

Phonon-Induced Corrections to the Ground-State Splitting of S-State Ions in Cubic Crystals*

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The ground 6S and excited 4L states of the Mn^{2+} ion are perturbed by the cubic crystalline field and mixed by the spin-orbit coupling. A two-phonon Raman process, second order in the orbit-lattice interaction, is found to contribute to the ground-state splitting. The theory is developed within the framework of Van Vleck's small-wave-vector averaging procedure for acoustic phonons. Both the zero-point vibrational contribution and the temperature-dependent parts are calculated and compared with experimental measurements in Mn^{2+} -doped MgO. Good qualitative agreement between the theory and experiment is found but quantitative agreement is not obtained.

I. INTRODUCTION

IN 1934 Van Vleck and Penny¹ proposed that the admixture of excited orbitally asymmetrical states into the ground state via the spin-orbit coupling could lead to a ground-state splitting in the S -state $Mn^{2+}({}^6\Gamma_1)$ ion. Pryce² showed that Van Vleck and Penny's mechanisms were not adequate to give the experimentally measured magnitude of the anisotropy in magnetic susceptibility, and proposed that a contribution would be obtained in relatively low order by use of spin-spin interaction and the admixture of states outside the ground configuration. Watanabe³ not only calculated the zero-field splitting for the spin-spin contribution, but also considered the admixtures of the excited states into the ground state by the spin-orbit coupling. Since the calculated results of Watanabe were smaller than the experimental measurements, Kondo⁴ calculated the covalent contributions and managed to fit his calculations with the experiment in a somewhat phenomenological manner. Blume and Orbach⁵ calculated the cubic crystalline field perturbation of excited quartet states only, and admixed them into the ground 6S state by spin-orbit coupling. Leushin⁶ considered these admixtures not only by the spin-orbit coupling but also by the spin-spin interaction and calculated the ground-state splitting of the Mn^{2+} ion in low-symmetry systems. Bersohn and Das⁷ obtained the perturbation of the one-electron orbitals by an axial potential, using a variational technique and solving the first-order perturbation equations numerically. Chakraverti⁸ applied this method to a number of iron-group ions using

Slater wave functions for which one can obtain analytic expressions for the solutions of the first-order perturbation equations. Orbach, Das, and Sharma⁹ considered the configurational interaction and obtained numerical solutions of the one-electron Schrödinger equation using appropriate Hartree-Fock wave functions. We refer the reader to the work of Sharma *et al.*¹⁰ for a summary of some of these methods. In the case of rare-earth S -state ions, attempts¹¹ have been made to calculate the orbit-lattice-interaction contribution to the spectral shift using wave functions that were not perturbed by the crystalline field.

Within the framework of the rigid-lattice model the most satisfactory account of the cubic field splitting of Mn^{2+} in MgO is due to Gabriel, Johnston, and Powell.¹² In the present work, we propose the following mechanism: The ${}^6\Gamma_1$ ground state is split^{12,13} into a doublet ${}^2\Gamma_7$ and a quartet ${}^4\Gamma_8$ by the cubic field. The excited quartet states are also perturbed by the cubic field and admixed into the ground-state components ${}^2\Gamma_7$ and ${}^4\Gamma_8$ by the spin-orbit coupling. A two-phonon Raman process is then used to calculate the phonon-induced contribution to the ground-state splitting. The results of calculation are compared with experimental measurements in Mn^{2+} -doped MgO.

II. WAVE FUNCTIONS

The ground 6S state of the Mn^{2+} ion in a cubic crystalline field splits into a doublet and a quartet ${}^2\Gamma_7 + {}^4\Gamma_8(E_{5/2g} + G_g)$. The state 4P reduces into ${}^4\Gamma_4(T_{1g})$, 4D into ${}^4\Gamma_3 + {}^4\Gamma_5(E_g + T_{2g})$, 4F into ${}^4\Gamma_2 + {}^4\Gamma_4 + {}^4\Gamma_5(A_{2g} + T_{1g} + T_{2g})$, and 4G into ${}^4\Gamma_1 + {}^4\Gamma_3 + {}^4\Gamma_4 + {}^4\Gamma_5(A_{1g} + E_g + T_{1g} + T_{2g})$. The common subscript g in Γ_i is not indicated throughout this paper. The selection rules in

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¹ J. H. Van Vleck and W. G. Penney, *Phil. Mag.* **17**, 961 (1934).

