Spin-lattice relaxation in magnetic ion pairs

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A new theoretical model of spin-lattice relaxation for magnetic "ion pairs" has been developed in which both the "spin-phonon" and "spin-spin" interactions are jointly effective in producing a net relaxation transition. The Raman-type indirect two-phonon relaxation rate for non-Kramers as well as Kramers ion pairs shows T^7 dependence at low temperatures and T^3 dependence at high temperatures. The T^3 dependence is entirely a new result. The T^7 dependence for Kramers pairs is also a new result as it is not possible in the usual Van Vleck mechanism. Even the T^7 dependence for non-Kramers ion pairs is different from a similar standard result for unpaired ions. It appears that the electronic spin relaxation behavior of ion pairs may be quite different from that of unpaired ions.

I. INTRODUCTION

The electronic spin-relaxation rate of magnetic ions is a very important parameter in various magnetic resonance experiments as it affects the sharpness of the resonance peaks. It is also extremely important in the observation and analysis of the Mössbauer magnetic hyperfine spectra of paramagnetic ions at low temperatures.[1,2] It is well understood that electronic spin relaxation proceeds by the two distinct processes known as (i) spin-spin relaxation and (ii) spin-lattice relaxation.[3-6] The two relaxation mechanisms have always been considered to proceed independently without any mutual influence, that is, the spin-spin interaction and the spin-phonon interaction are treated as being completely independent of each other. However, in many cases (especially in crystals with a good concentration of magnetic ions) the exchange interaction and the dipolar interaction between a pair of magnetic ions may become quite significant, and the spin relaxation of such magnetically coupled (or exchange-coupled) ion pairs can proceed effectively under the joint effect of spin-spin and spin-phonon interactions. In a sense one considers a situation when a pair of magnetic ions besides being individually coupled to lattice vibrations are also magnetically coupled together. The aim of the present work is to explicitly calculate the spin-lattice relaxation rate of such "ion pairs" through a specific relaxation path which connects the two ions both vibronically and magnetically. Here the calculation will be presented for a Raman-type indirect two-phonon relaxation process which effectively utilizes the entire phonon spectrum of the lattice and is therefore quite dominant.[5] For the sake of completeness, a brief outline of "spin-spin" and "spin-phonon" interactions will be given and then the relaxation model for ion pairs will be taken up.

II. SPIN-SPIN INTERACTION

The electronic spin-spin interaction arises from the Heisenberg exchange and magnetic dipole-dipole interactions between a pair of ions. These interactions can be ex-pressed as a sum of various terms containing spin operators.[3,6] Among the various possible transitions induced by these terms the most dominant are those which conserve the net spin and the crystal-field energy of the system. Accordingly the spin-spin transitions are mainly induced by mutual spin flips at the two ions and the relevant interaction is effectively represented by

$$H_{ss}(1,2)=J[S_+(1)S_-(2)+S_-(1)S_+(2)] , \tag{1}$$

where $|J| = |\frac{1}{2}J_{12}+G|$ is the effective magnetic coupling constant. Here J_{12} is the Heisenberg exchange-coupling parameter and $G =(g_e^2\beta_e^2/4r_{12}^3)(1-3\cos^2\theta_{12})$ is the dipolar coupling constant between two ions.

III. SPIN-PHONON INTERACTION

The spin-phonon interaction is responsible for the exchange of energy between electronic spins and lattice vibrational phonons. With the use of the long-phonon-wavelength approximation the spin-phonon interaction is given by[5,7]

$$H_{s\text{-ph}}=\sum_k \sum_{n,m} \left[\frac{\hbar}{2M\omega_k}\right]^{1/2} V_n^m(L)k(a_k+a_k^*) , \tag{2}$$

where M is the mass of the crystal, ω_k is the phonon frequency of wave vector k, and $V_n^m(L)$ is the crystal-field potential with dynamic parameters. The properties of phonon annihilation and creation operators a_k and a_k^* are well known.[8]

