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Zero-Field Splitting of S-State Ions. III. Corrections to Parts I and II and Application to Distorted Cubic Crystals*

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The procedures developed in two previous papers by the authors for calculating the parameters D and E in the spin Hamiltonian $\mathcal{H}_s = D[3S_z^2 - S(S+1)] + E(S_x^2 - S_y^2)$ for iron-group $3d^5(^6S)$ ions are applied to a distorted cubic system, namely, that of a Mn^{++} ion in a MgO host lattice under uniaxial stress. The parameters D and E for this system are specified respectively by two stress coefficients C_{11} and C_{44}, which contain contributions from point-charge and overlap mechanisms of the amounts: C_{11} (point charge) $=2.10$, C_{11} (overlap) $=-0.14$, C_{44} (point charge) $=-1.44$, C_{44} (overlap) $=-0.28$ all in units of 10^{-13} cm/dyn. The totals, $C_{11}=1.96$, $C_{44}=1.16\times10^{-13}$ cm/dyn are in resonable agreement with the values $C_{11}=7.1$, $C_{44}=-2.1\times10^{-13}$ cm/dyn measured by Feher. An Appendix is included which lists corrections to the spin-spin contributions to D and E that were derived in two earlier papers.

I. INTRODUCTION

IN two earlier papers[1,2] (to be referred to as SDO I and SDO II), we have analyzed the various mechanisms that contribute to D and E in the spin Hamiltonian,

$$\mathcal{H}_s = D[3S_z^2 - S(S+1)] + E(S_x^2 - S_y^2),$$

for Mn^{++} ions in noncubic crystalline fields. It has been shown that the combined effects of the spin-spin[3] and Blume-Orbach spin-orbit[4] mechanisms, taken together with overlap effects can account reasonably well for the magnitudes and signs of the D and E terms in Mn^{++}:$\mathrm{ZnF_2}$. In the present paper, we consider Mn^{++} ion in MgO crystal which was originally cubic, but which has had its cubic symmetry destroyed by uniaxial stress.[5]

The coupling parameters for the uniaxially distorted Mn^{++}–MgO system will be calculated including both point-charge–point-multipole and overlap effects. These parameters are defined by the spin Hamiltonian[5]

$$\mathcal{H} = \mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}, \tag{1}$$

where $\mathbf{D}$ is a second-rank tensor, the components of which are given by

$$D_{ij} = \sum_{kl} C_{ijkl} X_{kl}, \tag{2}$$

where X_{kl} are components of the external stresses and C_{ijkl} is referred to as the stress coefficient. For a cubic (unstrained) environment, it turns out that only two independent stress coefficients survive. Using the Voigt notation, these are C_{11} and C_{44} with $C_{12} = -\frac{1}{2}C_{11}$ using the requirement that the trace of D must vanish.

II. SPIN HAMILTONIAN FOR Mn^{++} IN MgO UNDER UNIAXIAL STRESS

A. Point-Charge Contribution to D

The calculation of the point-charge–point-multipole and overlap contributions to D and E follows the same lines as in SDO I and SDO II. However, we have recently discovered some unfortunate errors in our algebra for the spin-spin contributions in both cases. The modified algebraic expressions are listed in the Appendix together with some of the numerical results that change as a consequence of the changes in the algebra for the spin-spin contribution. For convenience, the formulas derived for D and E for the point-charge-multipole model will be repeated here. They are based on a value of the one-electron spin-orbit coupling constant $\tau = 300\ \mathrm{cm}^{-1}$ and the expectation values[1] $\langle r^2\rangle = 1.5482\ a_0^2$ and $\langle r^4\rangle = 5.5126\ a_0^2$ for the Hartree-Fock $3d$ wave functions of Mn^{++} ion. According to SDO I:

$$\begin{aligned}
&D_{WC} = -1.7417(B_2^0)^2;\\
&D_{\mathrm{O\text{-}D\text{-}S}} = 2.1044(B_2^0)^2;\\
&D_{\mathrm{ss}}(d\to s) = -0.05218B_2^0; && E_{\mathrm{ss}}(d\to s) = -0.06392B_2^2;\\
&D_{\mathrm{ss}}(d\to d) = +0.00506B_2^0; && E_{\mathrm{ss}}(d\to d) = +0.00617B_2^2;\\
&D_{\mathrm{ss}}(d\to g) = -0.02594B_2^0; && E_{\mathrm{ss}}(d\to g) = -0.03494B_2^2;\\
&D_{\mathrm{B\text{-}O}} = 4.3404(B_4^0)'; && E_{\mathrm{B\text{-}O}} = -16.47275B_4^2.
\end{aligned} \tag{3}$$

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[1] R. R. Sharma, T. P. Das, and R. Orbach, Phys. Rev. **149**, 257 (1966), hereafter referred to as SDO I.

[2] R. R. Sharma, T. P. Das, and R. Orbach, Phys. Rev. **155**, 338 (1967), hereafter referred to as SDO II.

[3] M. H. L. Pryce, Phys. Rev. **80**, 1107 (1950); R. Bersohn and T. P. Das, *ibid.* **100**, 1792 (1955); A. S. Chakravarty, J. Chem. Phys. **39**, 1004 (1963); R. Orbach, T. P. Das and R. R. Sharma, in *Proceedings International Conference of Magnetism, Nottingham, 1964* (The Institute of Physics and the Physical Society, London, 1965), p. 330.

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

[5] G. D. Watkins and E. Feher, Bull. Am. Phys. Soc. **7**, 29 (1962); N. S. Shiren, *ibid.* **7**, 29 (1962); E. Feher, Phys. Rev. **136**, A145 (1964).

The subscripts refer to the various mechanisms that have been discussed in SDOI. WC denotes the Watanabe mechanism[6] involving two orders each in the spin-orbit interaction and the distorted crystal-field component B_2^0 considering only the excited states within the d^5 configuration. The O–D–S mechanism[3] also includes two orders each in spin-orbit interaction and B_2^0, but involves excited states outside d^5 configuration in the perturbation treatment. The spin-spin contribution D_{ss} represents a more complete evaluation of the Pryce mechanism,[3] involving one order in the spin-spin interaction and one order in B_2^0. Finally the B-O mechanism involves the spin-orbit interaction twice, and the unbalanced noncubic component of $(B_4^0)'$ in consort with the cubic crystalline field B_4^0. The expressions in (3) give the values of D and E in units of cm^{-1}. The distorted crystalline fields B_2^0 and B_2^2 are in natural units of $e^2/2a_0$,[3] and $(B_4^0)'$ and B_4^0 in units of $e^2/2a_0$.[5] The Watanabe and O–D–S mechanisms turn out to make very small contributions to D and therefore are not included in the expression for E.

