material can be deduced in as much detail as it is now known for several nontransition metals.

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[1] M. Ya. Azbel' and E. A. Kaner, J. Phys. Chem. Solids 6, 113 (1958).

[2] A. F. Kip, D. N. Langenberg, and T. W. Moore, Phys. Rev. 124, 359 (1961).

[3] E. Fawcett, Bull. Am. Phys. Soc. 7, 231 (1962), and to be published.

[4] M. S. Khaikin, J. Exptl. Theoret. Phys. (U.S.S.R.) 39, 212 (1960) [translation: Soviet Phys.-JETP 39(12), 152 (1961)].

[5] J. A. Rayne and H. Sell, Phys. Rev. Letters 8, 199 (1962).

SPIN-LATTICE RELAXATION IN MULTILEVEL SPIN SYSTEMS

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We wish to report the possibility of a new temperature dependence for the spin-lattice relaxation time due to two-phonon Raman processes in multilevel spin systems. The process is simply an extension of the Van Vleck[1] "cancellation" argument for a Kramers doublet lowest to the case when there is a multilevel Kramers state lowest in energy. In the former case Van Vleck found $T_1 \propto T^{-9}$ in the Raman region. We find for the latter case, in addition to the T^{-7} dependence of T_1 found by Van Vleck, a T^{-5} dependence of T_1 in the low-temperature part of the Raman region. The T^{-5} law competes with the T^{-7} term, but should be relatively more important in the rare-earth group and third transition group than in the first and second transition groups. A very rough order-of-magnitude argument gives the criterion,

$$\lambda(\lambda/\Delta) > kT,$$

for the dominance of the T^{-5} term over the T^{-7} term in the first two transition groups. Here, λ is the spin-orbit coupling constant, and Δ is an appropriate crystalline field splitting. In the rare-earth group, however, where the crystalline field splittings are small compared to the spin-orbit splittings, the criterion for the appearance of the T^{-5} law is simply:

$$\Delta > kT.$$

To be specific, let us examine a situation where the T^{-5} law is sure to dominate over at least a portion of the Raman region. Consider a rare-earth ion in a cubic environment such that a Γ_8 quartet is lowest in energy. Such would definitely be the case[2] for Ce^{3+}, Nd^{3+}, and Sm^{3+} in a cubal environment (eightfold coordination) and, depending on the relative size of the fourth and sixth order crystalline field terms, for Dy^{3+} in a cubal environment and for Nd^{3+}, Dy^{3+}, and Er^{3+} in an octahedral environment. Consider the case of Sm^{3+} in a cubal environment. The wave functions are[3]

$$|\Gamma_8, M_J = \tfrac{3}{2}\rangle = -(\tfrac{1}{6})^{1/2}|J = \tfrac{5}{2}, M_J = \tfrac{3}{2}\rangle - (\tfrac{5}{6})^{1/2}|J = \tfrac{5}{2}, M_J = -\tfrac{5}{2}\rangle;$$

$$|\Gamma_8, M_J = \tfrac{1}{2}\rangle = |J = \tfrac{5}{2}, M_J = \tfrac{1}{2}\rangle;$$

$$|\Gamma_8, M_J = -\tfrac{1}{2}\rangle = -|J = \tfrac{5}{2}, M_J = -\tfrac{1}{2}\rangle;$$

$$|\Gamma_8, M_J = -\tfrac{3}{2}\rangle = (\tfrac{5}{6})^{1/2}|J = \tfrac{5}{2}, M_J = \tfrac{5}{2}\rangle + (\tfrac{1}{6})^{1/2}|J = \tfrac{5}{2}, M_J = -\tfrac{3}{2}\rangle. \quad (1)$$

The wave functions for Nd^{3+}, Dy^{3+}, and Er^{3+} are not so simple because there is more than one Γ_8 quartet in the ground multiplet, and the detailed nature of the wave functions will depend on the ratio of the fourth to sixth order crystalline field terms. The orbit-lattice interaction is written[4]

$$V_{\mathrm{OL}} = \sum_{\substack{m=\theta,\epsilon \\ l=2,4,6}} V(\Gamma_{3g},l)C(\Gamma_{3g}l,m)e(\Gamma_{3g},m)$$

$$+ \sum_{\substack{m=0,\pm 1 \\ l=2,4,6}} V(\Gamma_{5g},l)C(\Gamma_{5g}l,m)e(\Gamma_{5g},-m)(-1)^m, \qquad (2)$$

where only $l=2,4$ terms contribute for Sm^{3+} if we remain in the ground $J=\frac{5}{2}$ manifold. The $V(\Gamma_{ig},l)$ are phenomenological coefficients; the $C(\Gamma_{ig}l,m)$ and the $e(\Gamma_{ig},m)$ are linear combinations of Racah's[5] $C_{\lambda\mu}$ and of the strain tensor, respectively, which transform as the mth subvector of the Γ_{ig} irreducible representation of the cubic group O_h. For the rare-earth group, the matrix elements of the $C_{\lambda\mu}$ are