IV. RELAXATION INTERACTION FOR ION PAIRS

In any theory of spin-lattice relaxation one has to take into account the electronic states of the magnetic ion, the phonon states (or lattice-vibrational states) of the crystal, and the perturbing interaction which can induce transitions between unperturbed electron-phonon states. The complete Hamiltonian for the electron-phonon system will be given by

$$H =H_0+H_{s\text{-ph}}(1)+H_{ss}(1,2)+H_{s\text{-ph}}(2) . \tag{3}$$

The Hamiltonian H_0 consists of the electronic and lattice-vibrational interactions, and it produces the unperturbed electron-phonon states of the system. The relevant electronic interactions are the crystal-field potential, the spin-orbit coupling, and the Zeeman interaction, and they decide the electronic states of the ion. The phonon state of the lattice is represented by the number of phonons (n_k) of varying energies and wave vectors, which is given by the Bose-Einstein distribution function. The relaxation transition between various unperturbed electron-phonon states of an ion pair are induced by the perturbing Hamiltonian $H_{s\text{-ph}}(1) + H_{ss}(1,2) + H_{s\text{-ph}}(2)$. While treating $H_{ss}(1,2)$ as a perturbing interaction one should be somewhat cautious. As mentioned earlier $H_{ss}(1,2)$ incorporates the exchange interaction which may become strong enough to give rise to ferromagnetic or antiferromagnetic ordering of the system (provided the concentration of magnetic ions is large and the temperature is suitable). In a magnetically ordered system the electronic spin states are widely separated so that only the ground state is mostly populated (i.e., the spin states are long lived) and such conditions are not favorable for the measurement of spin-relaxation times. Therefore one is always interested in cases where the exchange interaction is very small or zero (that is, the system tends to remain in a paramagnetic state) and then $H_{ss}(1,2)$ can very well be regarded as a perturbing interaction.

V. TWO-PHONON RELAXATION PROCESS

In the usual indirect two-phonon process the spin relaxation between the two electronic states of a ground doublet proceeds via an excited state with the emission and absorption of two phonons. In the case of an ion pair the proposed relaxation path has been shown in Fig. 1. For example, at the first ion a phonon of energy $\hbar\omega_k$ is absorbed which brings this ion into its excited state. Then there is a simultaneous spin flip at both the ions followed by the emission of a phonon of energy $\hbar\omega_{k'}$ at the second ion. During mutual spin flips if the spin of one ion changes by $+1$ that of the second ion changes by -1 so that the net spin and the energy of the system remains
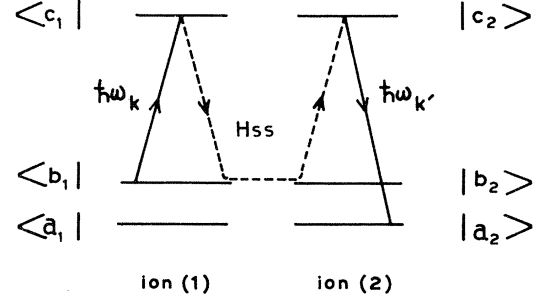

FIG. 1. Schematic representation of the relaxation path.

conserved. Finally, the emitted and the absorbed phonons have an energy difference equal to the energy separation between the electronic ground doublet.

The initial state of the relaxation path is

$$| b_1,b_2;n_k,n_{k'} \rangle ,$$

the intermediate states are

$$| c_1,b_2;n_k-1,n_{k'} \rangle, \quad | b_1,c_2;n_k-1,n_{k'} \rangle ,$$

the final state is

$$| b_1,a_2;n_k-1,n_{k'}+1 \rangle ,$$

and the energy separations are

$$\Delta b_1 = E_{b_1} - E_{a_1}, \quad \Delta c_1 = E_{c_1} - E_{a_1} ,$$

$$\Delta b_2 = E_{b_2} - E_{a_2}, \quad \Delta c_2 = E_{c_2} - E_{a_2} .$$

In Fig. 1, $| a_1 \rangle$, $| b_1 \rangle$, $| c_1 \rangle$, and $| a_2 \rangle$, $| b_2 \rangle$, $| c_2 \rangle$ are the electronic eigenstates of the first and the second ions, respectively, and $| n_k \rangle$ represents the phonon state of the crystal. The eigenstates of the ion pairs are represented by Born-Oppenheimer products of the electron-phonon states of the two ions and Fig. 1 shows one such scheme.