To calculate the crystal-field coefficients B_n^m, it is necessary first to know the positions of the ions in the axially distorted MgO crystal. These can be obtained from standard elastic theory if one assumes that the local elastic constants around a Mn^{++} ion are the same as for pure MgO lattice. Uniaxial stress measurements have been performed[5] for the directions [001], [110], and [111]. We shall impose a stress along the [001] direction in order to compute C_{11} and a stress along the [110] direction to compute C_{44}. In the former case, choosing the direction of stress [001] as along the Z direction, the strain components are given by

$$e_{xx}=-\frac{c_{12}P}{(c_{11}-c_{12})(c_{11}+c_{12})}=e_{yy},$$

$$e_{zz}=\frac{(c_{11}+c_{12})P}{(c_{11}-c_{12})(c_{11}+2c_{12})}, \tag{4}$$

where P is the external stress and c_{11} and c_{12} are the two elastic constants for a cubic crystal. For the MgO lattice,[7]

$$c_{11}=29.54\times10^{11}\text{ dyn/cm}^2,$$

$$c_{12}=8.49\times10^{11}\text{ dyn/cm}^2. \tag{5}$$

Thus, a uniaxial extensional stress $P=X_{33}=600$ kg/cm$^2=0.5886\times10^9$ dyn/cm^2 gives rise to strain components

$$e_{xx}=e_{yy}=-0.5103\times10^{-4},$$

$$e_{zz}=2.2859\times10^{-4}. \tag{6}$$

The changes in the dimensions of the unit cell along X, Y, Z directions are then given by

$$\Delta x=ae_{xx}=ae_{yy}=\Delta y,$$

$$\Delta z=ae_{zz}, \tag{7}$$

where $a=4.203$ Å is the cell dimension of the original cubic MgO unit cell.[5] There are several possible ways to determine the components of the crystal field due to the resultant tetragonal array of double-positive and double-negative point charges on the ions. We follow the procedure of Nijboer and de Wette[8] and obtain, in natural units,

$$B_2^0=0.52991\times10^{-4};$$

$$(B_4^0)'=(B_4^0)_{nc}-(14/5)^{1/2}(B_4^4)_{nc}$$

$$=0.15006\times10^{-4}. \tag{8}$$

The additional contributions to B_2^0 and $(B_4^0)'$ which arise from induced quadrupoles and higher multipole moments are currently unavailable so that we are forced to use only the point-charge estimates of the crystalline fields (8) to compute the various terms listed in (3). We find

$$D_{WC}=-0.00005\text{ cm}^{-1},$$

$$D_{\text{O-D-S}}=0.00006,$$

$$D_{(C)}=D_{\text{O-D-S}}+D_{WC}=0.00001,$$

$$D_{\text{ss}}(d\to s)=-0.0276,$$

$$D_{\text{ss}}(d\to d)=+0.0027,$$

$$D_{\text{ss}}(d\to g)=-0.0137,$$

$$D_{\text{ss}}(\text{total})=-0.0387,$$

$$D_{\text{B-O}}=+0.6531. \tag{9}$$

Summing, we find for the extensional stress $X_{33}=+600$ kg/cm^2,

$$D(\text{point charge})=0.62\times10^{-4}\text{ cm}^{-1}. \tag{10}$$

The terms in (9) display the same qualitative behavior as in SDO I for Mn^{++} in ZnF$_2$. The Watanabe and O–D–S mechanisms lead to individually small contributions of opposite sign, their combined effect after mutual cancellation being negligible. The reason for the small spin-spin contribution (more than a factor of fifteen smaller than the Blume-Orbach contribution) is discussed in connection with Eq. (82) in SDO I.

Using (2) and (10), we obtain

$$C_{11}(\text{point charge})=+2.10\times10^{-13}\text{ cm/dyn}. \tag{11}$$

This is to be compared with the experimental value[5]

$$C_{11}(\text{expt})=+7.1\times10^{-13}\text{ cm/dyn}. \tag{12}$$

The point-charge estimate is thus of the same sign as experiment but is nearly a factor of three smaller in

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[6] H. Watanabe, Progr. Theoret. Phys. (Kyoto) **18**, 405 (1957).

[7] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Co., Cleveland, Ohio, 1962), 44th ed., p. 2801.

[8] B. R. A. Nijboer and F. W. de Wette, Phys. Rev. **133**, A1327 (1964).

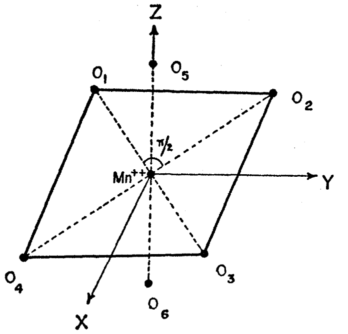

FIG. 1. Configuration of O^{--} ions around Mn^{++} for stress along the [001] direction. The equatorial axes of the tetragonal system are chosen along X and Y.

magnitude. In their earlier work, Blume and Orbach[4] had obtained a magnitude comparable to that given by (12), but of opposite sign. The reason for this was an unfortunate error in the choice of the phases of some of the many-electron determinantal functions for the ^4G state which occurs in the required wave functions of the excited states of the $3d^5$ configuration.

It is now of interest to compute the overlap contribution to D and E, as discussed in the Introduction. Our procedure is somewhat similar to Kondo's[9] but is considerably more complete and accurate, as discussed in SDO II.

B. Overlap Contribution to D

The expressions in SDO II were derived for the contributions to D and E in terms of overlap and other two-center integrals and the pertinent charge transfer parameters. We shall make use of these expressions to calculate D in the present case. In the absence of any knowledge about the charge-transfer coefficients γ, we are unable to include its effect and calculate the contributions to D which arise from overlap alone.

