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Mixed-spin-relaxation behaviour of paramagnetic Fe²⁺ ions in ZnCO₃

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Abstract. The mixed-spin-relaxation rates of substitutional paramagnetic Fe²⁺ (⁵D) ions in ZnCO₃ have been explicitly evaluated between 10 and 35 K. These results are then compared with the experimental data obtained earlier from the analysis of the Mössbauer magnetic hyperfine spectra of the above system at liquid-He temperature. It is found that at low temperatures the mixed-spin-relaxation process provides a competing mode for the exchange of energy between electronic spins and phonons.

1. Introduction

The well resolved Mössbauer magnetic hyperfine spectra for paramagnetic Fe²⁺ ions in ZnCO₃ have been obtained by Price *et al* (1977) down to liquid-helium temperature (4.2 K) owing to slow spin relaxation and the observed values of spin relaxation rates at various temperatures are available. The spin–lattice relaxation rates arising from Raman and Orbach processes have also been calculated by Price *et al* on a simple magnetic relaxation model and they are found to be less by the order of 10³–10⁴ than the experimentally measured values. Therefore a mixed-spin-relaxation process has been proposed in which both the spin–spin and spin–lattice (phonon) relaxation processes are jointly and simultaneously effective in completing a relaxation transition. The aim in the present paper is to discuss how the relaxation between the two close ground states of paramagnetic Fe²⁺ ions in ZnCO₃ proceeds via an excited state under the joint action of dipolar spin–spin and spin–lattice interactions. This type of relaxation mechanism has been conceived as a mixed-spin-relaxation process (Srivastava and Singh 1980). It is found that mixed spin relaxation is a dominant relaxation process at low temperatures (below 35 K) for paramagnetic Fe²⁺ ions in ZnCO₃ as the calculated mixed-spin-relaxation rates agree well with the experimental data of Price *et al* (1977).

2. Interaction of Fe²⁺ ions

2.1. Crystal-field interaction

The substitutional Fe²⁺ ions in ZnCO₃ as well as in various other carbonates occupy trigonally distorted sites. The symmetry axis for such cases is along <111> or the body

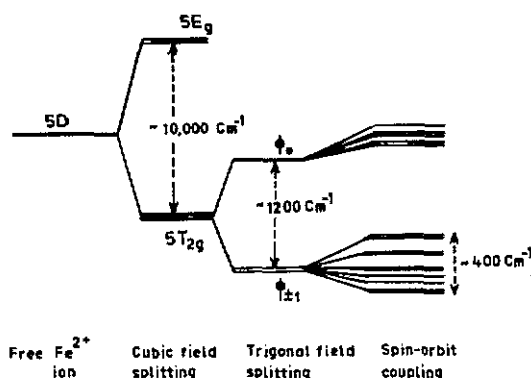


Figure 1. Energy level diagram of a high-spin Fe²⁺ (⁴D) ion with trigonal distortion and spin-orbit coupling.

diagonal of the cube. For such trigonal distortions, the cubic crystal-field interaction is given by Bleaney and Stevens (1953) and Ballhausen (1962):

$$V_c = B_4^0 [O_4^0(L) - 20\sqrt{2}O_4^2(L)]. \quad (1)$$

As a result of this cubic field the eigenstates of a free Fe²⁺ ion is split into an excited doublet 5E_g and ground triplet 5T_{2g} separated by an energy $|180B_4^0| \approx 10000 \text{ cm}^{-1}$ (Ingalls 1964). As the energy separation between the 5T_{2g} and 5E_g states is very high, any mixture between them by a small trigonal field component is expected to be very small and hence can be neglected. This is because, at all ordinary working temperatures, the Boltzmann population of the E_g states (excited doublet) is almost negligible, and therefore its contribution may be neglected in deciding any physical property of the system. The 5T_{2g} wavefunctions may be written as

$$\begin{aligned} \Phi_0 = |0\rangle & \quad \Phi_1 = [\sqrt{\frac{2}{3}}|-2\rangle + \sqrt{\frac{1}{3}}|1\rangle] \\ & \quad \Phi_{-1} = [\sqrt{\frac{2}{3}}|2\rangle - \sqrt{\frac{1}{3}}|-1\rangle]. \end{aligned} \quad (2)$$

These triplet orbital states become the orbital basis states for dealing with further perturbing interactions which are small in comparison with the cubic crystal-field interaction.