$$\langle f^n\tau'U'v'SL'J'J_z'|C_{\lambda\mu}|f^n\tau UvSLJJ_z\rangle$$

$$=(-1)^{J_z'+S-L}\begin{pmatrix} J' & \lambda & J \\ -J_z' & \mu & J_z \end{pmatrix}\begin{Bmatrix} L' & J' & S \\ J & L & \lambda \end{Bmatrix}[(2J+1)(2J'+1)]^{1/2}$$

$$\times(f^n\tau'U'v'SL'\|C_\lambda\|f^n\tau UvSL), \qquad (3)$$

upon rearranging the expression of Elliott, Judd, and Runciman.[6] The double bar matrix element in (3) is easily evaluated using Racah's[7] fractional parentage coefficients. For Sm^{3+} in the ground multiplet, we find

$$(\psi\|C_2\|\psi)=-\tfrac{1}{3}(143/14)^{1/2};$$

$$(\psi\|C_4\|\psi)=\tfrac{2}{3}(13/7)^{1/2}. \qquad (4)$$

The spin-lattice Raman relaxation rate for rare-earth ions for transitions between levels M_J and $M_{J'}$ due to interactions of the type (2) is given by[8]

$$A_{M_J\to M_{J'}}=\frac{9}{(2\pi)^3\rho^2v^{10}}\int\Bigg[\sum_{\substack{m,m' \\ i,i'}}\Bigg|\sum_{l,l',M_{J''}}\Bigg\{\frac{\langle M_{J'}|C(\Gamma_{ig}l,m)|M_{J''}\rangle\langle M_{J''}|C(\Gamma_{i'g}l',m')|M_J\rangle}{E_{M_J}-E_{M_{J''}}+\hbar\omega_{i'm'}}$$

$$+\frac{\langle M_{J'}|C(\Gamma_{i'g}l',m')|M_{J''}\rangle\langle M_{J''}|C(\Gamma_{ig}l,m)|M_J\rangle}{E_{M_J}-E_{M_{J''}}-\hbar\omega_{i'm'}}\Bigg\}V(\Gamma_{ig},l)V(\Gamma_{i'g},l')\Bigg|^2\Bigg]$$

$$\times\omega_{i'm'}{}^6\operatorname{csch}^2(\hbar\omega_{i'm'}/2kT)d\omega_{i'm'}, \qquad (5)$$

where E_{M_J} is the energy of the level $|J,M_J\rangle$; and we have set $\hbar\omega_{im}\sim\hbar\omega_{i'm'}$, the energy of the phonon destroyed by $e(\Gamma_{i'g},m)$, i.e., we have ignored the Zeeman energy in comparison with $\hbar\omega_{im}$, $\hbar\omega_{i'm'}$. In the case Van Vleck considered, $|M_{J''}\rangle$ was split apart from $|M_J\rangle$ and $|M_{J'}\rangle$ by a crystalline field energy $\Delta\sim 10\,000\ \mathrm{cm}^{-1}$. If $|M_J\rangle$ and $|M_{J'}\rangle$ are Kramers conjugates of one another (i.e., time reversed states of half integral spin), it is easily seen that the numerators of the two terms in the integrand of (5) are of equal magnitude, but are opposite in sign. Hence, a cancellation occurs, and if $E_{M_J}-E_{M_{J'}}\gg\hbar\omega_{i'm'}\sim kT$, the term in the curly brackets reduces to

$$\langle M_{J'}|C(\Gamma_{ig}l,m)|M_{J''}\rangle\langle M_{J''}|C(\Gamma_{i'g}l',m')|M_J\rangle$$

$$\times\frac{2\hbar\omega_{i'm'}}{(E_{M_J}-E_{M_{J''}})^2}.$$

This, when squared and inserted in (5), immediately gives $A_{M_J\to M_{J'}}\propto T^9$ for Kramers conjugate states $|M_J\rangle$, $|M_{J'}\rangle$. If, however, $|M_J\rangle$ and $|M_{J'}\rangle$ are not time reversed Kramers states, as for example in a multilevel spin system, then no cancellation occurs, and from (5), $A_{M_J \rightarrow M_{J'}} \propto T^7$. By assumption, $kT \ll \Delta$, and thus the T^9 terms will be negligible compared to the T^7 terms in a multilevel system, and the relaxation time T_1 should be proportional to T^{-7} in the Raman region.