For the sake of uniformity of notation, the six nearest-neighbor O^{--} ions, equidistant from the Mn^{++} ion, are denoted as shown in Fig. 1. The four equatorial O^{--} ions are denoted as O_1, O_2, O_3, O_4, and the ones along the direction of stress (Z axis) are denoted as O_5, O_6. This is equivalent to the notation used for the six nearest-neighbor F^- ions in MnF_2 except that the equatorial O^{--} ions are now arranged in a square and the angle subtended by O_1 and O_2 at the Mn^{++} site is now $\pi/2$. For $D_{ss}{}^{l}$, the local spin-spin interaction mechanism, the pertinent expressions we shall use are (42a), (42b), and (42c) of SDO II. For $D_{ss}{}^{nl}$, the nonlocal spin-spin contribution, the pertinent expressions are the revised versions of (58a), (58b), and (58c). For $D_{so}{}^{l}$, the local spin-orbit contribution, the pertinent expressions are (87a), (87b), and (87c) of SDO II. For $D_{so}{}^{nl}$, (99a), (99b), and (99c) are used, while for the distant spin-orbit contribution $D_{so}{}^{d}$, equation (110) of SDO II is used. We shall not reproduce these rather elaborate expressions here but consider instead a number of quantities which these expressions contain involving one- and two-center integrals. These quantities are listed below:

$$S_i(O_j) = \int u_{3d}{}^0 \alpha_2(O_j LM \mid a_j, r)\, dr; \tag{13}$$

$$g_{3d,l_2}{}^{n,n+3}(O_j, i) = \int_0^\infty dr_1 \frac{(u_{3d}{}^0(1))^2}{r_1{}^{n+3}} \times \int_0^{r_1} dr_2 u_{3d}{}^0(2) \alpha_{l_2}(O_j \mid a, r_2) r_2{}^n; \tag{14}$$

$$h_{3d,l_2}{}^{n,n+3}(O_j, i) = \int_0^\infty dr_2 \frac{u_{3d}{}^0(2) \alpha_{l_2}(O_j \mid a, r_2)}{r_2{}^{n+3}} \times \int_0^{r_2} dr_1 (u_{3d}{}^0(1))^2 r_1{}^n; \tag{15}$$

$$\zeta_{3d,2}(O_j LM) = \int u_{3d}{}^0 \zeta(r) \alpha_2(O_j LM \mid a_j, r)\, dr; \tag{16}$$

$$\zeta_{p,p}(O^{--}) = \int u_{2p}{}^0(O^{--}) \zeta(r) u_{2p}{}^0(O^{--})\, dr; \tag{17}$$

with

$$\zeta(r) = (e^2 h^2/4m^2 c^2 a_0{}^3) r^{-1} (dV/dr). \tag{18}$$

Here $V(r)$ is the one-electron Hartree-Fock potential and $\zeta(r)$ represents the strength of the spin-orbit interaction at a distance r from the attractive oxygen or manganese center. $\zeta_{p,p}(O^{--})$ is thus the conventional spin-orbit constant for the O^{--} ion. The integrals in (13), (14), and (15) arise from the two-center matrix elements between orbitals of Mn^{++} and O^{--} ions. $S_i(O_j)$ arises from the overlap between $3d$ orbitals of Mn^{++} and $2s$ and $2p$ orbitals on O^{--} ions, the suffix j referring to the particular neighbor $j=1, 2\cdots$ and i to the $2s$, $2p_\sigma$, or $2p_\pi$ orbital with ($L=0$, $M=0$), ($L=1$, $M=0$), and ($L=1$, $M=\pm1$), respectively. The integrals $g_{3d,l_2}{}^{n,n+3}(O_j, i)$ and $h_{3d,l_2}{}^{n,n+3}(O_j, i)$ arise from the matrix element between Mn^{++} $3d$ orbitals and O^{--} orbitals, the subscripts j and i having the same meaning as in $S_i(O_j)$. The integral $\zeta_{3d,2}(O_j LM)$ arises from the matrix element of the spin-orbit operator (18) between Mn^{++} $3d$ and O^{--} orbitals. In Eq. (17), where the spin-orbit operator is referred to the oxygen nucleus, we use for V the usual expression derived from the electronic $2p$ wave function:

$$V = (1/u_{2p}{}^0)(d^2 u_{2p}{}^0/dr^2) - (2/r^2). \tag{19}$$

Here $u_{2p}{}^0$ represents r times the normalized radial wave function for the $2p$ orbitals. Similarly, in the integral (15) where one is concerned with the spin-orbit

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

TABLE I. Table of overlap integrals and two-center spin-orbit integrals.

j	S_s (O_j)	S_σ (O_j)	S_π (O_j)	$\zeta_{3d,\,2}$ (O_j00)	$\zeta_{3d,\,2}$ (O_j10)	$\zeta_{3d,\,2}$ (O_j11)
1	0.067999	0.083138	0.062768	0.305889	0.663676	0.407618
5	0.067928	0.083128	0.062713	0.305486	0.772631	0.406933

operator on the Mn^{++} ion, one uses

$$V=(1/u_{3d}^0)(d^2u_{3d}^0/dr^2)-(6/r^2), \qquad (20)$$

where u_{3d}^0 is r times the normalized radial wave function[10] for Mn^{++} $3d$ orbitals. In Eqs. (13), (14), and (15), a_j represents the distance between the Mn^{++} ion and the jth O^{--} ion. The functions $\alpha_l(OLM \mid ar)$ are defined by the relation

$$\Phi(OLM \mid R\Theta\Phi)=\sum_{l=0}^{\infty} r^{-1}\alpha_l(OLM \mid ar)\,Y_l^M(\theta,\varphi), \qquad (21)$$

where $(R\Theta\Phi)$ represent polar coordinates of a point with respect to the O^{--} ion, the Mn^{++}–O^{--} line being taken as the polar axis, while (r, θ, φ) represent the polar coordinates with respect to the Mn^{++} ion and the same polar axis. The methods for obtaining the α functions and the two-center integrals have already been described in SDO II and will not be repeated here. We shall remark merely on the choice of O^{--} wave functions that were employed in the evaluation of the integrals. For the $2p$ wave function of the O^{--} we used the wave function employed by Yamashita and Kojima[11] in their calculations on MgO. This function was expressed in terms of the sum of two exponentials:

$$u_{2p}^0=6.872r^2[\exp(-2.9r)+0.15\exp(-1.1r)]. \qquad (22)$$

Since no $2s$ wave functions for the O^{--} ion in MgO are available at this time, we made use of the $2s$ Hartree-Fock wave function for the O^- ion calculated by Hartree, Hartree, and Swirles.[12] The $2s$ function is more extended than the $1s$ wave function, and there will thus be some variation in the radial wave function upon going from the O^- to the O^{--} ion. However, this variation will be less pronounced than for the more spread out $2p$ wave functions.

For $\zeta_{d,d}(Mn^{++})$, which occurs in the direct contribution to D through the spin-orbit mechanism, we have taken the value 300 cm^{-1} used in SDO I and by Kondo[9] in his calculations. The value of $\zeta_{p,p}(O^{--})$, the spin-orbit coupling constant for a $2p$ electron on O^{--}, comes out as 67 cm^{-1}, using Eqs. (17), (18), (19), and (22).

