RELAXATION OF IMPURITY NUCLEI IN FERRODIELECTRICS

N. P. GIORGADZE and G. A. KHARADZE

Physics Institute, Georgian Academy of Sciences

Submitted March 13, 1971

Zh. Eksp. Teor. Fiz. 61, 826–831 (August, 1971)

The effect of low-frequency quasilocal spin excitations on the relaxation rate of impurity-atom nuclei in ferrodielectrics is investigated. It is shown that the rates of two- and three-quantum processes are much higher and that the temperature dependence of the impurity-nuclei relaxation time differs considerably from that for a regular crystal.

DURING the last decade there has been considerable progress in experimental and theoretical methods of investigating impurity states in solids. Interest in these questions is due to the fact that observation of the behavior of impurities makes it possible to trace, at the microscopic level, the character of the interactions of particles in condensed media and to "probe" the local characteristics of the excitation spectrum in them. At the present time, much material has been accumulated concerning the vibrational spectra of impurity atoms in nonmagnetic crystals, which was analyzed in light of modern attainments of the theory in this region (see the reviews[1,2]). The dynamics of impurity spins in magnetoactive solids has been investigated to a lesser degree, although for simple models a sufficiently detailed theory has been developed[3].

It is clear that many characteristic features of the dynamics of the impurities are reflected in the purely macroscopic measurements (specific heat, conductivity, susceptibility, etc.), but the main information on the local properties of impurity crystals can be obtained by direct methods, principal among which are inelastic neutron scattering, the Mössbauer effect, NMR, and also optical methods. Quite promising among the microscopic methods is observation of the character of nuclear-spin relaxation in impurity crystals. This concerns primarily the relaxation of the nuclei of the impurity atoms themselves, or else of the nuclei of atoms that neighbor on the impurities.

The character of the temperature dependence of the spin-lattice relaxation of the nuclei is determined by the spectrum of the local thermal fluctuations of the fields acting on the nuclear spin states. In nonmagnetic dielectrics, the relaxation of nuclei with spin $I > 1/2$ is realized via quadrupole interaction. In[4], a theoretical investigation was carried out of the quadrupole relaxation of impurity nuclei for a simple isotopic model, and it was shown that in the case of a heavy impurity the character of the low-temperature spin-lattice relaxation changes noticeably in comparison with the temperature course in a regular matrix. In a recent paper[5], on the basis of the same microscopic model, an analysis was made of the influence of an isolated impurity on the relaxation time of the nuclei of the neighboring atoms. An analogous question as applied to the relaxation of the electron spin was considered earlier in[6].

Of considerable interest is an investigation of the singularities of the spin relaxation of nuclei in impurity magnetically-ordered dielectrics. In these crystals, owing to the hyperfine and magnetic-dipole interaction of the nuclear spins with the electron subsystem, the mechanism of nuclear relaxation with participation of magnetic excitations is quite effective[7]. A recent experimental paper[8] reports an investigation of the characteristic features of magnetic resonance and of relaxation for F^{19} nuclei in impurity antiferromagnetic crystals $(Mn_{1-x}F_2)X_x$, where X = V, Fe, Co, Ni, and Zn, at concentrations $x \lesssim 0.01$. In pure MnF_2 samples, the relaxation of the fluorine nuclei (I = 1/2) was via anisotropic hyperfine coupling with the electron spins of the neighboring manganese atoms and magnetic dipole interaction. When the manganese atom is replaced by an impurity, the F^{19} nucleus neighboring on the impurity falls in a different surrounding, and the character of the nuclear relaxation should change, as was indeed observed in the already mentioned study[8], whose authors attributed these changes to a change in the constants of the coupling between the spin of the F^{19} nucleus and the magnetic surrounding, assuming that the dynamics of the spins is not significantly altered by introduction of the impurities. It is known, however, that in many cases the spectrum of the spin flucutations of the impurity and of the atoms surrounding it can become greatly modified compared with the picture characteristic of the initial regular magnetically-ordered crystal. It is clear that this can greatly influence the temperature variation of the rate of relaxation of the spins of the impurities themselves. We shall investigate this question below, using as an example a simple Heisenberg model of a ferrodielectric containing an isolated magnetic impurity.

