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Phonon-Induced Corrections to the Van Vleck Temperature-Independent Susceptibility*

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The dynamic spin-phonon correction to the Van Vleck temperature-independent susceptibility is computed for Eu^{3+} in a cubic crystalline-field environment. A T^4 law is predicted for the temperature-dependent part of the correction. A numerical estimate indicates the effect to be very small for orbit-lattice parameters appropriate to a "slow-relaxing" model, but a sizeable correction if parameters appropriate to a "fast-relaxing" model are assumed. It is shown that $U^{4+}(5f^2)$ in a cubic environment where the singlet (Γ_1) lies below the triplet (Γ_5) would be an excellent prospect for observation of this correction, in part because of the larger dynamic crystalline-field coefficients expected in the actinide series.

I. INTRODUCTION

THE spin-phonon interaction controls, in part, the dynamical behavior of the spin system when the spins have been forced out of an equilibrium condition with respect to the lattice. The return to thermal equilibrium, described by a characteristic time T_1, has been outlined in detail by Waller,[1] Kronig,[1] Van Vleck,[3] and others.[4] More recently, Inoue[5] has indicated how the spin-phonon interaction mechansim can affect the static properties of the spin system, deriving the expected corrections to the g value for Ho^{2+} and Tm^{2+} in CaF_2 and ytterbium gallium garnet (YbGaG), and the correction to the temperature-independent susceptibility for YbGaG. We wish in this paper to analyze the temperature-dependent effects of the spin-phonon interaction on the paramagnetic susceptibility of ions for which the ground state is a singlet.[6] This investigation has some relation to the controversy between the "slow" and "fast" relaxing theories of the rare-earth iron garnets. A T^4 correction to the normally temperature-independent Van Vleck paramagnetism will obtain in the presence of spin-phonon interactions, as stated by Inouse,[5] and, in a not unconnected paper, by Pincus and Winter.[7] This dependence will be large if coupling constants appropriate to a "fast" relaxing theory are assumed, but negligible for the rare-earth garnets for values of the coupling constants appropriate to a "slow" relaxing theory. Use is made of perturbation theory in the next section to derive an explicit expression for the contribution to the magnetic susceptibility from thermal excitation of perturbed lattice vibrations.

II. FORMULATION OF THE PROBLEM

The Hamiltonian for a paramagnetic salt can be broken into three parts,

$$\mathcal{H}=\mathcal{H}_L+\mathcal{H}_S+\mathcal{H}_{SL}. \tag{1}$$

The first term represents the lattice vibrations in the harmonic approximation. We assume $\mathcal{H}_L$ diagonal so that

$$\mathcal{H}_L=\sum_{fs}(n_{fs}+1/2)\hbar\omega_{fs}, \tag{2}$$

the sum going over the N reciprocal lattice values of the phonon wave vector **f**, and $s=1, 2, 3,\cdots$ labeling the polarization index of the phonon modes. We concern only ourselves with acoustic phonons, so that $s=1$, 2, or 3. We also shall take, eventually, directional averages of the square of the strain, at which time we shall assume a cubic lattice, but, for simplicity, vibrational modes which are purely longitudinal or transverse with velocities independent of **f**. This latter assumption should not affect the validity of our treatment, nor the rough magnitudes we estimate for the effect.

The second term $\mathcal{H}_S$ represents the static Hamiltonian governing the behavior of the paramagnetic electrons, and includes the free-ion Hamiltonian, the crystalline field, and the Zeeman interaction. We thus assume, contrary to more usual treatments, that the Zeeman interaction has been taken into account in $\mathcal{H}_S$. The correction to the magnetic moment will be computed directly, so that the evaluation of χ in the limit $H\rightarrow 0$ requires only the retention of first-order Zeeman terms in $\mathcal{H}_S$.