² M. H. L. Pryce, *Phys. Rev.* **80**, 1107 (1950).

³ H. Watanabe, *Progr. Theoret. Phys. (Kyoto)* **18**, 405 (1957).

⁴ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **23**, 106 (1960); **28**, 1026 (1962).

⁵ M. Blume and R. Orbach, *Phys. Rev.* **127**, 1587 (1962).

⁶ A. M. Leushin, *Fiz. Tverd. Tela* **5**, 2352 (1963) [English transl. *Soviet Phys.—Solid State*, **5**, 1711 (1964)].

⁷ R. Bersohn and T. P. Das, *Bull. Am. Phys. Soc.* **1**, 397 (1956).

⁸ A. S. Chakraverti, *J. Chem. Phys.* **39**, 1004 (1963).

⁹ R. Orbach, T. P. Das, and R. R. Sharma, in *Proceedings of the International Conference on Magnetism, Nottingham, September 1964* (The Institute of Physics and the Physical Society, London, 1965).

¹⁰ R. R. Sharma, T. P. Das, and R. Orbach, *Phys. Rev.* **149**, 257 (1966); **155**, 338 (1967); **171**, 378 (1968).

¹¹ C. Y. Huang, *Phys. Rev.* **159**, 683 (1967).

¹² J. R. Gabriel, D. F. Johnston, and M. J. D. Powell, *Proc. Roy. Soc. (London)* **A264**, 503 (1961).

¹³ W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960).

the Russell-Saunders coupling $\Delta S=0, \pm 1$ suggest that, for our purpose, only the excited quartets are important. Next, $\Delta L=0, \pm 1$, so that the maximum contribution arises from 4P , which in our case reduces to Γ_4 . The excited states are intermixed by the cubic-field operators as long as their symmetry is maintained. The state 4D drops out because it has no component transforming like Γ_4 . Thus, the only mixing states are the three Γ_4 's arising from 4P , 4F , and 4G . They may be written as

$$|i^4\Gamma_4\rangle = \alpha_i |{}^4P\rangle + \beta_i |{}^4F\rangle + \gamma_i |{}^4G\rangle. \quad (1)$$

The coefficients α_i , β_i , and γ_i are obtained by the diagonalization of the cubic matrices of Tanabe and Sugano¹⁴ and given in Table I. Next we apply the cubic crystalline field operator

$$\mathcal{H}_{\text{cubic}} = (a/6)[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)] \quad (2)$$

to the ground state, allowing the mixing of $|M_S\rangle$ states. It is found that there are four eigenfunctions $a_1|\mp\frac{5}{2}\rangle + a_2|\pm\frac{3}{2}\rangle$ and $|\pm\frac{1}{2}\rangle$ with energy equal to $+a$, and two eigenfunctions $a_2|\mp\frac{5}{2}\rangle - a_1|\pm\frac{3}{2}\rangle$ with energy $-2a$, where $a_1 = (\sqrt{5}/6)$, $a_2 = (\sqrt{1}/6)$, and the value of $|L=0, M_L=0\rangle$ is not stated. The ground-state splitting between these multiplets is, as usual, given by 3a:

$$3a = \Delta\Gamma_8 - \Delta\Gamma_7. \quad (3)$$

The mixing of upper states into ground state by the spin-orbit coupling is then

$$|M_S\rangle = |{}^6SM_S\rangle - \sum_{ijM_S'} \frac{\langle i^4\Gamma_4 j M_S' | \zeta \sum_k \mathbf{l}_k \cdot \mathbf{s}_k | {}^6SM_S \rangle}{\Delta_i} |i^4\Gamma_4 j M_S'\rangle, \quad (4)$$

