TEMPERATURE-HYPERFINE COUPLING CONSTANT OF Mn^{2+} IN MgO

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(Received 15 January 1967)

Abstract

The Van Vleck orbit-lattice interaction associated with an XY_6 cubic molecular cluster is used to calculate the phonon-induced hyperfine coupling constant of Mn^{2+} in MgO . Within the Debye approximation, the phonon-induced hyperfine fields is found to be proportional to the Debye-Waller factor. By introducing a "modified Debye temperature" which would calculate one would calculate on the assumption that only acoustic phonons were involved, we are able to compute the contributions attributed to acoustic and optical phonons separately. The agreement between experiment and theory is good. From the fitted curve, we find that the zero-point phonon contribution to the hyperfine coupling constant is 1.1 per cent and hence the hyperfine coupling constant in the "rigid lattice" at $T = 0^\circ K$ is $-82.4 \times 10^{-4} \text{ cm}^{-1}$.

1. Introduction

^VSIMÁNEK and Orbach [1] have proposed that the admixture of excited configurations of the form $3d^4ns$ into the ground $3d^5$ configuration by a dynamic phonon-induced non-cubic field is responsible for the temperature dependence of the hyperfine coupling constant of $(Mn^{55})^{2+}$ in MgO measured by Walsh *et al.* [2]. The temperature dependence predicted by Simánek and Orbach does not agree with the experimental points. In view of the fact that at high temperatures, optical phonon are very well excited, Orbach and Simánek [3] used the results of a diatomic linear chain to calculate the mean square amplitudes of normal coordinates attributed to acoustic and optical phonons. From this calculation, they found that zero-point optical phonon contribution to the hyperfine coupling constant is more important than that contributed by the acoustic phonons.

In this paper, we shall also use the Van Vleck orbit-lattice interaction, and compute the contributions by acoustic and optical phonons separately. However, we shall properly average the Van Vleck orbit-lattice interaction.

2. Theory

According to Van Vleck [4, 5] the orbit-lattice interaction associated with an XY_6 cubic molecular cluster is of the form

$$V_{ol} = \sum_{j=2}^6 v_j Q_j \quad (1)$$

where, to second order,

$$\begin{aligned} v_2 &= \sum_o A' r_o^2 (Y_2^2 + Y_2^{-2}), \\ v_3 &= - \sum_o \sqrt{6} A' r_o^2 Y_2^0, \\ v_4 &= - \sum_o i(2/3) A' r_o^2 (Y_2^2 - Y_2^{-2}), \\ v_5 &= - \sum_o (2/3) A' r_o^2 (Y_2^{-1} - Y_2^1), \\ v_6 &= \sum_o i(2/3) A' r_o^2 (Y_2^1 + Y_2^{-1}), \end{aligned} \quad (2)$$

$$A' \equiv 9 (2\pi)^{1/2} e e_{eff} / (15)^{1/2} R^4, \quad (3)$$

in which e is the electronic charge, e_{eff} the effective charge of an anion, R the anion-cation distance, r_o the radial distance of the $3d$ -electron from the center of the paramagnetic ion, and Y_2^m are the spherical harmonics. The normal coordinate Q_j can be written as [5]

$$Q_j = \sum_{m=1}^3 \sum_{i_m=1}^{N_c} a_{ji_m} q_{i_m} \quad (4)$$

for acoustic phonons, and [6]

$$Q_j = \sum_{i_r=1}^{N_c} a_{ji_r} q_{i_r} \quad (5)$$

for optical phonons. Here m denotes the acoustic phonon polarization, N_c the number of unit cells in the crystal, and r the r -th optical branch. q_{i_m} and q_{i_r} are the acoustic and optical

phonon operators respectively, and a_{ji_m} and a_{ji_m} are the appropriate coefficients. The average values of these coefficients associated with small values of the phonon wave vectors k have been calculated by Van Vleck [5]. However, because we are interested in the temperature region where phonons with large values of k are excited, and because the phonon density of states is higher at larger values of k , at which the phonon dispersion is smaller, we should average a_{ji} for large values of k . Accordingly, we have [6, 7]

$$\left\langle a_{ji_s} a_{li_t} \right\rangle_{av} \simeq \left[\frac{1}{3} \right] \delta_{jl} \delta_{st} \quad (6)$$

for both acoustic and optical phonons.

