first order term in w in V_q with the third order term in w in V_e, i.e., with the anharmonic term. Such a process occurs in the second approximation of perturbation theory). The calculations of nuclear magnetic relaxation time due to quadrupole effects give

$$T_1 = (C_1/\omega_m)(Mv^2/b)^2(\Theta/T)^4 \quad \text{for} \quad T > \Theta, \tag{1}$$

$$T_1 = (C_2/\omega_m)(Mv^2/b)^2(\Theta/T)^7 \quad \text{for} \quad T \ll \Theta, \tag{2}$$

where ω_m is the maximum frequency of the acoustic vibrations, M is the nuclear mass, v is the velocity of propagation of elastic waves, C_1 and C_2 are numerical coefficients which are not determined by our crude calculations, and b is given by

$$b \approx e^2Q/a^3, \tag{3}$$

where e is the elementary charge, a is the distance to nearest neighbor ions, and Q is the nuclear quadrupole moment. A more detailed treatment shows that b is actually somewhat greater than the value given by formula (3), because of the so-called antishielding effect[6,7].

There is no point in making a more exact calculation of T_1 at present, since almost nothing is known about the coefficients in the expansions of V_q and V_e, except their order of magnitude.

We note that Ref. 7 is also concerned with the theoretical treatment of nuclear magnetic relaxation caused by quadrupole effects. In that paper, the pure quadrupole two-phonon effect was calculated; however, we see from our calculations that, for $T > \Theta$, the four-phonon interference process is more important.

Since there are at present no experimental data concerning the temperature dependence of T_1 (for nuclei with spins greater than ½), we shall make a qualitative comparison with experiment in the following way: we calculate the constant b, using formula (1) and the experimental data on the relaxation time of Na in $NaNO_3$ at room temperature[5]. This gives $b \sim 3 \times 10^{-20}$ ergs.

This value of b corresponds to e^2Q/a^3 with a approximately equal to one Angstrom. (We take the value[8] $Q = 10^{-25}$ cm^2 for the quadrupole moment of Na^{23}.) Our calculations are quite crude, but still the value obtained for b is reasonable.

3. Bloembergen[9] has shown experimentally that in many nonconducting solids nuclear magnetic relaxation is due to paramagnetic impurities. In this paper the following mechanism for relaxation was proposed: the spin of a paramagnetic ion (for example, Cr^{+++} or Fe^{+++}), because of its interaction with the lattice, changes its direction periodically, with a period of the order of ρ, where ρ is the paramagnetic relaxation time. Therefore, a time-varying local magnetic field acts on the nuclear spins in the neighborhood of the paramagnetic ion and tends to reorient them. Because of this, the nuclear spins which are close to the paramagnetic ions rapidly approach thermal equilibrium with the lattice vibrations. A gradient of spin temperature is thus produced, which gives rise to spin diffusion, as a result of which equilibrium of the nuclear spins and lattice is finally established throughout the body.

In Ref. 9, a calculation was made of the time for direct nuclear magnetic relaxation at a distance r from a paramagnetic ion. In treating the spin diffusion, several doubtful assumptions were made in Ref. 9. In addition, the solution of the differential equation was carried out by numerical methods, so that it is of interest to consider once again the process of spin diffusion.

We have solved the differential equation for M (the nuclear magnetization) subject to the appropriate boundary conditions. The calculation was made for a nuclear spin ½, and the spatial dependence $M(r)$ was obtained. From the asymptotic form of this function, it is easy to obtain the flux of nuclear magnetic moment and then find the nuclear magnetic relaxation time. We obtain

$$T_1 = 1/4\pi DcN, \tag{4}$$

where N is the number of paramagnetic ions per unit volume, D is the diffusion coefficient for the nuclear spin, and c is given by

$$c = 2^{-5/4}\pi\Gamma^{-2}(5/4)\,\beta^{1/4} = 0.68\,\beta^{1/4}; \tag{5}$$

where

$$\beta = (\gamma\gamma'\hbar)^2 S(S+1)/5\pi\rho\nu^2, \tag{6}$$

γ, γ' are the gyromagnetic ratios of nucleus and paramagnetic ion , respectively, S is the spin of the paramagnetic ion, ν is the resonance frequency of the nuclear spin in the external magnetic field.

Our treatment is valid only for sufficiently low concentrations of paramagnetic ions. The quantitative criterion for the validity of the approximation we have considered is that the magnetic interaction energy of nearest neighbor paramagnetic ions be small compared to the interaction energy of the paramagnetic ion with the nearest nuclear spins.

In particular, Ref. 9 gives experimental data on the dependence, on temperature and concentration of Cr atoms, of the relaxation time for protons in potassium-chrome alums highly diluted with aluminum. A simple estimate shows that the condition for applicability of our treatment is fulfilled for $N_{Cr}/N_{Al} < 10^{-3}$. In particular, samples I, II and III of Ref. 9 satisfy this condition.

The dependence of T_1 on the concentration of paramagnetic atoms, given by formula (4), is confirmed by experiment. As for the temperature dependence of T_1 (where our result is the same as the dependence obtained in Ref. 9 by a numerical method), unfortunately, it is impossible at present to make a quantitative comparison with experiment, since there are no experimental data on the temperature dependence of the paramagnetic relaxation time of highly diluted alums. However, we note that with the value of ρ for undiluted potassium-chrome alums, formula (4) gives, for samples I, II and III of Ref. 9, satisfactory agreement with the experimental data for $T = 20°$ K.

4. Summarizing, we see that our calculations are in accord with the generally accepted picture of the mechanism of nuclear magnetic relaxation in ionic crystals. In the case of a nuclear spin equal to ½, the nuclear magnetic relaxation is always caused by the interaction of the nuclear spins with the spins of paramagnetic impurities. In the case of a nuclear spin greater than ½, nuclear magnetic relaxation at high temperatures is produced by quadrupole effects, and at low temperatures by the interaction of the nuclear spins with the spins of paramagnetic impurities. The temperature at which these two interactions are equally effective decreases with decreasing concentration of paramagnetic impurities .

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