The perturbing Hamiltonian to be considered here is given by

$$H = B_2^0 O_2^0(L) + \lambda L \cdot S \quad (3)$$

where the first term in equation (3) represents the trigonal field distortion and the second term the spin-orbit coupling between the total spin and the orbital angular momentum. The trigonal crystal field V_{trig} splits the 5T_{2g} orbitals into a singlet Φ₀ and a ground doublet Φ_{±1}, the energy separation being equal to $9|B_2^0|$. The magnitude of the trigonal field splitting in carbonates such as MnCO₃ is known to be of the order of 1200 cm⁻¹ as shown in figure 1, and the sign of B₂⁰ determines whether the singlet Φ₀ or the doublet Φ_{±1} is lower in energy. The Mössbauer quadrupole splitting data (Ok 1969, Forester and Koon 1969) indicates that the doublet Φ_{±1} is the ground state in FeCO₃, and similar results have been obtained for Fe²⁺ in ZnCO₃, MgCO₃, CaCO₃ and CdCO₃ (Price and Srivastava 1976, Price *et al* 1977).

Table 1. The wavefunctions and eigenvalues.

Eigenfunction	Eigenvalue (cm ⁻¹)
$\psi_{15} = 0.129 \Phi_1, -1\rangle + 0.983 \Phi_0, 0\rangle + 0.129 \Phi_{-1}, 1\rangle$	1432.0
$\psi_{14} = 0.141 \Phi_1, 0\rangle + 0.984 \Phi_0, 1\rangle + 0.098 \Phi_{-1}, 2\rangle$	1425.0
$\psi_{13} = 0.098 \Phi_1, -2\rangle + 0.984 \Phi_0, -1\rangle + 0.141 \Phi_{-1}, 0\rangle$	1425.0
$\psi_{12} = 0.140 \Phi_1, 1\rangle + 0.989 \Phi_0, 2\rangle$	1404.3
$\psi_{11} = 0.989 \Phi_0, -2\rangle + 0.140 \Phi_{-1}, -1\rangle$	1404.3
$\psi_{10} = \Phi_1, 2\rangle$	416.0
$\psi_9 = \Phi_{-1}, -2\rangle$	416.0
$\psi_8 = 0.989 \Phi_1, 1\rangle - 0.140 \Phi_0, 2\rangle$	297.7
$\psi_7 = -0.140 \Phi_0, -2\rangle + 0.989 \Phi_{-1}, 1\rangle$	297.7
$\psi_6 = 0.986 \Phi_1, 0\rangle + 0.130 \Phi_0, 1\rangle + 0.103 \Phi_{-1}, 2\rangle$	193.0
$\psi_5 = -0.103 \Phi_1, -2\rangle - 0.130 \Phi_0, -1\rangle + 0.986 \Phi_{-1}, 0\rangle$	193.0
$\psi_4 = -0.707 \Phi_1, -1\rangle - 0.179 \Phi_0, 0\rangle + 0.694 \Phi_{-1}, 1\rangle$	115.0
$\psi_3 = 0.694 \Phi_1, -1\rangle - 0.179 \Phi_0, 0\rangle + 0.694 \Phi_{-1}, 1\rangle$	71.0
$\psi_2 = 0.989 \Phi_{-1}, 2\rangle - 0.111 \Phi_0, 1\rangle + 0.089 \Phi_1, 0\rangle$	0.0
$\psi_1 = 0.989 \Phi_1, -2\rangle - 0.111 \Phi_0, -1\rangle + 0.089 \Phi_{-1}, 0\rangle$	0.0