The distance a_j for $j=1$, 2, 3, 4 are the equatorial distances $\frac{1}{2}a(1+e_{xx})$ and the distance a_j for $j=5$, 6 are the polar distances $\frac{1}{2}a(1+e_{zz})$, as calculated in Sec. II A. In Table I, we have tabulated the values of the overlap integrals $S_i(O_j)$ and the two-center spin-orbit integrals $\zeta_{3d}(O_jLM)$. In Tables II and III the quantities pertinent to the spin-spin contribution calculation are tabulated for the distances corresponding to equational and polar O^{--} ions. Finally, Table IV lists the significant local, nonlocal, and distant contributions to D arising from the spin-spin and spin-orbit mechanisms.

From Table IV, several interesting observations may be made. First we notice that the relative signs of the local and nonlocal spin-spin contributions are the same as those found in SDO II for Mn^{++}–ZnF_2 system. The same remark applies to the relative signs for the local, nonlocal, and distant spin-orbit contributions. Again, the nonlocal spin-spin terms dominate over the local terms. However, the nonlocal and spin-orbit contributions are more than an order of magnitude smaller than the local contribution. This is in contrast to the situa-

TABLE II. List of quantities $g_{d,\,l_2}^{l'-1,\,l'+2}$ (OLM) and $h_{d,\,l_2}^{l'-1,\,l'+2}$ (OLM) for overlap contributions to D and E,[a] $a_1=3.9734979a_0$.

l'		1		3		5
l_2, L, M	$M_{3d,\,l_2}^{L,M}$	g	h	g	h	h
0, 0, 0			−0.01020426	−0.00303941	···	···
2, 0, 0	−0.06781956	−0.00092085	−0.00522873	−0.00060189	−0.00170658	
4, 0, 0	···	···	−0.00179174	−0.00008444	−0.00043718	−0.00027477
0, 1, 0			−0.05176313	−0.01887031	···	···
2, 1, 0	−0.08213056	−0.00249536	−0.01055871	−0.00161289	−0.00392449	···
4, 1, 0	···	···	−0.00213220	−0.00015697	0.00061104	−0.00030338
2, 1, 1	0.06252914	0.00128116	0.00592425	0.00082997	0.00209888	···
4, 1, 1	···	···	0.00186975	0.00008331	0.00468840	0.000217820

[a] Blank spaces in the Table indicate that these integrals are not required.

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[10] R. E. Watson, Phys. Rev. **118,** 1036 (1960).

[11] J. Yamashita and M. Kojima, J. Phys. Soc. Japan **7,** 261 (1952).

[12] D. R. Hartree, W. Hartree, and B. Swirles, Phil. Trans. Roy. Soc. London **A238,** 229 (1939).

TABLE III. List of quantities $g_{d,l_2}{}^{l'-1,l'+2}$ (OLM) and $h_{d,l_2}{}^{l'-1,l'+2}$ (OLM) for overlap contributions to D and E,[a] $a_5=3.9723771\ a_0$.

$l_2, L^{l'}, M$	$M_{3d,l_2}{}^{L,M}$	1		3		5
		g	h	g	h	h
0, 0, 0	···	···	−0.01021921	−0.00304400	···	···
2, 0, 0	−0.06788788	−0.00092242	−0.005233652	−0.00060292	−0.00170932	···
4, 0, 0	···	···	−0.00179635	−0.00008519	−0.00044177	−0.00028081
0, 1, 0	···	···	−0.05180850	−0.01888779	···	···
2, 1, 0	−0.08216232	−0.00249765	−0.01056707	−0.00161436	−0.00392786	···
4, 1, 0	···	···	−0.00214024	−0.00016491	−0.00061635	−0.00030781
2, 1, 1	0.06258668	0.00128275	0.00593101	0.00083099	0.00210137	···
4, 1, 1	···	···	0.00187422	0.00009904	0.00047253	0.00022159

[a] Blank spaces in the Table indicate that these integrals are not required.

tion in Mn^{++}–ZnF_2 where the distant term was only a factor of 4 smaller. This behavior can be understood by noticing that the spin-orbit constant $\zeta_{pp}(O^{--})$ is more than five times smaller than $\zeta_{dd}(Mn^{++})$, while $\zeta_{pp}(F^-)$ is only about a third smaller than $\zeta_{dd}(Mn^{++})$. The magnitudes of the total spin-spin and spin-orbit contributions through the overlap effect are comparable as was the case in Mn^{++}-ZnF_2. The signs of the two contributions are, however, opposite to those in Mn^{++}-ZnF_2.

The total overlap contribution to D, combining the separate parts in Table III, is given by

$$D=-0.04\times10^{-4}\ \text{cm}^{-1}. \tag{23}$$

On combining this result with the point-charge value in (10), one finds

$$C_{11}=1.96\times10^{-13}\ \text{cm/dyn}. \tag{24}$$

This value is again to be compared with Feher's result[5]:

$$C_{11}(\text{expt})=7.1\times10^{-13}\ \text{cm/dyn}. \tag{25}$$

C. Point-Charge and Overlap Contributions to E

Before discussing the nature of agreement between theory and experiment for C_{11} we shall evaluate C_{44}. The procedure for doing so is essentially identical to that for C_{11}, and therefore will be described rather briefly. In the presence of stress along the [110] direction the distorted lattice has the structure shown in Fig. 2. Thus, the square pattern in Fig. 1 is replaced by a rhombuslike pattern with the angle $2p<\pi/2$. In other words, we now have an orthorhombic lattice with a and b directions, as indicated in Fig. 2.

To obtain the point-charge contribution to E, one utilizes the relevant equations in (3). From our analysis in SDO II of results for E in Mn^{++}:ZnF_2, it is clear that the Blume-Orbach mechanism gives almost the entirety of point-charge contribution to E, and hence C_{44}. A pressure P applied in the [110] direction results in the angle (defined in Fig. 2)

$$\cos(2p)=P/2c_{44}. \tag{26}$$

The Mn–O lengths in the equatorial and polar directions in the linear approximation are given respectively by

$$r_{\text{Mn–O}_1}=a[1+P/2(c_{11}-c_{12})],$$
$$r_{\text{Mn–O}_5}=a[1+P/(c_{11}-c_{12})]. \tag{27}$$

Using these dimensions and angle, one obtains $B_4{}^2=0.01283\cos(2p)$ in units of $e^2/2a_0$.[5] From (3), one therefore finds

$$E=-0.2113\cos(2p), \tag{28}$$

so that

$$C_{44}(\text{point charge})=2E/P=-1.44\times10^{-13}\ \text{cm/dyn}. \tag{29}$$

For the overlap contributions to E, we note that pressure applied along the [110] direction results in the same distortion of the oxygen ions in the equatorial plane as for the corresponding F^- ions in ZnF_2. One can therefore utilize the corresponding expressions (68), (69), (119), (120), and (125) in SDO II for E to calculate the overlap contributions to E. Because this quantity depends sensitively on cos $2p$ and is relatively

TABLE IV. Various contributions to D in units of 10^{-4} cm^{-1} for stress along the [001] direction.