as shown in Fig. 1. The composite result of calculations is

$$\begin{aligned} |_{1,2}\Gamma_8\rangle &= (\sqrt{\frac{5}{6}})(|{}^6S\mp\frac{5}{2}\rangle) + (\sqrt{\frac{1}{5}}|{}^6S\pm\frac{3}{2}\rangle) \\ &\quad - (\sqrt{\frac{5}{6}}) \sum_i (\alpha_i \zeta / \Delta_i) [\sqrt{5} |i^4\Gamma_4 \mp 1, M_S \pm 1\rangle \\ &\quad + (\sqrt{\frac{3}{5}}) |i^4\Gamma_4 \pm 1, M_S \mp 1\rangle \mp (\sqrt{\frac{2}{5}}) |i^4\Gamma_4 0, M_S\rangle], \\ |_{3,4}\Gamma_8\rangle &= |{}^6S\mp\frac{1}{2}\rangle - \sum_i (\alpha_i \zeta / \Delta_i) \\ &\quad \times [(\sqrt{\frac{1}{2}}) |i^4\Gamma_4 \pm 1, M_S \mp 1\rangle \\ &\quad + (\sqrt{\frac{3}{2}}) |i^4\Gamma_4 \mp 1, M_S \pm 1\rangle + \sqrt{3} |i^4\Gamma_4 0, M_S\rangle], \\ |_{1,2}\Gamma_7\rangle &= (\sqrt{\frac{1}{6}})[|{}^6S\mp\frac{5}{2}\rangle] - (\sqrt{5}) |{}^6S\pm\frac{3}{2}\rangle \\ &\quad - \sum_i (\alpha_i \zeta / \Delta_i) [\sqrt{5} |i^4\Gamma_4 \mp 1, M_S \pm 1\rangle \\ &\quad - \sqrt{3} |i^4\Gamma_4 \pm 1, M_S \mp 1\rangle \pm \sqrt{2} |i^4\Gamma_4 0, M_S\rangle], \quad (5) \end{aligned}$$

TABLE I. Values^a of α_i , β_i , γ_i , and Δ_i for $D_q=900 \text{ cm}^{-1}$.

i	α_i	β_i	γ_i	Δ_i
1	0.633	-0.127	0.763	15905
2	0.761	0.285	-0.583	35380
3	0.143	-0.950	-0.277	44805

^a M. J. D. Powell (unpublished), quoted in Ref. 5. See also Ref. 10.

where

$$\begin{aligned} |i^4\Gamma_4 1, M_S\rangle &= \{\alpha_i |P1\rangle + \beta_i [(\sqrt{\frac{3}{8}}) |F1\rangle + (\sqrt{\frac{5}{8}}) |F-3\rangle] \\ &\quad - \gamma_i [(\sqrt{\frac{7}{8}}) |G1\rangle + (\sqrt{\frac{1}{8}}) |G-3\rangle]\} | \frac{3}{2}, M_S \rangle, \\ |i^4\Gamma_4 0, M_S\rangle &= \{\alpha_i |P0\rangle + \beta_i |F0\rangle + \gamma_i (-\sqrt{\frac{1}{2}} |G4\rangle \\ &\quad + \sqrt{\frac{1}{2}} |G-4\rangle)\} | \frac{3}{2}, M_S \rangle \\ |i^4\Gamma_4 -1, M_S\rangle &= \{\alpha_i |P-1\rangle \\ &\quad + \beta_i [(\sqrt{\frac{5}{8}}) |F3\rangle + (\sqrt{\frac{3}{8}}) |F-1\rangle] \\ &\quad + \gamma_i (-\sqrt{\frac{1}{8}} |G3\rangle + (\sqrt{\frac{7}{8}}) |G-1\rangle)\} | \frac{3}{2}, M_S \rangle. \quad (6) \end{aligned}$$

Δ_i denotes the energy separations of $i^4\Gamma_4$ from the ground state, ζ is the spin-orbit coupling constant $\sim 300 \text{ cm}^{-1}$ for our case.

III. CRYSTAL-FIELD SPIN-ORBIT ORBIT-LATTICE MECHANISM

The orbit-lattice interaction^{15,16} is the change in the local crystalline electric field upon a microscopic deformation of the equilibrium configuration of the surrounding ions by lattice vibrations. The situation was