The transition probability per unit time for the transition $| b_2 \rangle \rightarrow | a_2 \rangle$ will be given by

$$P_{b_2 \rightarrow a_2} = \frac{2\pi}{\hbar} \sum_k \sum_{k'} \left| \frac{\langle b_1,a_2;n_k-1,n_{k'}+1 | H_{s\text{-ph}}(2) | b_1,c_2;n_k-1,n_{k'} \rangle \langle b_1,c_2;n_k-1,n_{k'} |}{\Delta c_2 - \hbar\omega_{k'}} \right.$$

$$\left. \times \frac{JS_{\mp}(1)S_{\pm}(2) | c_1,b_2;n_k-1,n_{k'} \rangle \langle c_1,b_2;n_k-1,n_{k'} | H_{s\text{-ph}}(1) | b_1,b_2;n_k,n_{k'} \rangle}{(\Delta c_1 - \Delta b_1) - \hbar\omega_k} \right|^2 \delta(\hbar\omega_{k'} - \hbar\omega_k - \Delta b_2) \quad (4)$$

$$= \frac{2\pi}{\hbar} \left[\frac{\hbar}{2M} \right]^2 J^2 M_1^2 \sum_k \sum_{k'} \frac{k^2 k'^2 n_k(n_{k'}+1)\delta(\hbar\omega_{k'} - \hbar\omega_k - \Delta b_2)}{\omega_k \omega_{k'}(\Delta c_2 - \Delta b_2 - \hbar\omega_k)^2(\Delta c_1 - \Delta b_1 - \hbar\omega_k)^2} , \quad (5)$$

where, effectively,

$$M_1 = \left\langle a_2 \left| \sum_{n,m} V_n^m \right| c_2 \right\rangle \langle b_1 | S_{\mp}(1) | c_1 \rangle \langle c_2 | S_{\pm}(2) | b_2 \rangle \left\langle c_1 \left| \sum_{n,m} V_n^m \right| b_1 \right\rangle . \quad (6)$$

The density of phonon states may be approximated to be continuous and Debye-type, which is given by[9]

$$g(k)dk = (V/2\pi^2)k^2 dk , \quad (7)$$

where V is the volume of the crystal. Then the summation over phonon states is replaced by an integration and the expression (5) reduces to

$$P_{b_2 \to a_2} = \frac{2\pi}{\hbar} \frac{\hbar^2 J^2 M_1^2}{16\pi^4 p^2 v^{10}} \int \int \frac{\omega_k^3 \omega_{k'}^3 n_k (n_{k'}+1) \delta(\hbar\omega_{k'} - \hbar\omega_k - \Delta b) d\omega_k d\omega_{k'}}{(\Delta_0 - \hbar\omega_k)^4} , \tag{8}$$

where $k = \omega/v$, v is the velocity of acoustic phonons in the crystal, p is the density of the crystal, and it has been assumed that $\Delta c_1 - \Delta b_1 \simeq \Delta c_2 - \Delta b_2 \simeq \Delta_0$. Completing the integration over the δ function, which exists only when $\hbar\omega_{k'} = \hbar\omega_k + \Delta b$, and using the expression for the phonon occupation number, one finally obtains

$$P_{b_2 \to a_2} = \frac{J^2 M_1^2}{8\pi^3 p^2 v^{10}} \int \frac{\omega^3 (\omega + \Delta b/\hbar)^3}{(\Delta_0 - \hbar\omega)^4} \frac{\exp[(\hbar\omega + \Delta b)/k_B T] d\omega}{[\exp(\hbar\omega/k_B T) - 1]\{\exp[(\hbar\omega + \Delta b)/k_B T] - 1\}} . \tag{9}$$

(now the label k has been removed from ω_k).

The transition probability for the reverse transition $|a_2\rangle \to |b_2\rangle$ may be similarly obtained by using the initial state

$$|b_1, a_2; n_k, n_{k'}\rangle ,$$

the intermediate states

$$|b_1, c_2; n_k, n_{k'} - 1\rangle, \quad |c_1, b_2; n_k, n_{k'} - 1\rangle ,$$

and the final state

$$|b_1, b_2; n_k + 1, n_{k'} - 1\rangle .$$

Then one obtains

$$P_{a_2 \to b_2} = \frac{J^2 M_1^2}{8\pi^3 p^2 v^{10}} \int \frac{\omega^3 [\omega + (\Delta b/\hbar)]^3}{(\Delta_0 - \hbar\omega)^4} \frac{\exp(\hbar\omega/k_B T) d\omega}{[\exp(\hbar\omega/k_B T) - 1]\{\exp[(\hbar\omega + \Delta b)/k_B T] - 1\}} . \tag{10}$$