Mechanism	Local	Nonlocal	Distant	Total
Spin-spin	0.0337	−0.1287		−0.0950
Spin-orbit	0.0560	−0.0043	+0.0019	0.0536
Total				−0.0414

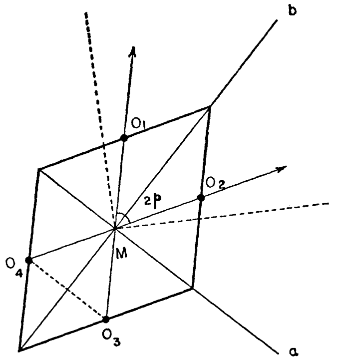

FIG. 2. Distorted environment of Mn^{++} in MgO for stress along the [110] direction. The orthogonal axes of the equivalent orthorhombic lattice are indicated as a and b.

independent of the small difference between $r_{\mathrm{Mn-O}}$ and a, we can set $r_{\mathrm{Mn-O_1}} \simeq r_{\mathrm{Mn-O_5}} \simeq a$ when calculating the two-center integrals involved in the overlap contributions to E. This situation is in sharp contrast to the situation for D where the difference $r_{\mathrm{Mn-O_1}}$ and $r_{\mathrm{Mn-O_5}}$ is responsible for determining the value of D. In Table V we list the local, nonlocal, and distant contribution to E from both the spin-spin and spin-orbit interactions. Summing the various contributions, we find

$$C_{44}(\text{overlap}) = -0.28 \times 10^{-13}\ \text{cm/dyn}. \qquad (30)$$

As in the case for C_{11}, the nonlocal spin-spin process is the leading contributor to C_{44}.

Upon combining the point-charge value for C_{44} in (29) with the above overlap value, we obtain

$$C_{44}(\text{theory}) = -1.16 \times 10^{-13}\ \text{cm/dyn}, \qquad (31)$$

which should be compared with Feher's value

$$C_{44}(\text{expt}) = -2.1 \times 10^{-13}\ \text{cm/dyn}. \qquad (32)$$

The agreement is better than for C_{11}.

It is interesting to note that the predicted values of C_{11} and C_{44} have the same sign as experiment. However, while the theoretical value of (12) of C_{11} is only 27% of experiment (13), there is somewhat better agreement between theory (31) and experiment (32) for C_{44}. One might be tempted to blame the remaining discrepancy between theory and experiment on the neglect of charge-transfer covalency. However, chemical considerations, considering the electronegativity difference between manganese and oxygen atoms, do not lead one to expect any significant covalency in the Mn–O bond. Therefore, we feel that, while covalency effects can perhaps explain part of the discrepancy, one has to look elswhere for a complete explanation of the discrepancy for C_{11} and c_{44}. The expressions for D in SDO II indicate that small differences in the overlap are two-center integrals for equatorial and polar distances are involved, while for E only integrals between electrons on ions in the equatorial plane are to be considered. Small errors in these overlap effects can therefore effect D considerably more than they do E. These errors can arise from causes such as (1) inaccuracies in the one-electron wave functions, (2) neglect of correlation effects, and (3) the radial deformation of the ionic wave functions in the crystal under stress, particularly for the loosely bound O^{--} ion.

III. CONCLUSION

Our results for Mn^{++}:MgO under uniaxial stress indicate that a combination of point-charge crystal-field overlap mechanisms can account for the spin-Hamiltonian parameters D and E reasonably well if the distorted configuration under the action of the stress is known. To obtain better quantitative agreement, one would require a better knowledge of the actual displacements of ions around the Mn^{++} ion itself, the induced quadrupole moments on the O^{--} ions, better electronic wave functions for the ions, and a knowledge of the charge-transfer covalency between the Mn^{++} ion and its O^{--} neighbors.

TABLE V. Various contributions to E in units of $(\cos 2p)$ (cm^{-1}) in MgO for stress along the [110] direction.

Mechanism	Local	Nonlocal	Distant	Total
Spin-spin	0	0.0416	···	0.0416
Spin-orbit	0	+0.0007	−0.0014	−0.0007
Total				0.0409

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APPENDIX

Corrections to SDO I and SDO II

The major changes to be made in the spin-spin sections of these two papers are the result of an error in the evaluation of the spin-spin energy expressions in Eqs. (43) and (44) of SDO I using Eq. (50). Thus, consider the evaluation of $\langle \Psi \mid \mathcal{H}_{\mathrm{ss}} \mid \Psi' \rangle$, where Ψ' is a determinant function that is different from Ψ as a consequence of the perturbation of one-electron orbitals by the crystalline field or by overlap and covalency effects:

$$\iint \Psi \mathcal{H}_{\mathrm{ss}} \Psi' d\tau_1 d\tau_2$$

$$= \left[\int_0^\infty r_1^2 dr_1 d\Omega_1 \int_0^{r_1} r_2^2 dr_2 d\Omega_2 \Psi \mathcal{H}_{\mathrm{ss}}(r_2 < r_1) \Psi' \right.$$

$$\left. + \int_0^\infty r_1^2 dr_1 d\Omega_1 \int_{r_1}^\infty r_2^2 dr_2 d\Omega_2 \Psi \mathcal{H}_{\mathrm{ss}}(r_2 > r_1) \Psi' \right]. \qquad (A1)$$

These two terms lead to two different types of integrals, namely,

$$g_{d\to{}^k l}{}^{n,m} = \int_0^\infty dr_1 \frac{(u_d{}^0(1))^2}{r_1{}^m} \int_0^{r_1} dr_2 u_d{}^0(2) u_{d\to{}^k l}{}^0(2) r_2{}^n,$$

$$h_{d\to{}^k l}{}^{n,m} = \int_0^\infty dr_2 \frac{u_d{}^0(2) u_{d\to{}^k l}{}^0(2)}{r_2{}^m} \int_0^{r_2} dr_1 (u_d{}^0(1))^2 r_1{}^n, \qquad (A2)$$

for the point-charge–point-multipole case in SDO II, and

$$g_{d,l_2}{}^{n,m}(\mathrm{F}LM) = \int_0^\infty dr_1 \frac{(u_d{}^0(1))^2}{r_1{}^m}$$

$$\times \int_0^{r_1} dr_2 u_d{}^0(2) \alpha_{l_2}(\mathrm{F}LM \mid a, r_2) r_2{}^n,$$

$$h_{d,l_2}{}^{n,m}(\mathrm{F}LM) = \int_0^\infty dr_2 \frac{u_d{}^0(2) \alpha_{l_2}(\mathrm{F}LM \mid a, r_2)}{r_2{}^m}$$

$$\times \int_0^{r_2} dr_1 (u_d{}^0(1))^2 r_1{}^n, \qquad (A3)$$

TABLE V. Table of two-electron integrals $g_{d\to k_{l'}}{}^{l''-1,l''+2}$ and $h_{d\to k_{l'}}{}^{l''-1,\,l''+2}$ appearing in Eqs. (47) and (56).