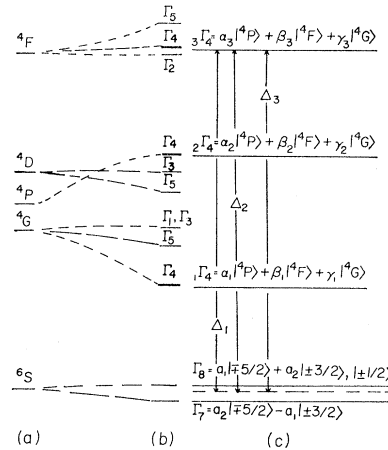


FIG. 1. Low-lying energy levels of Mn^{2+} : (a) Free ion, (b) splitting of states in cubic crystalline field. The figure is not drawn to scale, particularly, the 6S is shown raised up and its splitting amplified. (c) mixing of states $|LM_LSM_S\rangle$ by the cubic crystalline field. The symmetry rules show that states of different symmetry cannot mix, i.e., all matrix elements of Γ_1 , Γ_2 , Γ_3 , and Γ_6 with Γ_4 are identically zero, so that only the Γ_4 's can mix with Γ_4 (4P). Note that 4D completely drops out. For upper states the spin degeneracy $2S+1$ and L values are indicated. For ground states only M_S is written and $S=\frac{5}{2}$, $L=0$ are not given. The final step in which the excited $i\Gamma_4$ states are admixed into ground-state components Γ_7 and Γ_8 by the spin-orbit coupling is not depicted.

¹⁴ Y. Tanabe and S. Sugano, J. Phys. Soc. Japan 9, 753 (1954); 9, 766 (1954).

¹⁵ J. H. Van Vleck, Phys. Rev. 57, 426 (1940).

¹⁶ J. H. Van Vleck, J. Chem. Phys. 7, 72 (1939).

first examined by Van Vleck¹⁶ who calculated all the possible normal-mode vibrations for octahedral cubic crystals. Working within a d electron system the orbitals of which transform like $\Gamma_{5g}(T_{2g}; d_{xy}, d_{yz}, \text{ and } d_{zx})$ and $\Gamma_{3g}(E_g; d_{3z^2-r^2}, d_{x^2-y^2})$ it is important to admix only those vibrations which have the same symmetry as E_g or T_{2g} . The symmetry rules dictate that the vibrations of symmetry other than E_g or T_{2g} give identical zero contributions to the d electron wave functions. Thus, the totally symmetric vibration $A_1(\Gamma_1)$ and all the odd vibrations (which transform like $E_u, T_{1u}, \text{ or } T_{2u}$) must be excluded. This result follows directly from Jahn-Teller theorem and has been realized by Van Vleck¹⁵ and Blume and Orbach⁵ and discussed in detail in the author's work¹⁷ on the phonon-induced contribution to the transferred hyperfine coupling which appears as a superhyperfine splitting of Mn^{2+} lines in fluoride crystals. Thus, the orbit-lattice interaction in terms of Racah's¹⁸ C_l^m is written as⁵

$$V_{0L} = \sum_{l=2,4} \sum_{m=0,e} V(\Gamma_{3gl}) C(\Gamma_{3gl} m) \epsilon(\Gamma_{3gm}) + \sum_{l=2,4} \sum_{m=0,\pm 1} (-1)^m V(\Gamma_{5gl}) C(\Gamma_{5gl} m) \epsilon(\Gamma_{5g-m}), \quad (7)$$

where the coefficients $V(\Gamma_{3gl})$ and $V(\Gamma_{5gl})$ are calculated from the point-charge model and $\epsilon(\Gamma_{3gm})$ and $\epsilon(\Gamma_{5g-m})$

are the strain-tensor components with their symmetry given in the parenthesis. $C(\Gamma_{ig} l m)$ is the appropriate linear combination of normalized spherical harmonics, $C_l^m = [4\pi/(2l+1)]^{1/2} Y_l^m$ which transform like m th row of the i th irreducible representation of the octahedral group.

The wave functions given in the previous section involve the crystal field and the spin-orbit coupling. To specify them completely, for our purpose, we need the vibrational quantum number N_k . The phonon-induced shift of a particular Born-Oppenheimer state

$$|\Gamma_0 N_k\rangle = |\Gamma_0\rangle |N_k\rangle \quad (8)$$

by a two-phonon process¹⁹ may then be written as

$$\Delta\Gamma_0 = \sum_i \sum_{l=2,4} \sum_{m=0,e} V^2(\Gamma_{3gl}) \sum_{N_k'} \Delta_i^{-1} \times \langle N_k | \epsilon(\Gamma_{3gm}) | N_{k'} \rangle \langle N_{k'} | \epsilon(\Gamma_{3gm}) | N_k \rangle \times \langle \Gamma_0 | C(\Gamma_{3gl} m) | \Gamma_i \rangle \langle \Gamma_i | C(\Gamma_{3gl} m) | \Gamma_0 \rangle \quad (9)$$