2.2. Spin-orbit coupling

The spin-orbit interaction may be written as

$$H_{so} = \lambda \mathbf{L} \cdot \mathbf{S} = \alpha^2 \lambda_0 [L_z S_z + \frac{1}{2}(L_+ S_- + L_- S_+)]. \quad (4)$$

The coupling constant $\lambda = \alpha^2 \lambda_0$ where $\lambda_0 = -103 \text{ cm}^{-1}$ for the free ion and the factor α^2 accounts for the decrease in its magnitude due to covalency effects. S_{\pm} are the raising and lowering operators for the spin and L_{\pm} are those for the orbital angular momentum. The value of α^2 lies between 0.60 and 0.90 for Fe²⁺ in various ferrous compounds (Ingalls 1964, Okiji and Kanamori 1964, Kanamori 1958). Prinz *et al* (1973) have used the value of $\lambda = -105 \text{ cm}^{-1}$ in the analysis of far-infrared spectra of FeCO₃ and Meshcheryakov *et al* (1974) have used the value of $\lambda = -100 \text{ cm}^{-1}$ to explain the paramagnetic resonance lines of Fe²⁺ in CaCO₃. Hence a representative value of λ has been taken to be -100 cm^{-1} for Fe²⁺ in ZnCO₃.

When the net spin of Fe²⁺ is taken into account, the $5T_{2g}$ wavefunctions are 15-fold degenerate. These 15 spin-orbitals can be represented by $|\Phi_i, M_g\rangle$, where $i = 0, \pm 1$ and $M_g = 0, \pm 1, \pm 2$ are the five spin states of $S = 2$. Then for these 15 basic states the eigenvalue and the eigenfunction of the perturbing Hamiltonian in equation (3) are calculated. The wavefunctions and eigenvalues are listed in table 1.

The spin-orbit coupling leaves the ground doublet ψ_1 and ψ_2 degenerate in energy. These states have extremely anisotropic magnetic properties ($g_{\parallel} = 10, g_{\perp} = 0$) and it is between these two states that the Fe²⁺ ion relaxes at low temperatures. The two states of the ground doublet (ψ_1, ψ_2) will produce equal but opposite magnetic field at the Fe nucleus. For the first excited state ψ_3 , one obtains $\langle S_z \rangle = \langle S_x \rangle = 0$ and $\langle L_z \rangle = \langle L_x \rangle = 0$. Hence this state is completely non-magnetic, i.e. it cannot produce any magnetic field at the nucleus. At low temperatures the ground doublet is most dominant in deciding the nature of the Mössbauer spectrum. The ion can relax between the states ψ_1 and ψ_2 and the effective magnetic hyperfine interaction will depend upon the rate of spin

fluctuations between these states. Therefore our aim is to calculate the spin relaxation rate between ψ_1 and ψ_2 .

It may be further noted that $\langle \psi_1 | S_{\pm} | \psi_2 \rangle = 0$, which means that between these states themselves the spin-spin relaxation cannot proceed at all, irrespective of the concentration of Fe^{2+} ions. Therefore, in the case of Fe^{2+} in ZnCO_3 at low temperatures, the dominant relaxation mechanism can be expected to arise from the spin-lattice (or spin-phonon) interaction only. The spin-lattice relaxation proceeds mainly through the indirect Raman and Orbach processes, except at extremely low temperatures when the direct one-phonon process may be more important. The spin relaxation rate of Fe^{2+} in ZnCO_3 shows a strong temperature dependence (Price *et al* 1977) as the fully resolved magnetic hyperfine spectrum at 4.2 K completely collapses into a quadrupole doublet at about 50 K. From the changing pattern of the hyperfine spectrum, Price *et al* (1977) have measured the experimental values of the spin relaxation rate by using the stochastic method of simulating the Mössbauer lineshape in the presence of a time-dependent axial magnetic field given by Blume and Tjon (1968). They have further calculated the spin relaxation rates for the Raman and Orbach processes and then fitted them with the experimental data. They have used the simple phenomenological model of Orbach for the orbit-lattice interaction and their calculations are no doubt subject to the accuracy of the simple model for orbit-lattice interaction. It is found that their calculated spin-lattice relaxation rates and the observed values (Price *et al* 1977) differ by a factor of 10^3 – 10^4 over the temperature range of measurement.