The last term, $\mathcal{H}_{SL}$, represents the interaction between the orbital moment of the paramagnetic electrons and the change in the electric crystalline field brought about by the lattice vibrations. It has the form, for cubic crystals,[8]

$$\mathcal{H}_{SL}=\sum_{l=2,4,\cdots}\sum_{m=\theta,\epsilon}V(\Gamma_{3g}l)C(\Gamma_{3g}l,m)\epsilon(\Gamma_{3g},m)+\sum_{l=2,4\cdots}\sum_{m=\pm1,0}V(\Gamma_{5g}l)C(\Gamma_{5g}l,m)\epsilon(\Gamma_{5g},-m)(-1)^m, \tag{3}$$

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[1] I. Waller, Z. Physik **79**, 370 (1932).

[2] R. de L. Kronig, Physica **6**, 33 (1939).

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

[5] M. Inoue, Phys. Rev. Letters **11**, 196 (1963).

[6] This condition is necessary because otherwise the temperature-dependent corrections to the Van Vleck susceptibility will be masked by the usual Curie term.

[7] P. Pincus and J. Winter, Phys. Rev. Letters **7**, 269 (1961).

[8] M. Blume and R. Orbach, Phys. Rev. **127**, 1587 (1962).

where the sum over l stops at 4 for d electrons, 6 for f electrons, etc. The coefficient $V(\Gamma_{ig}l)$ is an interaction constant for the lth component of the expansion in spherical harmonics (Y_l^m) of the potential produced by a vibration transforming as the mth row of the ith even irreducible representation of the cubic group. $C(\Gamma_{ig}l,m)$ is the appropriate linear combination of normalized spherical harmonics [i.e. $C_l^m=(4\pi/2l+1)^{1/2}Y_l^m$] which transform as the mth row of the ith irreducible representation of the cubic group, and $\epsilon(\Gamma_{ig},m)$ is a similar combination of the strain tensor. Reference 8 lists the linear combinations appropriate to $C(\Gamma_{ig}l,m)$ and $\epsilon(\Gamma_{ig},m)$ of which we shall make use in this paper.

The unperturbed wave functions for the spins and phonons are the simple product functions

$$|\mathbf{f}s,j\rangle=|\mathbf{f}s\rangle|j\rangle,$$

where $|j\rangle$ refers to the eigenvalues of $\mathcal{H}_S$.

Regarding $\mathcal{H}_{SL}$ as a perturbation, second-order perturbation theory yields

$$|\mathbf{f}s,j\rangle'=|\mathbf{f}s,j\rangle+\sum_{r,\mathbf{f}'s'}{}'\frac{(\mathcal{H}_{SL})_{\mathbf{f}'s',r;\mathbf{f}s,j}|\mathbf{f}'s',r\rangle}{(E_{\mathbf{f}s,j}-E_{\mathbf{f}'s',r})}$$
$$+\sum_{r,t,\mathbf{f}'s',\mathbf{f}''s''}{}'\frac{(\mathcal{H}_{SL})_{\mathbf{f}''s'',t;\mathbf{f}s,j}(\mathcal{H}_{SL})_{\mathbf{f}'s',r;\mathbf{f}''s'',t}|\mathbf{f}'s',r\rangle}{(E_{\mathbf{f}s,j}-E_{\mathbf{f}'s',r})(E_{\mathbf{f}s,j}-E_{\mathbf{f}''s'',t})}-\tfrac{1}{2}|\mathbf{f}s;j\rangle\sum_{r,\mathbf{f}'s'}{}'\frac{|(\mathcal{H}_{SL})_{\mathbf{f}'s',r;\mathbf{f}s,j}|^2}{(E_{\mathbf{f}s,j}-E_{\mathbf{f}'s',r})^2},\quad(4)$$

where

$$(\mathcal{H}_{SL})_{\mathbf{f}'s',r;\mathbf{f}s,j}=\langle\mathbf{f}'s',r|\mathcal{H}_{SL}|\mathbf{f}s,j\rangle,$$

and the primes indicate $|\mathbf{f}'s',r\rangle\neq|\mathbf{f}s,j\rangle$, etc. Choosing the Z direction to be parallel to the external field, we find the correction to the magnetic moment to be