The relaxation rate $(1/T_1 \text{ sec}^{-1})$ is equal to the sum of the two transition probabilities given by expressions (9) and (10) and hence it is equal to

$$\frac{1}{T_1} = \frac{J^2 M_1^2}{8\pi^3 p^2 v^{10}} \int_0^{\omega_D} \frac{\omega^3 (\omega + \Delta b/\hbar)^3}{(\Delta_0 - \hbar\omega)^4} \frac{\{\exp(\hbar\omega/k_B T) + \exp[(\hbar\omega + \Delta b)/k_B T]\} d\omega}{[\exp(\hbar\omega/k_B T) - 1]\{\exp[(\hbar\omega + \Delta b)/k_B T] - 1\}} . \tag{11}$$

This is the general expression for the relaxation rate. The integration extends over the entire phonon spectrum and hence the upper limit goes up to Debye frequency (ω_D) of the crystal. The integral in expression (11) can be evaluated under different approximations.

A. Case 1: $\Delta_0 \gg \hbar\omega$

This condition is usually satisfied when the Debye energy of the lattice is less than Δ_0. In this case, $\hbar\omega$ may be neglected compared to Δ_0 in the denominator (apart from $\Delta b/\hbar$ being always neglected compared to ω) and the expression (11) reduces to

$$\frac{1}{T_1} = \frac{J^2 M_1^2}{4\pi^3 p^2 v^{10} \Delta_0^4} \left[\frac{k_B T}{\hbar} \right]^7 \int_0^{\Theta_D/T} \frac{x^6 e^x dx}{(e^x - 1)^2} , \tag{12}$$

where $\hbar\omega/k_B T = x$ and Θ_D is the Debye temperature of the crystal. This shows that the relaxation rate of ion pairs is proportional to T^7, which is similar to the standard Raman T^7 process[5] for an unpaired non-Kramers ion, but where the absolute values are different for the two cases. At low temperatures $(\Theta_D/T > 12)$ the upper limit of the integral in expression (12) may be replaced by ∞ and then its value approximates to $6!$. At higher temperatures the value of the integral diminishes sharply; this can be obtained from standard tables.[10]

B. Case II: $\Delta_0 \ll \hbar\omega$

This condition may be satisfied at sufficiently high temperatures and then Δ_0 may be neglected compared to $\hbar\omega$. The expression (11) then reduces to

$$\frac{1}{T_1} = \frac{J^2 M_1^2}{4\pi^3 p^2 v^{10} \hbar^4} \left[\frac{k_B T}{\hbar} \right]^3 \int_0^{\Theta_D/T} \frac{x^2 e^x dx}{(e^x - 1)^2} . \tag{13}$$

This indicates that for high-energy (or swift) phonons the relaxation rate is proportional to T^3 which is entirely a new result for non-Kramers ion pairs.

C. Case III: Kramers ion pairs

For Kramers ion pairs expression (11) will be modified to give

$$\frac{1}{T_1} = \frac{J^2 M_1^2}{4\pi^3 p^2 v^{10} \Delta_0^4} \int_0^{\omega_D} \left[\frac{1}{(\Delta_0 - \hbar\omega)^2} + \frac{1}{(\Delta_0 + \hbar\omega)^2} \right]^2$$

$$\times \frac{\omega^6 \exp(\hbar\omega/k_B T) d\omega}{[\exp(\hbar\omega/k_B T) - 1]^2} . \tag{14}$$

In the case of slow phonons at low temperatures $(\hbar\omega \ll \Delta_0)$ the term within the large parentheses in (14) can be or approximated to be $4/\Delta_0^4$ so that

$$\frac{1}{T_1} = \frac{J^2 M_1^2}{\pi^3 p^2 \nu^{10} \Delta_0^4} \left[\frac{k_B T}{\hbar} \right]^7 \int_0^{\Theta_D} \frac{x^6 e^x dx}{(e^x - 1)^2} . \qquad (15)$$

This gives a relaxation rate proportional to T^7 which is a new result for Kramers systems. Similarly for swift phonons at high temperatures $(\hbar\omega \gg \Delta_0)$ the term within the large parentheses can be approximated to $4/(\hbar\omega)^4$ so that

$$\frac{1}{T_1} = \frac{J^2 M_1^2}{\pi^3 p^2 \nu^{10} \hbar^4} \left[\frac{k_B T}{\hbar} \right]^3 \int_0^{\Theta_D/T} \frac{x^2 e^x dx}{(e^x - 1)^2} . \qquad (16)$$

This gives a relaxation rate proportional to T^3 which is again a new result for Kramers systems.

