PHYSICAL REVIEW VOLUME 158, NUMBER 2 10 JUNE 1967

Temperature-Dependent Hyperfine Interactions of Mn^{2+} in Alkali Halides

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(Received 16 January 1967; revised manuscript received 27 February 1967)

The Van Vleck orbit-lattice interaction is used to calculate the phonon-induced hyperfine coupling constants of $(Mn^{55})^{2+}$ in alkali halides. We find that the phonon-induced field is proportional to the Debye-Waller factor. From the best fit of the theoretical curve to the experimental data for $(Mn^{55})^{2+}$ in NaCl, we find that the zero-point phonon contribution to the hyperfine coupling constant is only 0.41%, and hence the hyperfine coupling constant in the "rigid lattice" at $T=0$ is -83.5×10^{-4} cm^{-1}, which is smaller than the hyperfine coupling constants of $(Mn^{55})^{2+}$ in KCl, KBr, NaF, and LiF measured at elevated temperatures. Except for NaF, we find that the zero-point optical-phonon contributions to the hyperfine interactions for Mn^{2+} in these host crystals are less important than those contributed by the acoustic phonons.

I. INTRODUCTION

RECENTLY, Walsh, Jeener, and Bloembergen[1] showed experimentally and theoretically that the temperature dependence of the hyperfine coupling constant of $(Mn^{55})^{2+}$ in some host crystals arises from the lattice vibrations of the host lattices. Based on this fact, Šimánek and Orbach[2] proposed a mechanism which involves the admixture of excited configurations of the form $3d^4ns$ into the ground $3d^5$ configuration by means of the Van Vleck orbit-lattice interaction.[3,4] Their theoretical values turned out to be smaller than the experimental data by a factor of 10. Knowing that[5] the point-charge model is not appropriate for Mn^{2+} in MgO, Šimánek and Nai Li Huang[6] introduced the covalent model which they found agrees with experiment. In view of the fact that at high temperatures optical phonons are well excited, Orbach and Šimánek[7] used the result of the diatomic linear chain to calculate the mean-square amplitude of lattice vibrations, and then calculated the phonon-induced hyperfine fields. From this calculation, and based on the experimental data obtained by Rosenthal *et al.*,[8] they found that the zero-point optical-phonon contributions to the hyperfine coupling constants of Mn^{2+} in MgO, SrO, and CaO are more important than those contributed by the acoustic phonons, and also found that the hyperfine coupling constants of Mn^{2+} in these oxides in the "rigid lattice" at $T=0$ are equal within their approximation. However, in these calculations, these authors[2,6] used the Van Vleck orbit-lattice interaction averaged only for phonons with small wave vectors. Therefore, their interaction is not appropriate for accounting the experimental data obtained at the higher temperatures at which phonons with large wave vectors are well excited.

In view of this, in this paper, we shall use the Van Vleck orbit-lattice interaction with proper averaging as the mechanism to calculate the phonon-induced hyperfine coupling constant of $(Mn^{55})^{2+}$ in NaCl, and then compare this theoretical value with the experimental hyperfine coupling constants of $(Mn^{55})^{2+}$ in NaCl, KCl, KBr, NaF, and LiF.

II. THE DEBYE-MODEL APPROXIMATION

The Van Vleck orbit-lattice interaction associated with an XY_6 cubic molecular cluster is of the form[3,4]

$$V_{ol}=\sum_{j=2}^{6} v_jQ_j, \tag{1}$$

where the electronic operators to second order are

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

$$A'=9(2\pi)^{1/2}ee_{\text{eff}}/(15)^{1/2}R^4, \tag{3}$$

in which e is the charge of the bonding electron of the paramagnetic ion, 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 the spherical harmonics. According to Van Vleck, the normal coordinate can be written as

$$Q_j=\sum_{m=1}^{3}\sum_{i_m=1}^{N} a_{ji_m}q_{i_m}. \tag{4}$$

Here m denotes the phonon polarization, and N the

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[2] E. Šimánek and R. Orbach, Phys. Rev. **145**, 191 (1966).