$$\langle\mathbf{f}s,j|\mu_Z|\mathbf{f}s,j\rangle=\sum_{r,t,\mathbf{f}'s',\mathbf{f}''s''}\left\{\frac{\langle\mathbf{f}s,j|\mu_Z|\mathbf{f}'s',r\rangle\langle\mathbf{f}'s',r|\mathcal{H}_{SL}|\mathbf{f}''s'',t\rangle\langle\mathbf{f}''s'',t|\mathcal{H}_{SL}|\mathbf{f}s,j\rangle}{(E_{\mathbf{f}s,j}-E_{\mathbf{f}'s',r})(E_{\mathbf{f}s,j}-E_{\mathbf{f}''s'',t})}\right.$$
$$+\frac{\langle\mathbf{f}s,j|\mathcal{H}_{SL}|\mathbf{f}'s',r\rangle\langle\mathbf{f}'s',r|\mu_Z|\mathbf{f}''s'',t\rangle\langle\mathbf{f}''s'',t|\mathcal{H}_{SL}|\mathbf{f}s,j\rangle}{(E_{\mathbf{f}s,j}-E_{\mathbf{f}'s',r})(E_{\mathbf{f}s,j}-E_{\mathbf{f}''s'',t})}$$
$$\left.+\frac{\langle\mathbf{f}s,j|\mathcal{H}_{SL}|\mathbf{f}'s',r\rangle\langle\mathbf{f}'s',r|\mathcal{H}_{SL}|\mathbf{f}''s'',t\rangle\langle\mathbf{f}''s'',t|\mu_Z|\mathbf{f}s,j\rangle}{(E_{\mathbf{f}s,j}-E_{\mathbf{f}'s',r})(E_{\mathbf{f}s,j}-E_{\mathbf{f}''s'',t})}\right\}-\langle\mathbf{f}s,j|\mu_Z|\mathbf{f}s,j\rangle\sum_{f's'r}{}'\frac{|\langle\mathbf{f}s,j|\mathcal{H}_{SL}|\mathbf{f}'s',r\rangle|^2}{(E_{\mathbf{f}s,j}-E_{\mathbf{f}'s',r})^2}.\quad(5)$$

Though this is a quite standard formula for the matrix element of $\boldsymbol{\mu}$ in third-order perturbation theory, we have written it out in detail in order to clarify our treatment for the specific case of Eu^{3+} discussed in the next section. The assumption that the spin eigenvectors $|j\rangle$ have been formed in the presence of the magnetic field has the consequence of imparting to the ground state of the spin system a magnetic moment even if the level is a singlet. This is, of course, the origin of the usual Van Vleck temperature-independent paramagnetism, but modified here because of the presence of $\mathcal{H}_{SL}$.

III. APPLICATION TO TRIVALENT EUROPIUM

Rather than go on to discuss the general form of the contribution to $\langle\boldsymbol{\mu}\rangle$ arising from the phonons, we shall treat the specific example of Eu^{3+} in a cubic salt. Such a salt may offer the best opportunity for the observation of this correction because the ground state is a singlet, the first excited state is 480°K higher in energy, and no other close-lying excited multiplet contributions to the unperturbed second-order Zeeman term.[9] At low temperatures, in the absence of $\mathcal{H}_{SL}$, we would expect to find only the Van Vleck temperature-independent paramagnetism. However, (5) will give an additional contribution to the susceptibility of the form

$$\chi\sim(\beta^2\mu^2/\Delta)(V^2\langle\epsilon^2\rangle/\Delta^2).\quad(6)$$

The first parenthesis in (6) is the Van Vleck result; the last is the second-order effect of $\mathcal{H}_{SL}$. Here, Δ refers to the spin-orbit splitting (~480°K) between the ground and excited multiplet, and V the orbit-lattice interaction constants found in (3). We would expect $V\gtrsim\Delta$, so that the correction is "reduced" from the Van Vleck result by the square of the strain, $\langle\epsilon^2\rangle$. Because the temperature-dependent part of $\langle\epsilon^2\rangle$ is proportional to T^4, however, we would expect this additional contribution to be readily distinguishable from the temperature-independent susceptibility, even if it be small. It will turn out that the actual matrix elements in (5) reduce the effect somewhat for the particular case of Eu^{3+}; but in the actinide series, where $\mathcal{H}_{SL}$ is much larger, a significant correction can obtain.

