

## TEMPERATURE DEPENDENCE OF SPIN-LATTICE RELAXATION TIMES

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The problem of the temperature dependence of spin-lattice relaxation times  $T_1$  in paramagnetic crystals is considered for direct resonance energy exchange processes. It is shown that the form of this relation depends essentially on the structure of the spin-system energy levels, the magnitude of the splitting between them as compared with the lattice temperature ( $kT$  level), and also on the ratio of the relaxation transition probabilities between the various levels. In particular, when the level splitting is much less than  $kT$ , the relaxation times vary as  $T_1 \sim T^{-1}$ , while for large level splittings exceeding  $kT$ , both weaker and stronger (exponential) dependence of  $T_1$  on the temperature can occur.

THE exchange of energy between the spin system of a paramagnet and the thermal vibrations of the lattice can, as is well known, be brought about by two processes: direct resonance processes in which the frequencies of the lattice phonons are identical with the transition frequencies between the spin-system energy levels, and combination processes in which the differences in the phonon frequencies coincide with the transition frequencies in the spin-system (see, for example, <sup>[1]</sup>). Direct processes are as a rule responsible for spin-lattice relaxation at low temperatures, while the combination processes are important at much higher temperatures.

It is usually assumed that the temperature dependence of the spin-lattice relaxation times  $T_1$  for the direct processes should obey the  $T_1 \sim 1/T$  law, whereas a much stronger temperature dependence of  $T_1$  should be characteristic of the combination processes. However, as has already been shown, <sup>[2]</sup> for direct resonance relaxation processes, there can be significant departures from the  $T_1 \sim 1/T$  law, in the direction of both stronger and weaker temperature dependences. The concrete form of the dependence  $T_1(T)$  is determined by the structure of the spin-system energy levels, the magnitude of the splitting between them as compared with the lattice temperature (the quantity  $kT$ ), and the ratio of the probabilities of relaxation processes between the various levels.

The purpose of the present work is a more detailed analysis of the temperature dependence of the spin-lattice relaxation times for direct resonance processes.

We consider several special cases.

1. In the simple case of a two-level system ( $E_2 > E_1$ ) the establishment of equilibrium with the thermal oscillations of the lattice follows the exponential law

$$n_2 - n_1 = A \exp(-t/T_1) + (n_2 - n_1)_{\text{eq}}, \quad (1)$$

where  $A$  is a constant determined by the initial conditions;  $(n_2 - n_1)_{\text{eq}}$  is the equilibrium difference in populations, corresponding to the Boltzmann distribution;  $T_1 = 1/(w_{12} + w_{21})$  is the spin-lattice relaxation time;  $w_{ik}$  is the  $E_i \leftrightarrow E_k$  transition probability. For direct resonance processes, the temperature dependence of the relaxation transition probabilities is determined by the factors <sup>[3]</sup>

$$\begin{aligned} w_{12} &\sim 1 / [\exp(h\nu_{21}/kT) - 1], \\ w_{21} &\sim \exp(h\nu_{21}/kT) / [\exp(h\nu_{21}/kT) - 1] \end{aligned} \quad (2)$$

It is thus seen that when  $h\nu_{21} = E_2 - E_1 \ll kT$  the temperature dependence of the spin-lattice relaxation times will follow the well-known  $T_1 \sim 1/T$  law. However,  $T_1$  is practically independent of the temperature for large level splittings ( $h\nu_{21} \gg kT$ ).

2. We now consider two special cases of three-level systems.

a) Let the energy of the levels ( $E_3 > E_2 > E_1$ ) be such that  $E_3 - E_2 \ll kT$ ,  $E_2 - E_1 \gg kT$ ; we shall be interested in the relaxation rate between the upper levels 3 and 2. Such a case can be realized, for example, for paramagnetic ions of the iron group (such as  $\text{Cr}^{3+}$  or  $\text{Fe}^{3+}$ ) having large initial splitting of the spin levels in the crystalline field, when the investigations of the relaxation are carried out

at comparatively low frequencies ( $h\nu \ll kT$ ). We assume that the relaxation for the transitions  $2 \leftrightarrow 3$  takes place principally through the lower level, i.e., we neglect the probability of relaxation transitions between the levels 2 and 3 ( $w_{23}$  and  $w_{32}$ ) in comparison with the corresponding transition probabilities  $1 \leftrightarrow 2$  and  $1 \leftrightarrow 3$  ( $w_{12}$ ,  $w_{21}$ ,  $w_{13}$ , and  $w_{31}$ ). Such a situation can exist in cases in which the direct relaxation transitions between the investigated levels are forbidden (for example, for the levels  $M = \pm 1/2$  in the case of  $\text{Cr}^{3+}$  ions). We then have the following kinetic equations for change in the level populations:

$$dn_3/dt = -n_3w_{31} + n_1w_{13}, \quad dn_2/dt = -n_2w_{21} + n_1w_{12} \quad (3)$$

under the condition that the total number of particles  $n = n_1 + n_2 + n_3$  is conserved. The solution of the system (3) has the form

$$n_3 - n_2 = A \exp(\alpha_1 t) + B \exp(\alpha_2 t) + (n_3 - n_2)_{\text{eq}}, \quad (4)$$

where

$$\alpha_{1,2} = \frac{1}{2} \left[ - (w_{31} + w_{13} + w_{21} + w_{12}) \pm \sqrt{(w_{31} + w_{13} - w_{21} - w_{12})^2 + 4w_{12}w_{13}} \right].$$

