appropriate choice of trial function. Further investigation along these lines, with a view to performing calculations for realistic potentials, is in progress.

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WEAKLY ALLOWED TRANSITIONS IN THE SPIN-LATTICE RELAXATION OF SPIN PAIRS

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Weakly allowed transitions alter the magnitude and dependence on temperature and frequency of the spin lattice relaxation rate of antiferromagnetically coupled pairs of spins. These transitions, allowed because the phonon wavelength is finite, appear to have been observed in $(NH_4)_2PtCl_6$:Ir.

In a recent paper [1] it was shown that the acoustic resonance spectrum of pairs of ions with effective spin $\frac{1}{2}$ contained lines which were allowed because the phonon wavelength was finite. These transitions, forbidden when the phonon phase is the same at both the ions in the pair, give large contributions to the moments of the acoustic resonance line shape [1, 2] but have very low intensity and should be very difficult to detect directly. It is shown here that for antiferromagnetically coupled pairs the temperature dependence of the relaxation rate in the excited state is altered by these transitions, which appear to have been detected in $(NH_4)_2PtCl_6$:Ir [3].

The eigenstates of a pair of spins $\frac{1}{2}$ with isotropic exchange $JS_1 \cdot S_2$ can be expressed in terms of the states $|S_{1z}, S_{2z}\rangle$. The antisymmetric state $|a\rangle = \{|+-\rangle - |-+\rangle\}/\sqrt{2}$ is the ground state at energy zero; $|s\rangle$, the symmetric state $\{|+-\rangle + |-+\rangle\}/\sqrt{2}$ lies at energy J, and $|\pm\rangle = |\pm\pm\rangle$ are at $J \pm \delta$, where $\delta = g\beta H$ is the Zeeman energy. We omit anisotropic exchange terms as they produce no new effects, unless the modulation of the spin-spin interaction contributes appreciably to the relaxation rate. Explicit calculation shows that this is not the case.

The spin-lattice interaction for the pair can be written $h = h_1 + h_2$, where h_i only involves the spin operators of the ith spin. h has no matrix elements between $|++\rangle$ and $|--\rangle$. Two relaxation mechanisms are important at low temperatures - the usual direct process transitions between $|s\rangle$ and $|\pm\rangle$, and those from the transitions between $|a\rangle$ and $|\pm\rangle$ which are slightly allowed by the finite phonon wavelength. The relaxation rates associated with these mechanisms are $1/\tau_p^i$ and $1/\tau_p^\pi$ respectively, the observed rate $1/\tau_p$ being the sum of the two.

The transition probabilities $W(a \rightarrow b)$ can be written in terms of temperature independent probabilities U, V for convenience, where

$$W(s \rightarrow +) = W(+ \rightarrow s)\exp(-\delta/kT) = n(\delta)\cdot U$$
$$W(a \rightarrow +) = W(+ \rightarrow a)\exp(-J/kT) = n(J)\cdot V \qquad (1)$$

in which $n(E) = [\exp(E/kT) - 1]^{-1}$ and we have

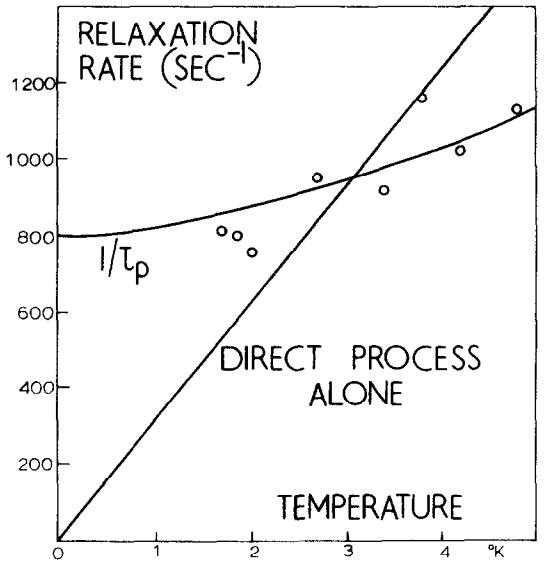

Fig. 1.

assumed $J \gg \delta$; other transition probabilities are simply related to those given, e.g. $W(s \rightarrow +) = W(- \rightarrow s)$. As mentioned earlier $W(+ \rightarrow -)$ is zero as $\langle ++|h|--\rangle$ vanishes. U and V are related by

$$V/U = \{\tfrac{1}{3}(\tfrac{1}{2}qa)^2\}(J/\delta)^3 = a^2J^5/12\hbar^2v^2\delta^3 \ , \qquad (2)$$

where q is the wave vector of phonons of energy J, a the separation of the spins in the pair and v the velocity of sound. The factor $\frac{1}{12}q^2a^2$ in eq. (2) is obtained in ref. 1, and the second factor comes from the standard dependence of spin lattice transition probabilities on the cube of the energy [4] for a Debye density of states. The increase in density of states of phonons of energy J over those of energy δ is important in making $1/\tau_p''$ appreciable.

The usual direct process contribution to the relaxation rate is, noting $kT \gg \delta$,

$$1/\tau_p' = U[n(\delta) + \tfrac{1}{2}] \approx UkT/\delta \ , \qquad (3)$$

from transitions within the triplet. The contribution of the weakly allowed transitions between $|a\rangle$ and the triplet is

$$1/\tau_p'' = V[1 - \exp(-J/kT)]^{-1} \ . \qquad (4)$$

$1/\tau_p''$ is temperature independent at low temperatures, but linear in T when $kT \gg J$; this contribution to the relaxation rate is independent of the resonance energy δ. $1/\tau_p'$ is proportional to δ^2 * so the relative contributions of the two mechanisms depend on both temperature and resonant frequency. The observed relaxation rate is

$$1/\tau_p = [1 + A\chi/(1 - e^{-\chi})]/\tau_p' \ , \qquad (5)$$

in which $x = J/kT$ and $A = (a^2/12\hbar^2v^2)J^4/\delta^2$. At very low temperatures eq. (5) tends to the *finite* value $V = A/\tau_p'$. From this value the rate increases with temperature, linearly as $1/\tau_p'$ at first, and tending asymptotically to $(1 + A)/\tau_p'$ at high temperatures. Qualitatively this is quite different from the simple linear dependence of $1/\tau_p'$ on temperature, which omits the weakly allowed transitions.

As an example we use the data of refs. 3 and 5 for Ir^{4+} pairs in $(NH_4)_2PtCl_2$. For these $J = k \times 7.5^{\circ}$, $a = 6.98$ Å, $v \approx 2 \times 10^5$ cm/sec and $\delta/\hbar = 9.5 \times 10^9$ sec^{-1}. A is 4.67, and $1/\tau_p$ from eq. (5) is plotted in the figure. No theoretical estimate of U has been made, U being chosen so that the theoretical curve passes through the centre of gravity of the experimental points; this is the only arbitrary parameter. Although there is considerable scatter in the experimental results there is reasonable agreement with $1/\tau_p$ of eq. (5) and the results are inconsistent with a simple direct process alone, also shown in the figure. This confirms the existence of the weakly allowed transitions discussed in ref. 1.

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* The frequency dependence of $1/\tau_p'$ is δ^2, and not δ^4 which might be expected for Kramer's ions; it is the exchange interaction, rather than the applied magnetic field, which destroys the Kramer's degeneracy in this case.

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