The ground-state determinant for Mn^{2+} can be written as

$$|M_s\rangle = \left| \psi_{3d+2}^{\prime+} \psi_{3d+1}^{\prime+} \psi_{3d0}^{\prime+} \psi_{3d-1}^{\prime+} \psi_{3d-2}^{\prime+} \right\rangle \quad (7)$$

where $\psi_{3d\alpha}^{\prime+}$ is the $3d$ orbital with up spin perturbed by the orbit-lattice interaction, and is of the form

$$\psi_{3d\alpha}^{\prime+} = \psi_{3d\alpha} - \sum_n \frac{\langle \psi_{ns} | V_{ol} | \psi_{3d\alpha} \rangle}{E[3d\alpha] - E[ns]} \psi_{ns}.$$

Here ψ_{ns} is the excited state wave function. Hence the phonon-induced hyperfine field is

$$\begin{aligned} \left\langle H_{hyp} \right\rangle_{av} &= \left\langle M_s \left| (8\pi/3) \mu_o \sum_i s_{zi} \delta(\mathbf{r}_i) \right| M_s \right\rangle \\ &\simeq (8\pi/3) g \mu_o \left\langle S_z \right\rangle \sum_{j=2}^6 \sum_{n'} \frac{\langle M_s | v_j | \psi_{ns} \rangle \langle \psi_{n's} | v_j | M_s \rangle}{[E(3d) - E(ns)] [E(3d) - E(n's)]} \end{aligned} \quad (8)$$

$$\begin{aligned} &\times \frac{1}{3} \left[\sum_{m=1}^3 \sum_{i_m=1}^{N_c} \left(\frac{\hbar}{2\pi M} \right) \left(\frac{2 N_{i_m} + 1}{v_{i_m}} \right) \times \langle \psi_{ns} | \delta(\mathbf{r}) | \psi_{n's} \rangle \right. \\ &\left. + \sum_r \sum_{i_r=1}^{N_c} \left(\frac{\hbar}{2\pi M} \right) \left(\frac{2 N_{i_r} + 1}{v_{i_r}} \right) \right] \end{aligned}$$

where g is the g -value of the Mn^{2+} ion, μ_0 the Bohr magneton, s_{zi} the z -component of the electron spin at r_i , N_{i_m} the Bose-Einstein factor evaluated at $E = h \nu_{i_m}$, and M the mass of the crystal. It is interesting to see that within the Debye approximation, the quantity in the square bracket is proportional to the Debye-Waller factor, and hence equation (8) is proportional to the mean square amplitude of lattice vibrations. This is exactly what obtained by Walsh *et al.* [2]. To sum over the acoustic phonon states, we shall replace the summation by an integration as follows:

$$\sum_{m=1}^3 \sum_{i_m=1}^{N_c} = 4\pi V \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \int_0^{v_D'} v^2 \cdot dv \quad (9)$$

where V is the volume of the crystal, v_l and v_t are the longitudinal and transverse sound velocities respectively, and v_D' is the "modified Debye frequency" which would calculate one would calculate on the assumption that only acoustic modes were involved. Since only the optical phonons with large values of k are important in the spin-optical-phonon interaction [3, 6], we can approximately replace ν_{i_r} by the optical phonon frequency of the r -th optical branch at the Brillouin zone boundary, ν_{rB} . Hence equation (8) reduces to

$$\begin{aligned} \langle H_{hyp} \rangle_{av} &= (8\pi/3) g \mu_0 \langle S_z \rangle \sum_n \sum_{n'} B(n, n') \\ &\times \langle \psi_{ns} | \delta(r) | \psi_{n's} \rangle (296\pi \hbar / 25) (e e_{eff} / R^4)^2 \\ &\times \left\{ \frac{1}{\rho} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \int_0^{v_D'} \left[1 + \frac{2}{\exp(h\nu/k_B T) - 1} \right] v dv \right. \\ &\left. + \frac{N_c}{M} \sum_r \frac{1}{\nu_{rB}} \left[1 + \frac{2}{\exp(h\nu_{rB}/k_B T) - 1} \right] \right\} \quad (10) \end{aligned}$$

where

$$B(n, n') = \frac{\langle \psi_{3d} | r_0^2 | \psi_{ns} \rangle \langle \psi_{n's} | r_0^2 | \psi_{3d} \rangle}{[E(3d) - E(ns)] [E(3d) - E(n's)]}.$$