[3] J. H. Van Vleck, J. Chem. Phys. **7**, 32 (1939).

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[5] J. Kondo, Progr. Theoret. Phys. (Kyoto) **28**, 1026 (1962); M. Blume and R. Orbach, Phys. Rev. **127**, 1587 (1962).

[6] E. Šimáneck and Nai Li Huang, Phys. Rev. Letters **17**, 699 (1966).

[7] R. Orbach and E. Šimánek, Phys. Rev. (to be published).

[8] J. Rosenthal, L. Yarmas, and R. H. Bartram, Phys. Rev. **153**, 407 (1967).

total number of atoms in the crystal. The phonon operator q_{i_m} is defined as[4]

$$\langle N_{i_m} \mid q_{i_m} \mid N_{i_m}+1\rangle = \langle N_{i_m}+1 \mid q_{i_m} \mid N_{i_m}\rangle = [\hbar(N_{i_m}+1)/2\pi M \nu_{i_m}]^{1/2}, \quad (5)$$

where N_{i_m} is the Bose-Einstein factor evaluated at $E=h\nu_{i_m}$, and M is the mass of the crystal. a_{ji_m} are the appropriate coefficients. Van Vleck has calculated the average values of these coefficients for small values of the phonon wave vectors k. However, because the phonon density of states is higher at higher values of k, and because we are interested in the temperature range in which the phonons with large values of k are well excited, we should average a_{ji_m} for large values of k. Hence we get [9,10]

$$\langle a_{ji_m} a_{li_n}\rangle_{\mathrm{av}} \simeq \tfrac{1}{3}\delta_{jl}\delta_{mn} \quad (6)$$

for all j, l, m, and n.

Using the notations used in Ref. 2, we can write the ground-state determinant for Mn^{2+} as

$$|{}^6S'M_s=\tfrac{5}{2}\rangle = |\,\psi'^{+}{}_{3d_{+2}}\psi'^{+}{}_{3d_{+1}}\psi'^{+}{}_{3d_0}\psi'^{+}{}_{3d_{-1}}\psi'^{+}{}_{3d_{-2}}\rangle, \quad (7)$$

where $\psi'^{+}{}_{3d_\alpha}$ is the $3d$ orbital with up spin perturbed by the orbit-lattice interaction. Hence the phonon-induced hyperfine field is

$$\begin{aligned}\langle H_{\mathrm{hyp}}\rangle_{\mathrm{av}} &= \langle {}^6S'M_s \mid (8\pi/3) g\mu_o \sum_i s_{zi}\delta(\mathbf{r}_i) \mid {}^6S'M_s\rangle \\ &= (8\pi/3) g\mu_o \langle S_z\rangle \sum_n \sum_{n'} \sum_{j=2}^{6} \frac{\langle {}^6S'M_s \mid v_j \mid \psi_{ns}\rangle\langle \psi_{n's} \mid v_j \mid {}^6S'M_s\rangle}{[E(3d)-E(ns)][E(3d)-E(n's)]} \langle \psi_{ns} \mid \delta(r) \mid \psi_{n's}\rangle \\ &\quad \times (1/3)\Big[\sum_{m=1}^{3} \sum_{i_m=1}^{N} (\hbar/2\pi M)(2N_{i_m}+1)/\nu_{i_m}\Big], \quad (8)\end{aligned}$$

where $|\psi_{ns}\rangle$ and $|\psi_{n's}\rangle$ are, respectively, the wave functions of the excited configurations $(3d)^4ns$ and $(3d)^4n's$. We can easily show

$$\sum_{j=2}^{6} \langle {}^6S'M_s \mid v_j \mid \psi_{ns}\rangle\langle \psi_{n's} \mid v_j \mid {}^6S'M_s\rangle = (444\pi/25)(ee_{\mathrm{eff}}/R^4)^2 \langle \psi_{3d} \mid r_o^2 \mid \psi_{ns}\rangle\langle \psi_{n's} \mid r_o^2 \mid \psi_{3d}\rangle. \quad (9)$$