Let us consider the nuclear spin of an impurity atom interacting with its "own" electron spin via isotropic hyperfine coupling AIS_0. We shall assume below that the electron spin S_0 of the impurity has exchange coupling with the neighboring electron spins of the matrix characterized by the constant J_0. The relaxation rate of the impurity nucleus is determined by the Fourier component of the time-dependent correlator $\langle S_0^+(t)S_0^-\rangle$ at a nuclear frequency ω_N, where $S_0^\pm$ are the circular projections of the electron spin (in a coordinate system having the z axis directed along the quantization axis of the nuclear spin). If the direction of the quantization of the electron spin makes an angle ϑ with the nuclear-spin quantization axis, then the relaxation time of the latter spin must be calculated from the formula

$$1/T_1 = {}^1/_2A^2[\langle S_0^{x'}|S_0^{-'}\rangle_{\omega_N} + \langle S_0^{z'}|S_0^{z'}\rangle_{\omega_N}\sin^2\vartheta],$$

where $S_0^{\alpha'}$ is the projection of the impurity electron

spin in the coordinate system having an axis z′ directed along the equilibrium orientation of the electron spin, and $\langle S_0^{\alpha'} | S_0^{\beta'} \rangle_\omega$ denotes the Fourier component of the corresponding time-dependent correlator.

Since we plan to consider the low-temperature region, we change over to the Holstein-Primakoff representation

$$S_0^{z'} = S_0 - b^+ b, \quad S_0^{+'} = \sqrt{2S_0}\left(b - \frac{1}{4S_0} b^+ bb + \ldots\right),$$

where b^+ and b are the Bose operators for creation and annihilation of spin deviations in the impurity site, and introduce the single-particle, two-particle, and three-particle Green's functions

$$G^{(1)}(\omega) = -i\int_{-\infty}^{+\infty} \theta(t)\langle [b(t); b^+]\rangle e^{i\omega t}\, dt,$$

$$G^{(2)}(\omega) = -i\int_{-\infty}^{+\infty} \theta(t)\langle [b^+(t)\, b(t); b^+ b]\rangle e^{i\omega t}\, dt,$$

$$G^{(3)}(\omega) = -i\int_{-\infty}^{+\infty} \theta(t)\langle [b^+(t)\, b(t)\, b(t); b^+ b^+ b]\rangle e^{i\omega t}\, dt.$$

Using the standard technique, we can easily show that

$$\langle S_0^{+'} | S_0^{-'}\rangle_\omega \approx 2\pi\,[n(\omega)+1]\{2\langle S_0^{z'}\rangle[-\pi^{-1}\operatorname{Im} G^{(1)}(\omega + i\delta) + {}^1/_8\, S_0^{-1}[-\pi^{-1}\operatorname{Im} G^{(3)}(\omega + i\delta)]\},$$

$$\langle S_0^{z'} | S_0^{z'}\rangle_\omega \approx 2\pi\{[S_0^2 - 2S_0\langle b^+ b\rangle]\,\delta(\omega) + (n(\omega)+1)[-\pi^{-1}\operatorname{Im} G^{(2)}(\omega + i\delta)]\}$$

where $n(\omega)$ is the Bose distribution function.

The quantity $\rho(\omega) = -\pi^{-1}\operatorname{Im} G^{(1)}(\omega + i\delta)$ is the spectral density of the single-particle excitations and describes the oscillation spectrum of the impurity electron spin. Since $\rho(\omega_N) = 0$ for real systems possessing a gap in the spin-excitation spectrum, we arrive at the conclusion that

$$\frac{1}{T_1} = \pi A^2 [n(\omega_N)+1]\left\{\frac{1}{8S_0}\left[-\frac{1}{\pi}\operatorname{Im} G^{(3)}(\omega_N + i\delta)\right] + \left[-\frac{1}{\pi}\operatorname{Im} G^{(2)}(\omega_N + i\delta)\right]\sin^2\vartheta\right\}.$$