3. Evaluation of mixed-spin-relaxation rate

The electronic spin relaxation properties of any paramagnetic ion depend mainly on the nature of its low-energy electronic eigenstates. However, the calculation of the spin relaxation rate also requires the knowledge of various excited eigenstates of the ion, the vibrational states of the lattice and the dynamical crystal-field parameters. The calculation of the mixed-spin-relaxation rate will require the knowledge of the ground doublet (ψ_1, ψ_2) or (a, b) and the excited states (ψ_3, ψ_4) or (c, d) apart from the dynamical crystal-field parameters, the velocity of sound in the crystal and the Debye temperature of the crystal. The contribution of higher excited states will be small and hence can be neglected.

The dynamic crystal-field parameters are usually unknown and different approximations have been used to estimate them from a knowledge of the static crystal-field parameters. Huang has suggested that the dynamic parameters are greater than the static parameters by a factor of P_n which is equal to $n + 1$. In Orbach's (1961) view the dynamic and static crystal-field parameters are very similar and the different parameters for the same value of n are roughly equal. This is especially true for transition-metal ions. Scott and Jeffries (1962) have also commented on this aspect and they agree more or less with Orbach's proposition. Price *et al* (1977) have used the same approximation while calculating the spin-lattice relaxation rates of Fe^{2+} in ZnCO_3 .

In view of these comments, the dynamical crystal-field parameters for Fe^{2+} in ZnCO_3 may be reasonably taken as $|B_2^m| = |B_4^m| = 100 \text{ cm}^{-1}$, the values used by Price *et al* (1977).

Matrix elements such as $\langle \psi_1 | \sum_{n,m} V_n^m | \psi_3 \rangle$ can exist only between those basis states which have identical spin values. Hence the orbit-lattice interaction part can be calculated as follows:

$$\langle \psi_1 | \sum_{n,m} V_n^m | \psi_3 \rangle = \langle \psi_1 | B_n^m O_n^m | \psi_3 \rangle = - \{ -(0.111)(0.694) \langle \Phi_0 | B_2^2 O_2^2 + B_4^2 O_4^2 | \Phi_1 \rangle \} \\ - \{ (0.089)(0.179) \langle \Phi_{-1} | B_2^2 O_2^2 + B_4^2 O_4^2 | \Phi_0 \rangle \} \quad (5)$$

(dropping the identical spin parts). Substituting the values of the wavefunctions Φ_0 and Φ_{-1} and using the tables of Buckmaster (1962) and Abragam and Bleaney (1970), one finally obtains

$$\langle \psi_1 | \sum_{n,m} V_n^m | \psi_3 \rangle = 25.1 \text{ cm}^{-1}$$

and similarly

$$\langle \psi_3 | \sum_{n,m} V_n^m | \psi_1 \rangle = 25.1 \text{ cm}^{-1}.$$

Hence

$$\langle \psi_1 | \sum_{n,m} V_n^m | \psi_3 \rangle \langle \psi_3 | \sum_{n,m} V_n^m | \psi_1 \rangle = 630.01 \text{ cm}^{-2}.$$

The matrix elements over spin operators such as $\langle \psi_3 | S_{\pm} | \psi_2 \rangle$ can exist only between those basis states $|\Phi_i, M_g\rangle$ which have identical angular momentum parts (Φ_i) but differ in their spin values by ± 1 . Thus the spin-spin interaction part can also be evaluated as

$$\langle \psi_3 | S_- | \psi_2 \rangle = 0.061 \langle -1 | S_- | 0 \rangle + 0.019 \langle 0 | S_- | 1 \rangle + 0.686 \langle 1 | S_- | 2 \rangle = 1.57$$