Within the Debye approximation, we can write

$$\sum_{m=1}^{3} \sum_{i_m=1}^{N} = 4\pi V(v_l^{-3}+2v_t^{-3}) \int_0^{\nu_D} \nu^2 d\nu, \quad (10)$$

where V is the volume of the crystal, v_l and v_t are, respectively, the longitudinal and transverse sound velocities, and ν_D is the Debye frequency. Hence Eq. (8) reduces to

$$\begin{aligned}\langle H_{\mathrm{hyp}}\rangle_{\mathrm{av}} &= (8\pi/3) g\mu_o \langle S_z\rangle \sum_n \sum_{n'} B(nn') \langle \psi_{ns} \mid \delta(r) \mid \psi_{n's}\rangle (296\hbar\pi/25)(ee_{\mathrm{eff}}/R^4)^2 \\ &\quad \times \rho^{-1}(v_l^{-3}+2v_t^{-3}) \int_0^{\nu_D} \{1+[\exp(h\nu/k_BT)-1]^{-1}\}\nu d\nu, \quad (11)\end{aligned}$$

where

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

and ρ is the density of the crystal. It is interesting to see that Eq. (11) is proportional to the Debye-Waller factor.[11] This result is by no means surprising, because the phonon-induced hyperfine field is proportional to the mean square amplitude of lattice vibrations.[1,2,7] We can now write the temperature-dependent hyperfine coupling constant as

$$A(T) = A(0)\{1-[C(0)+C(T)]\}, \quad (12)$$

where

$$C(0) = KL(2\pi\nu_D^2/\rho)(v_l^{-3}+2v_t^{-3}), \quad (13)$$

$$C(T) = KL(8\pi/\rho)(v_l^{-3}+2v_t^{-3})(k_BT/h)^2 \int_0^{X} x[\exp(x)-1]^{-1}dx, \quad (14)$$

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[9] Chao-Yuan Huang, Phys. Rev. **154**, 215 (1967).

[10] Chao-Yuan Huang (unpublished).

[11] For example, C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963).

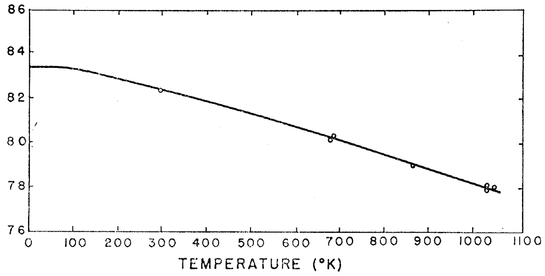

FIG. 1. The theoretical value of the phonon-induced shift of the hyperfine coupling constant A for $(\mathrm{Mn}^{55})^{2+}$ in NaCl as a function of temperature fitted to the experimental points, designated by circles, obtained by van Wieringen and Rensen (see Ref. 14).

in which[2]

$$K=\sum_n \sum_{n'} (8\pi/3) g\mu_o \langle S_z \rangle B(nn')/H_c \qquad (15)$$

$$=1.76\times10^{-10}\ \mathrm{sec}^4/\mathrm{g}^2\ \mathrm{deg}^8, \qquad (16)$$

$$L=(74\hbar/25)(ee_{\mathrm{eff}}/R^4)^2, \qquad (17)$$

$$X=h\nu_D/k_BT. \qquad (18)$$

Here H_c is the static hyperfine field resulting from core polarization. For NaCl, we have[12,13] $\rho=2.168$ g/cm^3, $e_{\mathrm{eff}}=e$, $R=2.783\times10^{-8}$ cm, $T_D=281$°K, $v_t=2.43\times10^5$ cm/sec, $v_l=4.78\times10^5$ cm/sec. In Fig. 1, we fit our theoretical curve to the experimental data obtained by van Wieringen and Rensen.[14] We find that the theoretical estimate based on Eq. (14) is smaller than the experimental result by a factor of 3.9. This fit gives $A(0)=-83.2\times10^{-4}$ cm^{-1}, and then we find $C(0)=0.41\times10^{-2}$. Hence the hyperfine coupling constant of Mn^{2+} in NaCl in the "rigid lattice" at $T=0$ is -83.5×10^{-4} cm^{-1}.