plus similar terms of Γ_{5g} symmetry. The \sum_i is summation over all excited states and over $N_{k'}$ on all phonon modes. Δ_i are the energy separations between the excited Γ_i and ground Γ_0 . Using expressions (3) and (9) the phonon-induced correction to the cubic-field splitting is found to be

$$\begin{aligned} \Delta a = & \sum_l \sum_i \sum_{M_L' M_L} \sum_{M_s' M_s} \sum_{N_k'} 12 \Delta_i^{-1} \left(\frac{ee_{\text{eff}} \langle r^2 \rangle}{R^3} \right)^2 \left\{ \sum_{m=0,e} \langle N_k | \epsilon(\Gamma_{3gm}) | N_{k'} \rangle \langle N_{k'} | \epsilon(\Gamma_{3gm}) | N_k \rangle \right. \\ & \times [\langle {}_1\Gamma_8 M_s M_L | C(\Gamma_{3gl} m) | {}_i^4 \Gamma_4 M_L' M_s' \rangle \langle {}_i^4 \Gamma_4 M_L' M_s' | C(\Gamma_{3gl} m) | {}_1\Gamma_8 M_L M_s \rangle - \langle {}_1\Gamma_7 M_L M_s | C(\Gamma_{3gl} m) | {}_i^4 \Gamma_4 M_L' M_s' \rangle \\ & \times \langle {}_i^4 \Gamma_4 M_L' M_s' | C(\Gamma_{3gl} m) | {}_1\Gamma_7 M_L M_s \rangle] + (4/9) \sum_{m=0,\pm 1} (-1)^m \langle N_k | \epsilon(\Gamma_{5g-m}) | N_{k'} \rangle \langle N_{k'} | \epsilon(\Gamma_{5g-m}) | N_k \rangle \\ & \times [\langle {}_1\Gamma_8 M_L M_s | C(\Gamma_{5gl} m) | {}_i^4 \Gamma_4 M_L' M_s' \rangle \langle {}_i^4 \Gamma_4 M_L' M_s' | C(\Gamma_{5gl} m) | {}_1\Gamma_8 M_L M_s \rangle - \langle {}_1\Gamma_7 M_L M_s | C(\Gamma_{5gl} m) | {}_i^4 \Gamma_4 M_L' M_s' \rangle \\ & \left. \times \langle {}_i^4 \Gamma_4 M_L' M_s' | C(\Gamma_{5gl} m) | {}_1\Gamma_7 M_L M_s \rangle \right\}. \quad (10) \end{aligned}$$

Using the small wave-vector averaging procedure¹⁵ for acoustic phonons, which is appropriate at low temperatures, the expression (10) is found to be

$$\Delta a = K \int_0^{\Theta/T} \left[\frac{1}{2} + \frac{1}{e^x - 1} \right] x^3 dx = \Delta a_{zp} + K T^4 \int_0^{\Theta/T} \frac{x^3 dx}{e^x - 1}, \quad (11)$$

where the first term represents the zero-point vibrational contribution

$$\Delta a_{zp} = \frac{1}{8} K \Theta^4, \quad (12)$$

and the second the temperature dependence with

$$K = \frac{36}{5} \left(\frac{ee_{\text{eff}} \langle r^2 \rangle}{R^3} \right)^2 \frac{\hbar}{\rho \pi^2} (v_i^{-5} + \frac{2}{3} v_l^{-5}) (k/\hbar)^4, \quad (13)$$

¹⁷ K. N. Shrivastava, J. Phys. **C2**, 777 (1969).

¹⁸ G. Racah, Phys. Rev. **63**, 367 (1943).

¹⁹ Compare with Ref. 11. See also, M. D. Sturge in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York, 1967), Vol. 20, p. 92.