In order to evaluate (5) for trivalent europium in a cubic salt we shall make two approximations, neither of which is crucial, but both of which materially reduce computational difficulties and enable us to see more clearly what is going on. We assume:

(i) We can cut off the sum over l in (3) to the single value, $l=2$;

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[9] In contrast with YbGaG where Inoue (Ref. 5) points out that the $J=\frac{5}{2}$ multiplet contributes a correction to χ of the same order as the spin-phonon correction.

(ii) we can ignore the cubic crystalline field splitting of the $J=2$, 3 multiplets.

The first approximation has little justification, other than the fact that in some materials (e.g., the garnets) the *static* $l=2$ terms in the crystalline potential seem to dominate the $l=4$ and 6 terms. We limit ourselves to $l=2$ because we only wish to consider the low-lying J multiplets (The triangle rule will allow us to stop at $J=3$). In any case, the $l=2$ terms will give an order of magnitude for, and provide a lower limit on, the size of the effect. The second approximation is less severe because the $J=1$ level is unsplit by a cubic field, and the crystalline field splitting of the $J=2$ and 3 levels will be small compared to the separation from the ground level (3Δ and 6Δ, respectively). There is not necessarily an inconsistency in taking $V(\Gamma_{ig}2)$ large and the static cubic crystalline field small. This follows because only $l=4$, 6 terms are present in the static field, arising only from ions in the immediate vicinity of the paramagnetic ion. The $l=2$ dynamic term, however, receives contributions from many ions outside the first shell of ligands. Hence, it may well be possible to have a large $V(\Gamma_{ig}2)$ and a relatively small static cubic crystalline field.

We need to compute the matrix element of $C_l{}^m$ assuming Russel-Saunders coupling. The standard formula is given by Elliott, Judd, and Runciman[10]:

$$\langle\alpha'S'L',J'M'|C_l{}^m|\alpha SL,J,M\rangle$$
$$=(-1)^{J'-M'}\begin{pmatrix} J' & l & J \\ -M' & m & M \end{pmatrix}(-1)^{L+S+J'+l}\delta(S',S)$$
$$\times[(2J'+1)(2J+1)]^{1/2}\begin{Bmatrix} J' & l & J \\ L & S' & L' \end{Bmatrix}(\alpha'L'\|C^{(2)}\|\alpha L). \tag{7}$$

The double-bar matrix elements are conveniently tabulated by Polo.[11] For our case, $L=L'=S=S'=3$ and $(\alpha'L\|C^{(2)}\|\alpha L)=\sqrt{(28/15)}$. The rest of the computation involves considerable algebra. Some simplification is obtained by making use of the orthogonality of the subvectors of the Γ_{ig} irreducible representations to eliminate cross terms in the strain tensor. We find, using (7) and (5) and carrying out all the sums, the perturbed low-temperature susceptibility (χ_p) for Eu^{3+}:

$$\chi_p=\frac{313}{14{,}175}\frac{\beta^3}{\Delta^3}\{V^2(\Gamma_{3g}2)$$
$$\times[(2\epsilon_{zz}-\epsilon_{xx}-\epsilon_{yy})^2+3(\epsilon_{xx}-\epsilon_{yy})^2]$$
$$+12V^2(\Gamma_{5y}{}^2)(\epsilon_{xy}{}^2+\epsilon_{xz}{}^2+\epsilon_{yz}{}^2)\}. \tag{8}$$