III. THE OPTICAL-PHONON CONTRIBUTION

In the last section, we have calculated the phonon-induced hyperfine coupling constant attributed to both acoustic and optical phonons in the Debye approximation. Here we shall try to estimate the optical-phonon contribution.

For optical phonons, we can write

$$Q_j=\sum_r \sum_{i_r=1i}^{N_c} a_{ji_r} q_{i_r}, \qquad (19)$$

where r denotes the rth optical branch, N_c the number of unit cells in the crystal, and[9,10]

$$\langle a_{ji_r} a_{ki_s} \rangle_{\mathrm{av}} = \tfrac{1}{3}\delta_{jk}\delta_{rs}, \qquad (20)$$

because optical phonons with large values of k are more important. Therefore, the optical-phonon-induced hyperfine field is

$$(\langle H_{\mathrm{hyp}}\rangle_{\mathrm{av}})_{\mathrm{op}}=(8\pi/3)g\mu_o\langle S_z\rangle \sum_n \sum_{n'} B(nn') \langle \psi_{ns} \,|\, \delta(r) \,|\, \psi_{n's} \rangle$$
$$\times(148\pi/25)(ee_{\mathrm{eff}}/R^4)^2 \Big\{ \sum_r \sum_{i_r=1}^{N_c} (\hbar/2\pi M)(2N_{i_r}+1)/\nu_{i_r} \Big\}. \qquad (21)$$

Since only optical phonons with large values of k are important,[7,9] and the frequencies of the optical phonons at large k are nearly constant, we can approximately replace ν_{i_r} by the optical-phonon frequency at the Brillouin-zone boundary ν_{rB}. Therefore, Eq. (21) becomes

$$(\langle H_{\mathrm{hyp}}\rangle_{\mathrm{av}})_{\mathrm{op}} \simeq (8\pi/3)g\mu_o\langle S_z\rangle \sum_n \sum_{n'} B(nn') \langle \psi_{ns} \,|\, \delta(r) \,|\, \psi_{n's} \rangle (74\hbar/25)$$
$$\times(ee_{\mathrm{eff}}/R^4)^2(N_c/M)\Big\{ \sum_r (2N_{rB}+1)/\nu_{rB} \Big\}. \qquad (22)$$

It follows that the fraction of the optical-phonon-induced hyperfine field is

$$C_{\mathrm{op}}(0)=KL(N_c/M)\sum_r (\nu_{rB})^{-1}, \qquad (23)$$

$$C_{\mathrm{op}}(T)=KL(2N_c/M)\Big\{ \sum_r [\exp(h\nu_{rB}/k_BT)-1]^{-1}(\nu_{rB}^{-1}) \Big\}. \qquad (24)$$

For NaCl, we have $\nu_{lB}=6.36\times10^{12}$ cps, $\nu_{tB}=5.19\times10^{12}$ cps obtained by Burstein *et al.*[15] We thus find theoretically

$$C_{\mathrm{op}}(T)/C(T)\simeq1/6 \qquad (25)$$

for $T\gtrsim280$°K. This clearly shows us that the contribution by optical phonons can be ignored in this temperature range. For the zero-point phonon contributions, Eqs. (13) and (23) give

$$C_{\mathrm{op}}(0)/C(0)\simeq1/2.7. \qquad (26)$$

The last equation also demonstrates that the acoustic phonons are more important than optical phonons in

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[13] Fred C. Rose, Phys. Rev. **49**, 50 (1936); Lloyd Hunter and Sidney Siegel, *ibid.* **61**, 841 (1942).

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TABLE I. The elastic constants, densities, anion-cation distances, optical-phonon frequencies, Debye temperatures, hyperfine coupling constants, and ratios of phonon contributions to the hyperfine interactions for $(Mn^{55})^{2+}$ in KCl, KBr, NaF, and LiF.