in which

$$\begin{aligned} \Gamma_{78} = & \sum_i \sum_l \sum_{M_s} \sum_{M_s'} \sum_{M_L} \sum_{M_L'} \Delta_i^{-1} \left\{ \sum_{m=\theta, e} \langle {}_1\Gamma_8 M_L M_s | C(\Gamma_{3\theta} l m) | {}_i^4\Gamma_4 M_L' M_s' \rangle \langle {}_i^4\Gamma_4 M_L' M_s' | C(\Gamma_{3\theta} l m) | {}_1\Gamma_8 M_L M_s \rangle \right. \\ & - \langle {}_1\Gamma_7 M_L M_s | C(\Gamma_{3\theta} l m) | {}_i^4\Gamma_4 M_L' M_s' \rangle \langle {}_i^4\Gamma_4 M_L' M_s' | C(\Gamma_{3\theta} l m) | {}_1\Gamma_7 M_L M_s \rangle + (4/9) \sum_{m=0, \pm 1} (-1)^m \\ & \times \langle {}_1\Gamma_8 M_L M_s | C(\Gamma_{5\theta} l m) | {}_i^4\Gamma_4 M_L' M_s' \rangle \langle {}_i^4\Gamma_4 M_L' M_s' | C(\Gamma_{5\theta} l m) | {}_1\Gamma_8 M_L M_s \rangle - \langle {}_1\Gamma_7 M_L M_s | C(\Gamma_{5\theta} l m) | {}_i^4\Gamma_4 M_L' M_s' \rangle \\ & \left. \times \langle {}_i^4\Gamma_4 M_L' M_s' | C(\Gamma_{5\theta} l m) | {}_1\Gamma_7 M_L M_s \rangle \right\}. \quad (14) \end{aligned}$$

Here, Θ is the Debye characteristic temperature. v_t and v_l are the transverse and longitudinal sound velocities, k is the Boltzmann constant, and ρ is the mass density of the crystal.

IV. COMPARISON WITH EXPERIMENT

The ground-state splitting of Mn^{2+} ion in MgO has been measured by Walsh *et al.*²⁰ as a function of temperature and as a function of externally applied hydrostatic pressure.²¹ Attempts have been made²⁰ to understand the temperature dependence in terms of thermal expansion alone, by arbitrary normalization procedure. In Fig. 2 we show the experimentally measured temperature dependence in a and its value expected on the basis of thermal expansion alone as deduced from the pressure experiments.²¹ It is noticed that at a given temperature there is a small (0–5%) “shift” between the values expected from thermal expansion and those measured. It is also realized that this shift increases with increasing temperature. Since the phonon-induced crystal field effects are electrostatic in nature and since they are expected to increase with increasing temperature because of increased amplitudes of lattice vibrations, we postulate that the shift in the values of a measured and calculated on the basis of thermal expansion alone is essentially due to lattice vibrations. This shift is rededuced on Fig. 3, and compared with

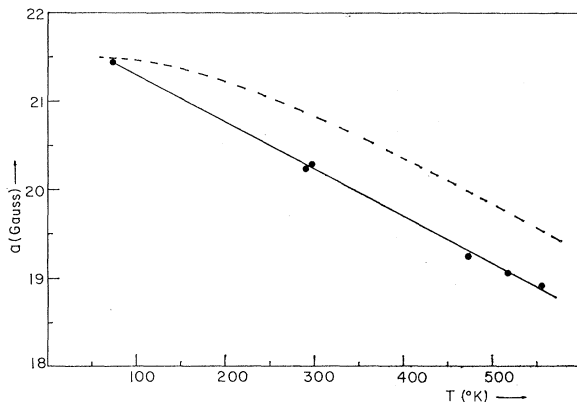


FIG. 2. Temperature dependence of the cubic field splitting parameter a of Mn^{2+} in MgO . The points and continuous curve give the experimental measurements. The dashed curve deduced from pressure experiments indicates the temperature dependence as expected on the basis of thermal expansion alone.

²⁰ W. M. Walsh, Jr., J. Jeener, and N. Bloembergen, *Phys. Rev.* **139**, A1338 (1965).

²¹ W. M. Walsh, Jr., *Phys. Rev.* **122**, 762 (1961).

that calculated from (11) with

$$\Delta a_{zp}^{\text{expt}} = (0.16 \pm 0.05) \times 10^{-4} \text{ cm}^{-1}, \quad (15)$$

and

$$K^{\text{expt}} = (3.2 \pm 0.5) \times 10^{-15} \text{ cm}^{-1} (\text{°K})^{-4}. \quad (16)$$

The fit is satisfactory.