(dropping the identical Φ_i parts). Similarly

$$\langle \psi_2 | S_+ | \psi_3 \rangle = 1.57.$$

Thus

$$\langle \psi_3 | S_- | \psi_2 \rangle \langle \psi_2 | S_+ | \psi_3 \rangle = (1.57)^2 = 2.46.$$

The calculation of the mixed-spin-relaxation rate (Srivastava and Singh 1980) also needs an estimate of various other parameters for the experimental lattice. For a $ZnCO_3$:20% Fe^{2+} Mössbauer sample (Price *et al* 1977), the separation (R_{jl}) between the j th and l th paramagnetic Fe^{2+} ions is of the order of 30 Å and here this value is found to be 25 Å. The effect of next-nearest neighbours on the relaxation rate will be small because $\langle R_{jl}^{-3} \rangle$ will be sufficiently reduced. The velocity of acoustic phonons in $ZnCO_3$: Fe^{2+} sample has been estimated as $v = 4 \times 10^5 \text{ cm s}^{-1}$ from the Debye temperature measured by the Mössbauer method (Price *et al* 1977) and $\rho = 4.4 \text{ g cm}^{-3}$.

Now the dipolar coupling constant G (Srivastava and Singh 1980) has a magnitude lying between -2 and 1 . Any central Fe^{2+} ion will have several other surrounding Fe^{2+} ions as its nearest neighbours in different directions. The neighbouring ion for which $1 - 3 \cos^2 \theta_{jl} \approx 0$ i.e. $\theta_{jl} = 55^\circ$, does not make any significant contribution towards the net relaxation rate. It is seen that this term assumes the maximum positive value of the order of unity for the angular region $\theta_{jl} = 90^\circ$. Therefore it is assumed that $1 - 3 \cos^2 \theta_{jl} = 1$. Now the lineshape function (or the density of states) $g(\omega)$ for the spin-spin transition depends upon the contribution of paramagnetic ions in the crystal and it

may be reasonable to assume that $g(\omega) \approx 10^{-4}$ s. Using these estimated values of various parameters and $\Delta_c = 71 \text{ cm}^{-1}$, the expression for the mixed-spin-relaxation rate (Srivastava and Singh 1980) is given as

$$(1/T_{\text{mixed}})\psi_3 = 3.769 \times 10^6 T^4 [2 \exp(\Delta_c/k_B T) + 1]^{-1} [\sin(kR_{ji})]/kR_{ji}. \quad (6)$$

The second excited state |d) (i.e. ψ_4) is situated at an energy $\Delta_d = 115.4 \text{ cm}^{-1}$ above the ground doublet. The spin relaxation can also proceed via this state whose rate is finally expressed as

$$(1/T_{\text{mixed}})\psi_4 = 2.4 \times 10^6 T^4 [2 \exp(\Delta_d/k_B T) + 1]^{-1} [\sin(kR_{ji})]/kR_{ji}. \quad (7)$$

Neglecting contributions from higher excited states one can write

$$1/T_{\text{mixed}} = (1/T_{\text{mixed}})\psi_3 + (1/T_{\text{mixed}})\psi_4. \quad (8)$$