The unperturbed Van Vleck temperature-independent susceptibility $\chi_{vv}=\sum\beta^2/\Delta$ for Eu^{3+}, so that (8) is indeed of the form (6). The coefficients of the coupling constants are such that the Γ_{5g} vibrational modes give a much larger contribution to χ than do the Γ_{3g} vibrational modes. This will also turn out to be the case for the case of U^{4+} (an f^2 configuration) to be considered later. Evaluating (8), assuming an isotropic solid with a Debye spectrum for the lattice vibrations, the temperature-dependent part of χ_p is found to be

$$\chi_p(T)=\frac{313}{14{,}175}\left(\frac{\pi^2}{25}\right)\frac{\beta^2}{\Delta^3}$$
$$\times[2V^2(\Gamma_{3g}2)+3V^2(\Gamma_{5g}2)]$$
$$\times\frac{\hbar}{\rho}\left(\frac{1}{v_t{}^5}+\frac{2}{3v_l{}^5}\right)\left(\frac{kT}{\hbar}\right)^4, \tag{9}$$

where v_l, v_t are the longitudinal and transverse sound velocities respectively, and ρ is the crystal mass density.

It is a difficult matter to estimate accurately the coupling coefficients $V(\Gamma_{ig}2)$ for Eu^{3+}. The experimental determination of these parameters is not an easy manner since one must work in the excited states of Eu^{3+} to obtain direct information on $V(\Gamma_{ig}2)$. We suspect that a figure of ~500 cm^{-1} for $V(\Gamma_{5g}2)$ may be somewhat of an overestimate but not unreasonable in view of the short lifetime of the $J=1$ level in the iron garnet.[12] Such a value, taken together with a density of ~3 g/cm^3, $v_t=2\times10^5$ cm/sec, and $\Delta=480$°K, results in a value for $\chi_p(T)$ from (9) of

$$\chi=\chi_{vv}\times1.3\times10^{-11}T^4, \tag{10}$$

where T is measured in degrees Kelvin. It is clear that this effect is probably below the borderline of detection. At $T=100$°K, the correction to the Van Vleck susceptibility is only $\frac{1}{2}$% and at higher temperatures the occupation of the $J=1$ level becomes important, tending to obscure (10). If, however, $V(\Gamma_{5g}2)$ were considerably larger (the fast-relaxing theory would require an increase of roughly one order of magnitude) then (9) might be appreciable. Unpublished measurements of Le Craw indicate no deviation of χ from the noninteracting value to within 1%, implying $V(\Gamma_{5g}2)$ is ≤500 cm^{-1} from (10). This indicates directly that the coupling constants are certainly smaller than the fast-relaxing theory would require.

IV. APPLICATION TO TETRAVALENT URANIUM

The energy levels of U^{4+} in an octahedral and cubic environment were first computed by Hutchison and Candela,[13] and are shown in Figures 1(a) and (b). For dilute solutions of UO$_2$ in ThO$_2$, an example of the latter

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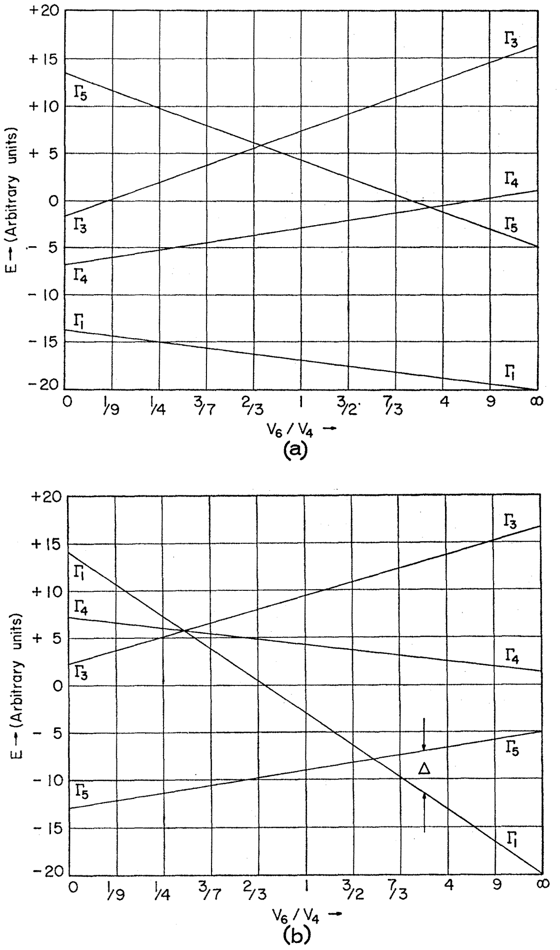