To check the quantitative validity of the theory we compute the value of Γ_{78} from (14). The matrix elements in Γ_{78} are calculated to the lowest order in orbit-lattice interaction using the method of Elliott *et al.*²² as given by Blume and Orbach and for which we took the coefficients of fractional parentage from the work of Racah¹⁸ and the $3-j$ and $6-j$ symbols from the tables of Rotenberg *et al.*²³ The computed value

$$\Gamma_{78} = 5.14 \times 10^6 \text{ ergs}^{-1} \quad (17)$$

substituted in (13) with $\rho = 3.7 \text{ g/cm}^3$, $\Theta = 750 \text{°K}$, $R = 2.1 \times 10^{-8} \text{ cm}$, $v_l = 8.8 \times 10^5 \text{ cm/sec}$, $v_t = 6.3 \times 10^5 \text{ cm/sec}$ appropriate²⁴ to MgO and the effective charge of a ligand, $e_{\text{eff}} = 2e$ and $\langle r^2 \rangle = 1.584 a_0^2$ for Mn^{2+} gives

$$K^{\text{cal}} = 7.5 \times 10^{-14} \text{ cm}^{-1} (\text{°K})^{-4} \quad (18)$$

to be compared with the experimental value (16). Using (18) and (12) we calculate the zero-point vibrational contributions

$$\Delta a_{zp}^{\text{cal}} = 3.2 \times 10^{-4} \text{ cm}^{-1} \quad (19)$$

to be compared with the experimental value (15) of $\approx 0.2 \times 10^{-4} \text{ cm}^{-1}$. The calculations do not agree with

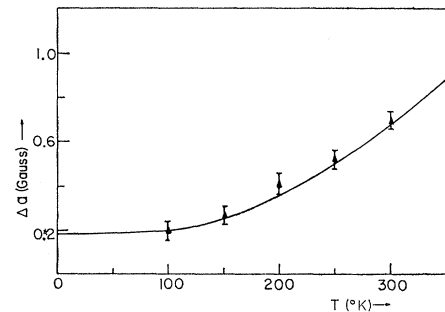


FIG. 3. The shift in cubic-field-splitting parameter between the experimental measurements and those expected from thermal expansion is represented as a function of temperature by triangular points and associated errors. The continuous curve is calculated from the expression (11) on the basis of small wave-vector averages for acoustic phonons with parameters of (15) and (16).

²² J. P. Elliott, B. R. Judd, and W. A. Runciman, *Proc. Roy. Soc. (London)* **A240**, 509 (1957).

²³ M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j symbols* (MIT Press, Cambridge, Mass., 1959).

²⁴ H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 214.

the experiment. Nevertheless, the calculated zero-point phonon contribution is reasonable because it is only about 14% of the low-temperature rigid-lattice value a of $20.1 \times 10^{-4} \text{ cm}^{-1}$. Comparison of (18) with (16) shows that the calculated value is high by a factor of 20. Part of this increase is due to the use of small wave-vector ($\sin kR = kR$) averages¹⁵ which overestimate the phonon contribution. The calculations are sensitive to the choice of the ratio ζ/Δ which is certainly not known with enough accuracy. Thus, it is obvious¹² that the calculated (18) and measured (16) estimates can be brought into closer agreement by adjusting the value of spin-orbit coupling parameter and the excited-state separations from the ground state. Part of the discrepancy between the measured (15) and calculated (19) zero-phonon contribution to the ground-state splitting could arise because of the use of small-wave-vector approximation in the calculation (12). In the work of Van Vleck,¹⁵ the Debye characteristic temperature was taken to be only 90°K so that in his case the approximation was described to break down at the liquid-air temperature. Further, Van Vleck had approximated the integral in (11) by replacing the limit Θ/T by infinity, in which case the value of the integral is $\pi^4/15$, so that his result remained good only at extremely low temperatures. It was also suggested by Van Vleck²⁵ that at higher temperatures the most important frequencies are those near the high-frequency "cutoff" to the Debye spectrum. These have wavelengths of the order of $hc/k\Theta$. In our case of MgO, the Debye temperature is 750°K, so that the small-wave-vector averaging procedure is valid over a larger range of temperatures than in Van Vleck's case. Nevertheless, we may recalculate (12) in the limit of temperatures high compared with the Debye Θ , so that the lattice frequencies may be assumed constant. This is very much like replacing the Debye ν^2 law by a $\nu = \text{const} = K\Theta/h$ "law." The calculations for this limit have been developed by Huang¹¹ using Van Vleck's suggestion.²⁵ In our case, this method gives

$$\delta a_{zp} = \frac{1}{2} \Theta^2 \times 36 \left(\frac{e e_{\text{eff}} \langle r^2 \rangle}{R^4} \right)^2 \frac{1}{2\rho} \Gamma_{78} \frac{\hbar}{2\pi} \times (v_l^{-3} + 2v_t^{-3}) \left(\frac{k}{2\pi\hbar} \right)^2. \quad (20)$$