It may be noted that the function $[\sin(kR_{ji})]/kR_{ji}$ also depends on temperature as the phonon wavelength ($k = 2\pi/\lambda$) depends on the temperature of the lattice. At a temperature T the acoustic phonons will have an energy $\hbar\omega \approx k_B T$ (k_B is Boltzmann's constant) and, assuming that phonon wave velocity $v = 4 \times 10^5 \text{ cm sec}^{-1}$, one obtains the phonon wavelength $\lambda = 200 \text{ \AA}$ at 10 K and $\lambda = 50 \text{ \AA}$ at 40 K. In the temperature range 10–35 K, it appears that $\lambda/2 > R_{ji}$ (for nearest Fe^{2+} pairs) and hence the mixed-spin-relaxation process may be physically allowed (Srivastava and Singh 1980). The contribution to relaxation rates from the next-nearest neighbours should not be taken into account in view of the added fact that the condition $\lambda/2 > R_{ji}$ breaks down at much lower temperatures. On the basis of these estimates, one finds that $[\sin(kR_{ji})]/kR_{ji} = 0.90, 0.78, 0.64, 0.47, 0.29$ and 0.14 at $T = 10 \text{ K}, 15 \text{ K}, 20 \text{ K}, 25 \text{ K}, 30 \text{ K}$ and 35 K , respectively, and using these values the relaxation rates can now be calculated from equations (6)–(8). The calculations indicate that the second term in equation (8) is less than one tenth of the first term.

4. Results and discussion

Using the Mössbauer method the electronic spin relaxation rates are measured by observing the broadening of the absorption peaks and for the ^{57}Fe isotope the relaxation rates can be measured within the range 10^9 – 10^{11} s^{-1} only, beyond which the absorption peaks assume the natural linewidth (Wickman 1966). The calculated values of the mixed-spin-relaxation rates have been compared with the experimentally observed values given by Price *et al* (1977) in figure 2. It is found that the calculated relaxation rates are about 1.3–9 times that of the observed values. In view of the fact that various parameters had to be estimated, the agreement between the calculated and observed values must be regarded as reasonably good. In the derivation of the expression (Srivastava and Singh 1980) for $1/T_{\text{mixed}}$ the integral

$$\int_0^{\theta_D/T} x^3 \exp(-x) dx$$

(where $x = \hbar\omega/2k_B T$) has been considered for very low temperatures where effectively the upper limit of integration extends to infinity and the value of the integral approximates to $3!$. However, as the temperature increases, the value of the integral progressively diminishes and, if this is taken into account, the calculated value of spin

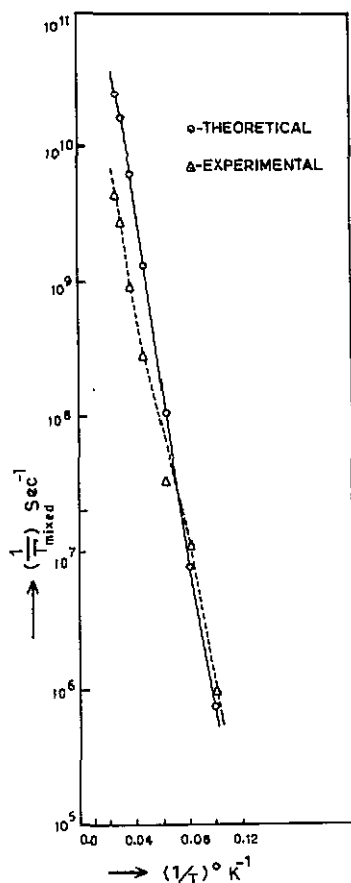


Figure 2. Mixed-spin-relaxation rate plotted against the inverse temperature.

relaxation rate will also be decreased accordingly. This will bring about better agreement between the calculated and observed data. Apart from this a small adjustment in the values of the crucial parameters R_{jl} , ν and $g(\omega)$ can also improve the agreement between the calculated and observed relaxation rates. It may be further noted that on a similar simple model of orbit-lattice interaction the calculated spin-lattice relaxation rates (Price *et al* 1977) for Raman and Orbach process were about 10^3 – 10^4 times smaller than the observed values.

5. Conclusion

On the basis of these observations and comments it can be said with confidence that at low temperatures the 'mixed-spin-relaxation process' is also a competing mode for the energy exchange between electronic spins and lattice vibrations.

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