l' \ l''	0		2		4	
	g	h	g	h	g	h
1		−0.238800	−0.241049	−0.162652		0.049662
3	−0.196293		−0.127463	−0.102676	0.010014	0.020631
5						0.012209

for the overlap and covalency mechanisms of SDO II. In the original articles, the erroneous assumptions were made that

$$g_{d\to}{}^{k}{}_{l}{}^{n,m}=h_{d\to}{}^{k}{}_{l}{}^{n,m}=\tfrac{1}{2}f_{d\to}{}^{k}{}_{l}{}^{n,m},$$

with $f_{d\to}{}^{k}{}_{l}{}^{n,m}$ as defined in Eq. (48) of SDO I and

$$g_{d,l_2}{}^{n,m}(\mathrm{F}LM)=h_{d,l_2}{}^{n,m}(\mathrm{F}LM)=\tfrac{1}{2}f_{d,l_2}{}^{n,m}(\mathrm{F}LM),$$

with $f_{d,l_2}{}^{n,m}(\mathrm{F}LM)$ as defined by Eq. (51) of SDO II for the nonlocal overlap contribution. Note, however, that for the local spin-spin contribution, the relation

$$g_{d,d}{}^{n,m}=h_{d,d}{}^{n,m}=\tfrac{1}{2}f_{d,d}{}^{n,m} \qquad \text{(A4)}$$

is a valid one.

Corrections in SDO I

In SDO I, as a consequence of the error in the spin-spin interaction integrals, the Eqs. (47)–(49), (52), (54)–(57), (60)–(62), and (82) and Tables V and VI have to be changed. The corrected forms of these equations and Tables are listed here.

$$D_{\mathrm{ss}}(d\to l')=(-g^2\beta^2/20a^3{}_0)\,p_k{}^0 \times\sum_{l''}\{D_{k,l',l''}{}^{(1)}g_{d\to}{}^{k}{}_{l}{}^{l''-1,l''+2}+D_{k,l',l''}{}^{(2)}h_{d\to}{}^{k}{}_{l}{}^{l''-1,l''+2}\}. \qquad (47)$$

Equation (48) of SDO I is to be replaced by Eqs. (A2).

$$D_{k,l',l''}{}^{(1)}=\Big[C_{l'',0}\sum_{\alpha,\beta}F_{k,2}{}^{0,\beta}(l')(-)^{\alpha+\beta}F_{2,2}{}^{-\alpha,\alpha}(l''+1)F_{2,l'}{}^{-\beta,\beta}(l''-1) -\sum_{\alpha,\beta}C_{l'',\beta-\alpha}F_{k,2}{}^{0,\alpha}(l')F_{2,2}{}^{-\alpha,\beta}(l''+1)F_{2,l'}{}^{-\beta,\alpha}(l''-1)\Big]. \qquad (49)$$

$$D_{k,l',l''}{}^{(2)}=\Big[C_{l'',0}\sum_{\alpha,\beta}F_{k,2}{}^{0,\beta}(l')(-)^{\alpha+\beta}F_{2,2}{}^{-\alpha,\alpha}(l''-1)F_{2,l'}{}^{-\beta,\beta}(l''+1) -\sum_{\alpha,\beta}C_{l'',\alpha-\beta}F_{k,2}{}^{0,\alpha}(l')F_{2,2}{}^{-\alpha,\beta}(l''-1)F_{2,l'}{}^{-\beta,\alpha}(l''+1)\Big]. \qquad (49)$$

$$D_{\mathrm{ss}}(d\to s)=[-g^2\beta^2/20(\sqrt{5})a_0{}^3]B_2{}^0[3.58h_{d\to{}^2s}{}^{0,3}-5.37g_{d\to{}^2s}{}^{2,5}],$$
$$D_{\mathrm{ss}}(d\to d)=[-g^2\beta^2/20(\sqrt{5})a_0{}^3]B_2{}^0[-1.28g_{d\to{}^2d}{}^{0,3}+5.11h_{d\to{}^2d}{}^{0,3}-2.19g_{d\to{}^2d}{}^{2,5}-2.19h_{d\to{}^2d}{}^{2,5}],$$
$$D_{\mathrm{ss}}(d\to g)=[-g^2\beta^2/20(\sqrt{5})a_0{}^3]B_2{}^0[9.20h_{d\to{}^2g}{}^{0,3}-0.11g_{d\to{}^2g}{}^{2,5}-5.48h_{d\to{}^2g}{}^{2,5}-19.17h_{d\to{}^2g}{}^{4,7}]. \qquad (52)$$

$$D_{\mathrm{ss}}(d\to s)=-0.05218\,B_2{}^0\ \mathrm{cm}^{-1},$$
$$D_{\mathrm{ss}}(d\to d)=+0.00506\,B_2{}^0\ \mathrm{cm}^{-1},$$
$$D_{\mathrm{ss}}(d\to g)=-0.02594\,B_2{}^0\ \mathrm{cm}^{-1}. \qquad (54)$$
$$D_{\mathrm{ss}}=-0.07305\,B_2{}^0. \qquad (55)$$

TABLE VI. List of corrections to the spin-spin contribution due to errors in the evaluation of spin-spin integrals in SDO I. Only the corrected spin-spin results and the consequently changed total theoretical results are listed.