If we confine ourselves henceforth to the linear approximation, i.e., we disregard the interactions of the spin excitations with one another, we can express the quantities $-\pi^{-1}\operatorname{Im} G^{(2,3)}(\omega + i\delta)$ in simple fashion in terms of the single-particle spectral density. Noting, for example, that in the linear approximation

$$\langle [b^+(t)\, b(t);\ b^+ b]\rangle = \langle b^+(t) b\rangle\langle [b(t);\ b^+]\rangle + \langle b^+ b(t)\rangle\langle [b^+(t);\ b]\rangle,$$

it is easy to verify the validity of the following equation:

$$-\frac{1}{\pi}\operatorname{Im} G^{(2)}(\omega + i\delta) = \int_{-\infty}^{+\infty} n(\omega')\rho(\omega')\,[\rho(\omega'+\omega) - \rho(\omega'-\omega)]\, d\omega'$$

$$= \int_{-\infty}^{+\infty} [n(\omega') - n(\omega'+\omega)]\,\rho(\omega')\,\rho(\omega'+\omega)\, d\omega'.$$

Noting further that $\omega_N \ll T$, we can take the limit as $\omega_N \to 0$ and take into account the equality

$$\lim_{\omega\to 0}[n(\omega)+1]\left[-\frac{1}{\pi}\operatorname{Im} G^{(2)}(\omega + i\delta)\right] = \int_0^\infty n(\omega')\,[n(\omega')+1]\,\rho^2(\omega')\, d\omega' \equiv I_2(T).$$

We can show analogously that in the linear approximation

$$\lim_{\omega\to 0}[n(\omega)+1]\,[-\pi^{-1}\operatorname{Im} G^{(3)}(\omega + i\delta)] = 2\int_0^\infty d\omega' \int_0^\infty d\omega'' n(\omega') n(\omega'')\,[n(\omega'+\omega'')+1]\cdot \times \rho(\omega')\rho(\omega'')\rho(\omega'+\omega'') \equiv I_3(T).$$

As a result we arrive at the following expression for the reciprocal relaxation time of the impurity nucleus in a ferrodielectric at low temperatures:

$$\frac{1}{T_1} = \pi A^2\left[\frac{1}{4S_0} I_3(T) + I_2(T)\sin^2\vartheta\right].$$

This formula reflects the well known fact that the relaxation of nuclei in a ferrodielectric is determined by two- and three-quantum processes. It must be emphasized that the expressions for $I_2(T)$ and $I_3(T)$ contain the spectral density $\rho(\omega)$ of the single-particle excitations, which characterizes the local fluctuations of the impurity electron spin, which in turn can differ greatly from the spectrum of the spin excitations in a regular matrix. To ascertain the extent to which this circumstance can influence the rate of relaxation of the impurity nucleus, it is necessary to specify more concretely the expression for $\rho(\omega)$. We consider below a simple cubic ferromagnetic lattice, in which one of the atoms is replaced by an impurity possessing a spin S_0 and exchange $J_0 > 0$ with the nearest neighbors. Such an impurity model has been thoroughly investigated, and we shall use the results of the calculations reported in[3].

Introducing the spectral density $\rho_0(\omega)$ of the spin excitations in the initial regular matrix and considering the case of a weakly coupled impurity with $J_0 \ll J$ and $S_0 = S$, we can show that

$$\rho(\omega) = \frac{\omega_R^2}{(\omega - \omega_R)^2 + (\pi\omega^2\rho_0)^2}\,\rho_0(\omega),$$

where the resonant frequency $\omega_R \ll \omega_0$ and ω_0 is the maximum frequency of the spin-wave spectrum of an ideal crystal characterized by an exchange interaction J between the nearest neighbors. The foregoing expression approximates the spectral density of the single-particle excitations of the impurity electron spin at $\omega \ll \omega_0$. At low frequencies, the spectral density of the excitations in an isotropic ferromagnet can be approximately described by the formula

$$\rho_0(\omega) = \frac{3}{2}\frac{1}{\omega_0}\sqrt{\frac{\omega}{\omega_0}}, \quad \omega \ll \omega_0.$$