FIG. 1. (a) Energy-level diagram for the low-lying states of U^{4+} in an octahedral environment (Hutchison and Candela, Ref. 13) as a function of the ratio of the fourth- to sixth-order crystalline-field parameters. (b) Energy-level diagram for the low-lying states of U^{4+} in a cubic environment (Hutchison and Candela, Ref. 13) as a function of the ratio of the fourth- to sixth-order crystalline-field parameters.

case, it is known that the Γ_1 level lies lowest, with a Γ_5 level lying close by. The Γ_4 level is expected to lie at least 1000 cm^{-1} above the Γ_1. This arrangement of levels is interesting since the Zeeman interaction can only mix the Γ_4 into the Γ_1 ground state, whereas the dynamic spin-phonon interaction can mix the Γ_5 level into the ground level. The latter admixture, because of matrix elements of the Zeeman interaction *diagonal* in Γ_5, leads to a T^4 correction similar to (9), but with Δ representing the Γ_1-Γ_5 splitting. Thus, the dynamic spin phonon coupling allows a contribution to χ_p at low temperatures from a level which, in the absence of the spin-phonon interaction, would not contribute to χ_{vv}. Blume[14] has analyzed the susceptibility of UO_2 and argues for a $\Delta\sim 35$ cm^{-1}. This splitting is likely to be considerably smaller[15] for UO_2 dissolved in ThO_2, the dilution necessary to suppress the antiferromagnetic order characterizing UO_2 at $T<30$°K. The orbit-lattice coupling constants are expected to be an order of magnitude larger[16] for U^{4+} than for the comparable rare-earth ion, Pr^{3+}. This, in concert with the (assumed) small excitation energy Δ leads one to expect that the phonon correction to χ may be appreciable in this case. The analysis is considerably easier than that which led to (8) since the magnetic field cannot connect the ground and first excited levels. We find explicitly at temperatures $T\ll\Delta/k$,

$$\chi_p=\frac{\beta^2}{\Delta}(0.37)\frac{V^2(\Gamma_{5g}2)}{\Delta^2}\frac{\hbar}{\pi^2\rho}\left(\frac{1}{v_t^5}+\frac{2}{3v_l^5}\right)\left(\frac{kT}{h}\right)^4. \quad (11)$$

Only $V(\Gamma_{5g}2)$ appears in (11) since a Γ_{3g} vibration cannot connect Γ_1 with Γ_5. Because of the indeterminacy in the value of Δ for U^{4+} in ThO_2, it is difficult to make a quantitative estimate of χ_p in this case. Candela *et al.*[17] have shown that Pu^{4+} in an octahedral environment has a similar level structure to U^{4+} in a cubal environment. Since Δ for the latter ion may be too small to yield a region of temperature where (11) will be of a significant magnitude,[15] the former ion should be investigated to see if a more favorable level structure obtains.

The case of U^4 in an octahedral environment is also of interest, since from Fig. 1(a), the Γ_1 level is well isolated from all three other levels (The splitting to the Γ_4 being 992, 1097, and 1165 cm^{-1} for $[(CH_3)_4N]_2UCl_6$, Cs_2UCl_6, and PuO_2, respectively[17]). Here too a χ_p similar in form to (9) should be present. Rough estimates indicate a contribution 10 to 50 times larger than (10). It would be of great interest to see if this correction can be observed in these cases.

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