In order to compare this result with (12) we evaluate the dimensionless ratio

$$\frac{\Delta a_{zp}}{\delta a_{zp}} = \frac{2}{5} \left(\frac{k}{\hbar} \right)^2 R^2 \Theta^2 \frac{(v_l^{-5} + \frac{2}{3}v_t^{-5})}{(v_l^{-3} + 2v_t^{-3})} = 1.966 \quad (21)$$

which indicates that the small-wave-vector averaging procedure (12) overestimates the value of zero-point vibrational contribution to the ground-state splitting by a factor of about 2 compared to the one obtained (20) from " $\nu = \text{const}$ " law. The recalculated value of (19) would then be

$$\delta a_{zp}^{\text{cal}} = 1.6 \times 10^{-4} \text{ cm}^{-1}, \quad (22)$$

²⁵ See the argument below the expression (11) of Ref. 15.

which is in better agreement with (15) but still significantly off. One comment must be made on the optical phonon contribution to the ground state splitting. Using $\nu = \text{const}$ at the BZ boundary, we find

$$\delta a^{\text{opt}} = \delta a^{\text{opt}}(0) + \delta a^{\text{opt}}(T), \quad (23)$$

where

$$\delta a^{\text{opt}}(0) = 36 \left(\frac{e e_{\text{eff}} \langle r^2 \rangle}{R^4} \right)^2 \Gamma_{78} \frac{\hbar}{8\pi\rho R^3} \sum_r \nu_{rB}^{-1}, \quad (24)$$

and

$$\delta a^{\text{opt}}(T) = 36 \left(\frac{e e_{\text{eff}} \langle r^2 \rangle}{R^4} \right)^2 \times \Gamma_{78} \frac{\hbar}{8\pi\rho R^3} \sum_r \nu_{rB}^{-1} (e^{h\nu_{rB}/kT} - 1)^{-1}, \quad (25)$$

where the optical-phonon frequencies near the BZ boundary for the longitudinal and transverse branches are²⁶

$$\begin{aligned} \nu_{lB} &= 1.83 \times 10^{13} \text{ Hz}, \\ \nu_{t_1B} &= 1.53 \times 10^{13} \text{ Hz}, \\ \nu_{t_2B} &= 1.49 \times 10^{13} \text{ Hz}. \end{aligned} \quad (26)$$

From (22), (24), and (26) we calculate

$$\delta a_{zp}^{\text{cal}} / \delta a^{\text{opt}}(0) \simeq 8.0, \quad (27)$$

indicating that optical-phonon contribution to the zero-point ground-state splitting is small. Similarly, from (25), we find that in our system the contribution of optical phonons to the temperature dependence is also small. We would like to point out that it is dangerous to use the Debye model at high temperatures²⁷ and a study at these temperatures must wait until non-Debye calculations become available, and these calculations will have to be point-to-point computations taking explicitly the lattice spectrum and treating even the temperature dependence of sound velocities and the lattice spacing due to the anharmonic effects.

V. CONCLUSIONS

We have demonstrated that a very large ($\simeq 75\%$) part of the temperature dependence in the ground-state splitting parameter a of Mn^{2+} in MgO arises from thermal expansion alone. The remaining ($\simeq 25\%$) may be understood in terms of lattice vibrations.

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²⁶ J. P. Mon, J. Phys. (Paris) **26**, 611 (1965).

²⁷ The specific-heat data of W. F. Giaugne and R. C. Archibald, J. Am. Chem. Soc. **59**, 561 (1937), fit the Debye function for $\Theta = 750^\circ\text{K}$ quite accurately at temperatures below 270°K . At high temperatures substantial deviations are observed confirming the inadequacy of the Debye model. There is at least one more point to it. The sound velocities themselves are functions of temperature rather than constant. This inadequacy is also noted by G. F. Imbush, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, Phys. Rev. **133**, A1029 (1964), who phenomenologically fit the fluorescence of Cr^{3+} and V^{2+} in MgO for temperatures lower than 275°K .