If we assume that  $w_{31} + w_{13} = w_{12} + w_{21}$ , and take into account the connection between the relaxation probabilities

$$w_{13} = w_{31} \exp(-h\nu_{31}/kT), \quad w_{12} = w_{21} \exp(-h\nu_{21}/kT),$$

we can readily prove that  $B \approx 0$  when  $h\nu_{21} \gg kT$ , and the relaxation rate for the transition  $3 \leftrightarrow 2$  will be described by the single exponent

$$n_3 - n_2 = A \exp(\alpha_1 t) + (n_3 - n_2)_{\text{eq}} \quad (5)$$

with the relaxation time

$$T_1 = -1/\alpha_1 \approx 1/w_{31}. \quad (6)$$

It follows from (6) that a weak temperature dependence is observed for the spin-lattice relaxation times in the case under consideration, which disappears completely in the limit for  $h\nu_{31} \gg kT$ .

b) Let  $E_3 - E_2 \gg kT$ ,  $E_2 - E_1 \ll kT$ ; we are interested in the relaxation rate for the transition  $2 \leftrightarrow 1$ . By analogy with the case a) considered above, we assume that direct relaxation transitions between the levels 2 and 1 are forbidden (or weak), while the relaxations for these levels take place through the upper level 3. Then the kinetic equations for the rate of establishment of equilibrium with the lattice are similar to Eqs. (3), and under an assumption analogous to that given in case a) (namely,  $w_{31} + w_{13} = w_{32} + w_{23}$ ) we get

$$n_2 - n_1 = A \exp(\alpha_1 t) + B \exp(\alpha_2 t) + (n_2 - n_1)_p, \\ \alpha_{1,2} = - (w_{23} + w_{32}) \pm \sqrt{w_{31}w_{32}}. \quad (7)$$

Analysis shows that when  $h\nu_{32} \gg kT$  we have  $B \approx 0$ , and the relaxation rate for the transition  $2 \leftrightarrow 1$  is described by the single exponent

$$n_2 - n_1 = A \exp(\alpha_1 t) + (n_2 - n_1)_p \quad (8)$$

with the relaxation time

$$T_1 = -1/\alpha_1 \approx 1/w_{23}. \quad (9)$$

Since

$$w_{23} \sim 1 / [\exp(h\nu_{32}/kT) - 1],$$

we see that in the case considered ( $h\nu_{32} \gg kT$ ) a strong (exponential) temperature dependence should be observed for the spin-lattice relaxation time.

Recently, in the investigation of the spectra of paramagnetic resonance of ions of the iron group, significant splittings of the spin energy levels by the crystalline electric field have been discovered in certain crystals. As an example, one can use the single crystals of rutile with  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  impurities<sup>[4]</sup> and beryl with  $\text{Cr}^{3+}$  impurity.<sup>[5]</sup> The level splitting observed in them in the region of helium temperatures is comparable or even exceeds the value of  $kT$ . Therefore, spin-lattice relaxation in such crystals at helium temperatures can have the temperature dependence analyzed above. In particular, such a dependence has been discovered in rutile single crystals.<sup>[2]</sup>

Similar peculiarities of the spin-lattice relaxation can also take place in crystals containing rare earth ions, for which the excited orbital levels are separated from the ground level by an amount that exceeds  $kT$  several fold, and direct relaxation between the lower sublevels is forbidden. In a fashion similar to our analysis for the case b), Finn, Orbach, and Wolf<sup>[6]</sup> considered the relaxation process for the ground state of  $\text{Ge}^{3+}$  ions in cerium-magnesium nitrate through the neighboring upper excited level. Such a process differs from the relaxation process between the splitting of the spin levels of the ground state of ions of the iron group in that in the former case the lattice vibrations which modulate the crystalline electric field can act directly on the orbital momentum of the electrons, whereas the exchange of spin level energies with the lattice takes place in the second case through the medium of spin-orbit coupling. However, this difference is not fundamental for the temperature dependence of the spin-lattice relaxation times, brought about

by the direct resonance processes described above, which couple the lower and upper levels.

We note that the authors cited<sup>[6]</sup> consider the relaxation process under discussion (between two low levels through the upper level) as a new process, which differs from the combination and direct processes. We want to emphasize, however, that the process mentioned is in essence only a special case of the direct processes, inasmuch as it involves a resonant energy exchange between the lattice phonons and the various levels of the spin system.

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<sup>1</sup>S. A. Al'tshuler and B. M. Kozyrev, *Elektronnyĭ paramagnitnyĭ rezonans (Electron Paramagnetic Resonance)*, Fizmatgiz, 1961.

<sup>2</sup>Manenkov, Milyaev, and Prokhorov, *FTT* **4**, 388 (1962), *Soviet Phys. Solid State* **4**, 280 (1962).

<sup>3</sup>J. H. Van Vleck, *Phys. Rev.* **57**, 426 (1940).

<sup>4</sup>Gerritsen, Harrison, Levis, and Wittke, *Phys. Rev. Lett.* **2**, 153 (1959), Sierro, Muller, and Lacroix, *Arch. Sci. (Geneva)* **12**, 122 (1959), Gerritsen, Harrison, and Levis, *J. Appl. Phys.* **31**, 1566 (1960), Okaya, Carter, and Nash, *Bull. Amer. Phys. Soc.* **5**, 73 (1960).

<sup>5</sup>Geusic, Peter, and Schulz-Dubois, *Bell Syst. Tech. J.* **38**, 291 (1959).

<sup>6</sup>Finn, Orbach, and Wolf, *Proc. Phys. Soc. (London)* **A77**, 261 (1961).

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