Mechanisms		MnF_2-Mn^{+2} D	MnF_2-Mn^{+2} E	ZnF_2-Mn^{+2} D	ZnF_2-Mn^{+2} E	Single-point-charge model D
Spin-spin	$d\to s$	+3.69	+3.04	+4.53	+1.85	−9.59
	$d\to d$	−0.36	−0.29	−0.44	−0.18	−0.93
	$d\to g$	+1.84	+1.67	+2.25	+1.01	−4.76
Total		+5.17	+4.42	+6.35	+2.68	−13.42
Total theoretical result		+16.01	−92.98	+34.13	−96.57	+22.74

TABLE III. Table[a] of values of $g_{d,\,l_2}{}^{l'-1,\,l'+2}$ (FLM) and $h_{d,\,l_2}{}^{l'-1,\,l'+2}$ (FLM) as defined in Eq. (51) for $a=2.04$ Å.

l_2LM	$M_{3d,\,l_2}{}^{L,M}$ (F)	$l'=1$		$l'=3$		$l'=5$
		g	h	g	h	h
000			0.007664	0.002159		
200	0.066975	0.000812	0.004909	0.000541	0.001561	
400			0.001963	0.000079	0.000466	0.000210
010			−0.034824	−0.012559		
210	−0.078356	−0.002063	−0.009445	−0.001359	−0.003407	
410			−0.002682	−0.000148	−0.000743	−0.000357
211	0.050297	0.000906	0.004450	0.000597	0.001534	
411			0.001934	0.000090	0.000477	0.000220

[a] Only those numbers which are required in our calculations of $D_{\mathrm{ss}}{}^{\mathrm{nl}}$ and $E_{\mathrm{ss}}{}^{\mathrm{nl}}$ are entered in the Table.

$$E_{\mathrm{ss}}=\sum_{l'=|2-k|}^{|2+k|}E_{\mathrm{ss}}(d\to l'),$$

$$E_{\mathrm{ss}}(d\to l')=-(g^2\beta^2/20a_0^3)\tfrac{1}{2}p_k^{m_k}\sum_{l''}\{E_{k,l',l''}{}^{m_k}(1)\,g_{d\to{}^k l'}{}^{l''-1,l''+2}+E_{k,l',l''}{}^{m_k}(2)\,h_{d\to{}^k l'}{}^{l''-1,l''+2}\}. \tag{56}$$

$$E_{k,l',l''}{}^{m_k}(1)=-\sum_{\alpha,\beta}\{\delta_{m_k,-2}C_{l'',\alpha-\beta-1}{}'+\delta_{m_k,2}C_{l'',\beta-\alpha-1}{}'\}F_{k,2}{}^{m_k,\alpha}(l')\,F_{2,2}{}^{-\alpha,\beta}(l''+1)\,F_{2,l'}{}^{-\beta,\alpha+m_k}(l''-1),$$

$$E_{k,l',l''}{}^{m_k}(2)=(\delta_{m_k,-2}+\delta_{m_k,2})\,C_{l'',1}{}'\sum_{\alpha,\beta}(-)^{\alpha+\beta}F_{k,2}{}^{m_k,\alpha}(l')\,F_{2,l'}{}^{-\alpha,\alpha+m_k}(l''+1)\,F_{2,2}{}^{-\beta,\beta}(l''-1)$$
$$-\sum_{\alpha,\beta}\{\delta_{m_k,-2}C_{l'',\beta-\alpha+1}{}'+\delta_{m_k,2}C_{l'',\alpha-\beta+1}{}'\}F_{k,2}{}^{m_k,\alpha}(l')\,F_{2,2}{}^{-\alpha,\beta}(l''-1)\,F_{2,l'}{}^{-\beta,\alpha+m_k}(l''+1). \tag{57}$$

$$E_{\mathrm{ss}}(d\to s)=-[g^2\beta^2/40(\sqrt{5})\,a_0^3]B_2^2\,[8.76h_{d\to{}^2s}{}^{0,3}-13.15g_{d\to{}^2s}{}^{2,5}],$$
$$E_{\mathrm{ss}}(d\to d)=-[g^2\beta^2/40(\sqrt{5})\,a_0^3]B_2^2\,[-3.13g_{d\to{}^2d}{}^{0,3}+12.52h_{d\to{}^2d}{}^{0,3}-5.37g_{d\to{}^2d}{}^{2,5}-5.37h_{d\to{}^2d}{}^{2,5}],$$
$$E_{\mathrm{ss}}(d\to g)=-[g^2\beta^2/40(\sqrt{5})\,a_0^3]B_2^2\,[22.53h_{d\to{}^2g}{}^{0,3}-0.27g_{d\to{}^2g}{}^{2,5}-13.41h_{d\to{}^2g}{}^{2,5}-46.95h_{d\to{}^2g}{}^{4,7}]. \tag{60}$$

$$E_{\mathrm{ss}}(d\to s)=-0.06392B_2^2\ \mathrm{cm}^{-1},$$
$$E_{\mathrm{ss}}(d\to d)=+0.00617B_2^2\ \mathrm{cm}^{-1},$$
$$E_{\mathrm{ss}}(d\to g)=-0.03494B_2^2\ \mathrm{cm}^{-1}. \tag{61}$$
$$E_{\mathrm{ss}}=-0.09269B_2^2\ \mathrm{cm}^{-1}. \tag{62}$$
$$D(C):D_{\mathrm{ss}}:D_{\mathrm{B-O}}=\frac{1.45}{R^6}:\frac{-0.15}{R^3}:\frac{8.68}{R^5}. \tag{82}$$

We shall list only those rows of Table VI which are corrected. These rows are comprised of the spin-spin and the total theoretical contributions.

As a consequence of these corrections to the spin-spin contributions to D and E, a number of statements are no longer correct and should be changed:

(1) The second sentence on p. 264 should be changed to read: "It will be shown that both d-like and g-like admixtures are significant, the latter leading to a contribution of the same sign as s-like admixtures and about half in magnitude. The d-admixtures on the other hand lead to a contribution of opposite sign to that from the s-like admixture and of magnitude about a factor of ten lower."

(2) The third sentence in the second paragraph on p. 264 should be altered to read: "The inaccuracy of Slater orbitals leaves Chakravarty's results open to serious question quantitatively."

(3) The sentence following Eq. (62) on p. 266 should be altered to read: "Again we see that $d\to d$ admixtures give contributions to E of opposite sign to that from the $d\to s$ admixtures while the $d\to g$ admixtures give contributions of the same sign as $d\to s$."

(4) The last sentence in the paragraph following Eq. (82) on p. 268 has to be changed to: "However, the numerical coefficient for D_{BO} is about sixty times larger than that for D_{ss} which makes D_{BO} altogether about 2.5 times larger than D_{ss} as may be seen from Table VI.

In addition to these corrections there were a few minor typographical errors, corrections to which will now be listed.

(1) In the heading of Table III, $(4\pi/5)^{1/2}F_{2,4}{}^{m,m_k}(l')$ should be replaced by $[(4\pi)^{1/2}/5]F_{2,k}{}^{m,m_k}(l')$.

(2) In both Eqs. (31) and (32) the over-all negative sign on the right-hand side should be dropped.

(3) In Eq. (34) a negative sign has to be added on the right-hand side.