If we write the temperature-dependent hyperfine coupling constant as [2]

$$A(T) = A(0) \{1 - [C(0) + C(T)]\} \quad (11)$$

then we have

$$C(0) = KL \left[\frac{2\pi v_D'^2}{\rho} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) + \frac{N_c}{M} \sum_r (\nu_{rB})^{-1} \right] \quad (12)$$

$$C(T) = KL \left[\frac{8\pi}{\rho} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \left(\frac{k_B T}{h} \right)^2 \int_0^{T_D'/T} \frac{x dx}{\exp x - 1} \right. \quad (13)$$

$$\left. + \frac{2N_c}{M} \sum_r \left(\frac{1}{v_{rB}} \right) \frac{1}{\exp(hv_{rB}/k_B T) - 1} \right],$$

where [1]

$$K = \sum_n \sum_{n'} \frac{(8\pi/3) g \mu_0 \langle S_z \rangle B(n, n')}{H_c} \quad (14)$$

$$= 0.176 \times 10^{-9} \text{ sec}^4/\text{g}^2 - \text{deg}^8,$$

$$L = (74 h/25) (e e_{eff}/R^4)^2, \quad (15)$$

$$T_D' = hv_D'/k_B. \quad (16)$$

Here ρ is the density of the crystal, and H_c is the static hyperfine field resulting from core polarization.

For MgO , we have [8] $\rho = 3.7 \text{ g/cm}^3$, $R = 2.1 \times 10^{-8} \text{ cm}$, $e_{eff} = -2e$, $v_t = 6.3 \times 10^5/\text{sec}$, $v_l = 8.8 \times 10^5 \text{ cm/sec}$, and $T_D = 946^\circ\text{K}$. Because there are two atoms per unit cell in MgO the "modified Debye temperature", T_D' , is then $946/(2)^{1/3} = 750^\circ\text{K}$. The optical phonon frequencies are $v_{lB} = 1.83 \times 10^{13} \text{ c/s}$, $v_{t1B} = 1.53 \times 10^{13} \text{ c/s}$, $v_{t2B} = 1.49 \times 10^{13} \text{ c/s}$ obtained by Mon [9] from his Raman experiment. Using these quantities, we can now calculate $C(T)$, equation (13). By multiplying 0.42 to $C(T)$, we are able to fit our theoretical curve to the experimental data obtained by Walsh *et al.* [2] as shown in Fig. 1. The agreement between theory and experiment is excellent. We also find $C(0) = 0.011$ in which only 25 per cent is attributed to optical phonons. Hence, the zero-point phonon contribution to the hyperfine coupling constant is $-0.87 \times 10^{-4} \text{ cm}^{-1}$, and the hyperfine coupling constant in the "rigid lattice" at $T = 0^\circ\text{K}$ is $-82.4 \times 10^{-4} \text{ cm}^{-1}$.

3. Discussion

In the last section, we derived a theory appropriate to high temperatures. At very low temperatures, Orbach's theory [1] is still valid. The discrepancy between the temperature dependence predicted by Orbach's theory and that obtained by Walsh *et al.* [2] at low temperatures might be due to the fact that the Debye temperature decreases with increasing temperature at low temperatures [10]. Finally, in view of the agreement between theory and experiment, we should like to emphasize that the effect based on the point charge model is at least as important as that based on the covalent model.

FIGURE 1

The theoretical curve of the phonon-induced shift of the hyperfine coupling constant A for $(\text{Mn}^{55})^{2+}$ in MgO fitted to the experimental points, designated by o , obtained by Walsh *et al.* (see Ref. 2).

Acknowledgement

The author would like to express his gratitude to Professor R. Orbach for inducing him to be interested in this problem.

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