	In 10^{11} dyn/cm^2			ρ[a]	R[b]	In 10^{12} cps		Θ_D	A	
Sample	C_{11}[a]	C_{12}	C_{44}	(g/cm^3)	(Å)	ν_{lB}[c]	ν_{tB}	(°K)	(10^{-4} cm^{-1})	$C_{\mathrm{op}}(0)/C(0)$
KCl	3.98	0.625	0.62	1.98	3.108	4.6[d]	4.3	230[b]	88.5[g]	0.28
KBr	3.46	0.505	0.58	2.75	3.258	4.0[e]	3.4	177[b]	88.4[h]	0.35
NaF	9.71	2.43	2.80	2.81	2.283	8.1[e]	6.5	400[e]	92[i]	0.63
LiF	11.12	6.28	4.20	2.63	1.983	18.3[e]	12.7	708[f]	90[j]	0.09

[a] K. S. Aleksandrov and T. V. Ryzhova, Kristallografiya **6**, 289 (1961) [English transl.: Soviet Phys.—Crist. **6**, 228 (1961)].

[b] Reference 12.

[c] The optical-phonon frequencies at X are considered.

[d] J. R. Hardy, Phil. Mag. **7**, 315 (1962).

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[g] P. A. Forrester and E. E. Schneider, Proc. Phys. Soc. (London) **B69**, 833 (1956).

[h] W. Low, Proc. Phys. Soc. (London) **B69**, 837 (1956).

[i] W. Hays and D. A. Jones, Proc. Phys. Soc. (London) **71**, 503 (1958).

[j] T. T. Chang, W. H. Tanttilla, and J. S. Wells, J. Chem. Phys. **38**, 571 (1963).

inducing the excited configurations into the ground-state configuration.

IV. DISCUSSION

Table I gives the elastic constants, densities, anion-cation distances, optical-phonon frequencies at the symmetry point X, Debye temperatures, hyperfine coupling constants, and $C_{\mathrm{op}}(0)/C(0)$ for $(Mn^{55})^{2+}$ in KCl, KBr, NaF, and LiF. It is seen that the hyperfine coupling constants for these crystals measured at elevated temperatures are higher than that for NaCl in the "rigid lattice" at $T=0$ we found previously. Because the Van Vleck orbit-lattice interaction is electrostatic in character, it will only result in a net *decrease* of hyperfine field,[2] and hence the hyperfine coupling constants for $(Mn^{55})^{2+}$ in KCl, KBr, NaF, and LiF in the "rigid lattice" at $T=0$ will be greater than those values given in Table I. Therefore, we cannot draw a conclusion that the hyperfine coupling constants for $(Mn^{55})^{2+}$ in alkali halides in the "rigid lattices" at $T=0$ are equal, as Orbach and Šimánek[7] concluded for oxides. Furthermore, from Table I, it is interesting to see that the optical phonons in NaF contribute more to the zero-point phonon-induced hyperfine interaction than acoustic phonons.

In Sec. II, we have shown that our theoretical calculations agree with the experimental data within one order of magnitude. This result suggests that the point-charge model appears to correctly describe the temperature dependence of the hyperfine interaction. This conclusion is in agreement with the observation made by Walsh *et al.* in conjunction with the temperature-dependent hyperfine constants of Mn^{2+} in CaO and SrO.

Finally, we should like to emphasize that the theory presented by Orbach and Šimánek will correctly account for the phonon-induced hyperfine interaction at very low temperatures, while our theory, presented in Sec. II, will adequately describe the temperature-dependent hyperfine constant at the higher temperatures at which the experimental data are usually available.

ACKNOWLEDGMENTS

I would like to thank Professor R. Orbach for introducing me to this problem, and sending me the preprint before publication. Professor B. A. Green, Jr. helped with the numerical calculations and also helped to prepare this manuscript. Professor D. I. Bolef supplied a reference, and hence I would like to thank him.