VI. DISCUSSION

It appears that the spin-relaxation behavior of ion pairs may be much different from that of the unpaired ions.[5,11] Actually spin relaxation in a system may proceed through various possible paths and the dominant mechanism within a given temperature range can be decided only by matching experimental data with theoretical calculations. However, the proposed new relaxation for ion pairs can be identified by observing any T^3 dependence of relaxation rate which is predicted in the case of ion pairs only. Another distinct feature of the proposed relaxation mechanism is that the relaxation rate will be sensitive to temperature as well as ionic concentration and this may be utilized to identify the proposed mechanism.

It might be interesting from an experimental point of view to look into a system where there is no direct spin-spin relaxation within the ground doublet, that is, $\langle a \,|\, S_\pm \,|\, b \rangle = 0$ (or $g_\perp = 0$), which is often true for axial symmetries. For such a system the spin-relaxation rate at low temperatures should not depend upon the concentration of magnetic ions unless the proposed "pair relaxation mechanism" is operative. This can provide direct experimental evidence of the proposed relaxation process provided one studies the variation of spin-relaxation rate at low temperatures as a function of ion concentration.

It is appropriate to note that several authors have already described the cases of "cross relaxation" among "exchange-coupled ion pairs" where both spin-spin and spin-phonon interactions are operative and hence they may superficially appear similar to the relaxation mechanism proposed here. But this is not so, which will be evident from the following discussion.

Harris and Yngvesson[12] have considered the spin-lattice relaxation of exchange-coupled pairs of iridium ions. In their approach the effect of exchange interaction is only to modify the electronic wave function by introducing an admixture from other electronic states and by removing the spin degeneracy. After that the relaxation transitions are produced by the orbit-lattice interaction for the ion pair.

Gill and Ivey[13] have reported the observation of a cross spin-lattice relaxation in which the spin-lattice relaxation rate is affected by the presence of the exchange coupling. They believe that in Tutton salt $(NH_4)_2(Cu,Fe,Zn)(SO_4)_2 \cdot 6H_2O$ the spin-lattice relaxation of Cu^{2+} ions is mainly due to their coupling to very-fast-relaxing Fe^{2+} ions. Here a rapidly relaxing Fe^{2+} ion in effect produces a varying magnetic field on a neighboring Cu^{2+} ion. The magnetic field, whose magnitude and direction depend upon the strength of spin-spin coupling, in turn produces an admixture of high-energy electronic states into the ground Kramers doublet (which is mostly occupied at liquid-helium temperature), and consequently an orbit-lattice transition within the ground doublet becomes possible. This leads to an enhancement of the spin-lattice relaxation rate of Cu^{2+} in the presence of magnetic (or exchange) coupling with neighboring Fe^{2+} ions (a standard result for Kramers systems).

Recently Vasson et al.[14] have reported measurement of an electronic cross-relaxation rate of $Cr^{3+}(3d^3)$ in ruby crystals containing fast-relaxing $Ti^{3+}(3d^1)$ and other transition-metal ions. In order to explain the experimental data they have utilized a two-step relaxation mechanism represented by $Cr^{3+} \rightarrow Ti^{3+} \rightarrow$ lattice. The transition $Cr^{3+} \rightarrow Ti^{3+}$ is made possible by a dipolar spin-spin interaction and the transition $Ti^{3+} \rightarrow$ lattice proceeds by means of strong orbit-lattice interaction while Cr^{3+} itself is only weakly coupled to lattice. The theoretical framework of such a relaxation scheme has been discussed by Bates et al.[15]

In fact, the processes discussed by Harris and Yngvesson, Gill and Ivey, Bates et al., and Vasson et al. are very similar because in all these cases the spin-lattice relaxation rate of a weakly coupled ion is increased due to its magnetic coupling with a fast-relaxing ion. In perspective it appears that the spin-lattice relaxation mechanism for ion pairs, which has been proposed in the present work, is of a new kind where both the ions are strongly coupled to lattice vibrations besides being magnetically coupled together.

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