However, there is a possibility which is certainly unimportant for the multilevel ion (Cr^{3+}) Van Vleck considered, but which we feel is important for rare-earth ions and which may be important for third transition group ions. There is no reason to demand a priori that $|M_{J''}\rangle$ be another crystalline field level split apart from the ground levels by a large energy—it could also be another one of the ground levels. Thus, for Sm^{3+}, $|M_J\rangle$ and $|M_{J'}\rangle$ could be the $|\Gamma_8, M_J = \frac{1}{2}\rangle$ and the $|\Gamma_8, M_J = -\frac{1}{2}\rangle$ levels, respectively, and then $|M_{J''}\rangle$ would be the $|\Gamma_8, M_J = \pm\frac{3}{2}\rangle$ levels. Hence, in the Raman region, we can ignore $E_{M_J} - E_{M_{J''}}$ in comparison with $\hbar\omega_{i'm'} \sim kT$. When the "cancellation" occurs, the terms in the curly brackets of (5) now add to give

$$\langle M_{J'} | C(\Gamma_{ig} l, m) | M_{J''} \rangle$$

$$\times \langle M_{J''} | C(\Gamma_{i'g} l', m') | M_J \rangle \frac{2}{\hbar\omega_{i'm'}}.$$

When squared and inserted into (5), this term gives $A_{M_J \rightarrow M_{J'}} \propto T^5$. We assert that this term will be larger than the usual T^7 term by $(\Delta/kT)^2$ for rare-earth ions, and thus should be dominant over a significant part of the Raman process region.[9]

An order-of-magnitude approximation can be made for both temperature dependences of T_1 for Sm^{3+} using (1), (3), (4), and (5). We assume typical values of $V(\Gamma_{ig}, l) \sim 500\ \mathrm{cm}^{-1}$, $\Delta \sim 50\ \mathrm{cm}^{-1}$, $\rho \sim 2\ \mathrm{g/cm}^3$, $v \sim 3 \times 10^5$ cm/sec, and find

$$A_{\frac{3}{2} \rightarrow \frac{1}{2}} \sim 10^{-6} T^7\ \mathrm{sec}^{-1};$$

$$A_{\frac{1}{2} \rightarrow -\frac{1}{2}} \sim 10^{-3} T^5\ \mathrm{sec}^{-1};$$

where T is the temperature in °K.

We further suggest a possible experiment to check these ideas directly. The application of a large uniaxial stress will destroy the cubic symmetry of the paramagnetic ion's environment, and will split the Γ_8 quartet into two doublets. When this occurs, it is possible that $E_{M_J} - E_{M_{J''}}$ can be made sufficiently large compared to kT so that the temperature dependence of T_1 ought to change from a T^{-5} law to a T^{-7} law.

A word should be said concerning the situation in iron-group salts. It is easily shown that for Cr^{3+} in an octahedral environment where the ground level is a ${}^4\Gamma_2$, $\langle M_{J''} | C(\Gamma_{ig} l, m) | M_J \rangle \propto \lambda/\Delta$, if $|M_{J''}\rangle$ is a ${}^4\Gamma_4$ or a ${}^4\Gamma_5$; but proportional to $(\lambda/\Delta)^2$ if $|M_{J''}\rangle$ is another level within the ${}^4\Gamma_2$ ground level. Hence, the T^7 term in $A_{M_J \rightarrow M_{J'}}$ will be proportional to $(\lambda/\Delta)^4/\Delta^2$ [as can be seen from (5)], whereas our proposed T^5 term will be proportional to $(\lambda/\Delta)^8/(kT)^2$. Comparing, we see that, very roughly, if $\lambda(\lambda/\Delta) \gtrsim kT$, then $T_1 \propto T^{-5}$. Preliminary measurements of Castle and Feldman[10] on V^{2+} in cubic sites in MgO indicate that $T_1 \propto T^{-5}$ in the temperature region of $16 < T < 90$°K. Unfortunately, the relaxation mechanism we have presented here does not appear capable of entirely accounting for the dominance of the T^{-5} term over such a large temperature range, as λ/Δ is about the same for V^{2+} as for (isoelectronic) Cr^{3+}, and the latter ion's T_1 in MgO does seem proportional to T^{-7} over the same temperature range.

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[1] J. H. Van Vleck, J. Chem. Phys. 7, 72 (1939); Phys. Rev. 59, 730 (1941).

[2] K. R. Lea, M. J. M. Leask, and W. P. Wolf, Technical note 9/62, Oxford University, Oxford, England (unpublished).

[3] J. S. Griffith, The Theory of Transition Metal Ions (Cambridge University Press, New York, 1961), p. 393.

[4] M. Blume and R. Orbach (to be published).

[5] G. Racah, Phys. Rev. 62, 438 (1942).

[6] J. P. Elliott, B. R. Judd, and W. A. Runciman, Proc. Roy. Soc. (London) A240, 509 (1957).

[7] G. Racah, Phys. Rev. 76, 1352 (1949).

[8] R. Orbach, Proc. Roy. Soc. (London) A264, 458 (1961).

[9] We have not considered terms in V_{OL} which are proportional to e^2 and which contribute to the Raman processes in first order. Such terms can be shown to be of the same order of magnitude as those we have considered giving rise to the T^7 dependence, but they will not contribute to the T^5 dependence.

[10] J. G. Castle and D. W. Feldman (to be published).