Using the foregoing expressions, we arrive after simple transformations at the following result for the reciprocal relaxation time of the impurity nuclear spin:

$$\frac{1}{T_1} = \frac{9\pi}{16}\frac{A^2}{\omega_0}\left[\frac{3}{16S}\left(\frac{T}{\omega_0}\right)^{7/2}\mathcal{J}_3(T) + \left(\frac{T}{\omega_0}\right)^2\mathcal{J}_2(T)\sin^2\vartheta\right],$$

where

$$\mathcal{J}_2(T) = \int_0^{\omega_0/T} F^2(x, T)\, dx,$$

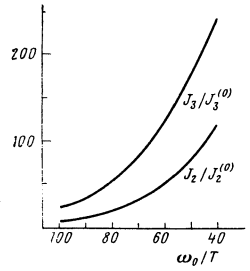
$$\mathcal{J}_3(T) = \int_0^{\omega_0/T} dx \int_0^{\omega_0/T} dx' F(x, T) F(x'\ T) F(x + x', T),$$

with

$$F(x, T) = \frac{\sqrt{x}}{\operatorname{sh}(x + \Delta/T)/2} R(x, T),$$

$$R(x, T) = \frac{(\omega_R/T)^2}{(x - \omega_R/T)^2 + (3\pi/2)^2 (T/\omega_0)^3 x^5}.$$

The expression for F(x, T) contains the parameter Δ, which has been introduced to take into account the presence of a gap in the spin-excitation spectrum of real



systems. We shall consider below the case when $\Delta \ll \omega_R \ll \omega_0$.

In order to clarify the extent to which the contribution of two- and three-quantum processes to the relaxation rate of the impurity nuclei differs from the corresponding quantities for a regular ferromagnet, it is necessary to construct the ratios $\mathcal{J}_2/\mathcal{J}_2^{(0)}$ and $\mathcal{J}_3/\mathcal{J}_3^{(0)}$, where $\mathcal{J}_{2,3}^{(0)}$ are the integrals calculated at $R \equiv 1$.

The figure shows the temperature dependence of the aforementioned ratios for the case of $\Delta/\omega_R = \omega_R/\omega_0 = 0.1$. As seen from the foregoing curves, the rates of relaxation transitions due to two- and three-quantum processes have greatly increased in comparison with the usual picture. It turns out here that the three-quantum processes are enhanced by a factor of several times in comparison with the two-quantum processes.

We have considered above the relaxation of magnetic-impurity nuclei in a ferromagnetic lattice. In conclusion, let us discuss briefly the relaxation of impurity nuclei replacing nonmagnetic atoms in nonconducting magnetically-ordered compounds, for example the replacement of the halide by an impurity in crystals of the already mentioned type, such as the antiferromagnet MnF_2. If the spin of the nonmagnetic impurity-atom nucleus is equal to one half, then there are no quadrupole effects and the coupling with the lattice is via the hyperfine and magnetic-dipole interaction with the surrounding magnetic atoms. If we disregard the thermal oscillations of the lattice and assume that upon introduction of nonmagnetic impurities the spectrum of the spin excitations remains unchanged, we arrive at the well known temperature dependence of the rate of relaxation of the nucleus, which is characteristic of two- and three-magnon processes in a regular lattice. When account is taken of the thermal oscillations, a contribution is made to the nuclear-spin relaxation by processes in which phonons and magnons take part. In particular, a relaxation mechanism is possible in which the reorientation of the nuclear spin is due to absorption of a phonon with subsequent emission of a spin wave with an excess energy equal to the energy of the nuclear spin transition[7]. It is clear that if the spectral distribution of the impurity oscillation amplitudes relative to the neighboring magnetic atoms differs noticeably from the picture characteristic of the regular crystal (for example, in the presence of a quasilocal vibrational level), the combined mechanism described above should lead to an anomalous temperature dependence of the nuclear-relaxation time of the nonmagnetic impurity, even if the spectrum of the electron spin excitations of the atoms neighboring on the impurity did not experience any changes.

The curves presented in the present paper were plotted on the basis of numerical calculations performed by Ts. T. Tarkashvili, B. N. Dzigava, and T. D. Kaladze, to whom the authors are sincerely grateful.

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Translated by J. G. Adashko
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