(4) In the first equation of (44), $3(z_{ij}^2-r_{ij}^2)$ has to be replaced by $(3z_{ij}^2-r_{ij}^2)$ and on the right-hand sides

TABLE IV. Table[a] of values of $g_{d,\,l_2}{}^{l'-1,\,l'+2}$ (FLM) and $h_{d,\,l_2}{}^{l'-1,\,l'+2}$ (FLM) as defined in Eq. (51) for $a=2.01$ Å.

l_2LM	$M_{3d,\,l_2}{}^{L,\,M}$ (F)	$l'=1$ g	$l'=1$ h	$l'=3$ g	$l'=3$ h	$l'=5$ h
000			0.008322	0.002353		
200	0.070824	0.000891	0.005329	0.000589	0.001705	
400			0.002125	0.000089	0.000512	0.000232
010			−0.036574	−0.013209		
210	−0.080930	−0.002205	−0.010012	−0.001453	−0.003629	
410			−0.002861	−0.000162	−0.000802	−0.000388
211	0.053107	0.000975	0.004768	0.000643	0.001648	
411			0.002093	0.000096	0.000520	0.000241

[a] Only those numbers which are required in our calculations of $D_{\rm ss}{}^{\rm nl}$ and $E_{\rm ss}{}^{\rm nl}$ are entered in the Table.

of both equations (44), a_0 in the denominator has to be replaced by $a_0{}^3$.

(5) The unlabelled equation following Eq. (50) should read

$$\frac{Y_2{}^0(1,2)}{r_{12}{}^3}=\sum_{l',m'}C_{l',m'}\frac{r_1{}^{l'-1}}{r_2{}^{l'+2}}Y_{l'-1}{}^{m'}(1)\,Y_{l'+1}{}^{m'*}(2).$$

(6) Equation (53) should be replaced by

$$\frac{B_2{}^0}{\sqrt{5}}\frac{u_{d\to{}^2s}{}'}{r}=u_{4s}{}^0\frac{\langle\psi_{3d}{}^0\,|\,\mathcal{H}_{\rm ax}\,|\,\psi_{4s}{}^0\rangle}{-\Delta_{ds}}. \tag{53}$$

(7) In the top row of Table VIII, $B_4{}^0$ should be replaced by $(B_4{}^0)'$.

Corrections in SDO II

In SDO II, as a consequence of errors in the spin-spin integrals, corrections have to be made in the spin-spin nonlocal contributions to D and E. By virtue of the Eq. (A4), the local spin-spin contributions obtained in SDO II are still correct. For the nonlocal spin-spin effect, the equations that have to be corrected are (47), (48), (49), (50a), (50b), (51), (52), (53), (54), (55), (56), (58a), (58b), (58c), (59), (60), (62), (63), (64), (65a), (65b), (66), (67), (69a), (69b), (69c), (70), and (71). The corrected forms of these equations will be listed here. Also listed will be the corrected forms of Tables III, IV, V, and VI.

$$D_{\rm ss}{}^{\rm nl}=-D_0\sum_{{\rm F}LM\,l_2m_2}b_{l_2,M,m_2}({\rm F})\,D_{L,l_2}{}^{M,m_2}({\rm F})\,\lambda_{LMm_2}{}^{\rm F}. \tag{47}$$

$$D_{L,l_2}{}^{M,m_2}({\rm F})=\sum_{l'}\{g_{d,l_2}{}^{l'-1,l'+2}({\rm F}LM)\,N_{l_2,m_2}{}^{l'}(1)$$
$$+h_{d,l_2}{}^{l'-1,l'+2}({\rm F}LM)\,N_{l_2,m_2}{}^{l'}(2)\}. \tag{48}$$

Equation (49) of the text should be omitted.

$$N_{l_2,m_2}{}^{l'}(1)=-\sum_{\beta}C_{l',\beta-m_2}F_{2,2}{}^{-m_2,\beta}(l'+1)\,F_{2,l_2}{}^{-\beta,m_2}(l'-1). \tag{50a}$$

$$N_{l_2,m_2}{}^{l'}(2)=C_{l',0}(-)^{m_2}[5/(4\pi)^{1/2}]F_{2,l_2}{}^{-m_2,m_2}(l'+1)\,\delta_{l',1}-\sum_{\beta}C_{l',m_2-\beta}F_{2,2}{}^{-m_2,\beta}(l'-1)\,F_{2,l_2}{}^{-\beta,m_2}(l'+1). \tag{50b}$$

$$g_{d,l_2}{}^{n,m}({\rm F}LM)=\int_0^\infty dr_1\frac{(u_d{}^0(1))^2}{r_1{}^m}\int_0^{r_1}dr_2u_d{}^0(r_2)\,r_2{}^n\alpha_{l_2}({\rm F}LM\,|\,a,r_2),$$

$$h_{d,l_2}{}^{n,m}({\rm F}LM)=\int_0^\infty dr_2\frac{u_d{}^0(2)\,\alpha_{l_2}({\rm F}LM\,|\,a,r_2)}{r_2{}^m}\int_0^{r_2}dr_1(u_d{}^0(1))^2r_1{}^n. \tag{51}$$

$$D_{\rm ss}{}^{\rm nl}=-D_0\sum_{l_2,L,M,m_2,l'}\{N_{l_2,m_2}{}^{l'}(1)\,P_{L,l_2}{}^{(1)M,m_2}(l')+N_{l_2,m_2}{}^{l'}(2)\,P_{L,l_2}{}^{(2)M,m_2}(l')\}. \tag{52}$$

TABLE V. Overlap contribution to the spin-Hamiltonian parameters D and E for Mn^{++}: ZnF$_2$ in units of 10^{-4} cm^{-1}.

	D Local	D Nonlocal	D Distant	E Local	E Nonlocal	E Distant
Spin-spin	−2.50	10.37	···	0	54.06	···
Spin-orbit	−4.24	+0.10	−1.15	0	+1.14	−6.47
Total		2.58			48.73	

TABLE VI. Compilation of results for D and E appropriate to Mn^{++}–ZnF_2 from SDO I and this paper, in units of 10^{-4} cm^{-1}.

	D	E		D	E
Point-multipole model	+34.13	−96.57	Total	36.71	−47.84
Overlap model	2.58	48.73	Experimental (Ref. 2)	10.50	−113.50

$$P_{L,l_2}{}^{(1)M,m_2}(l') = 4B_{l_2,M,m_2}(-\tfrac{1}{2}\pi)B_{2,M,m_2}(-\tfrac{1}{2}\pi)[M_{3d,2}{}^{L,M}(\mathrm{F}_1)+\gamma^{L,M}(\mathrm{F}_1)]g_{d,l_2}{}^{l'-1,l'+2}(\mathrm{F}_1LM)$$
$$+[M_{3d,2}{}^{L,M}(\mathrm{F}_5)+\gamma^{L,M}(\mathrm{F}_5)]g_{d,l_2}{}^{l'-1,l'+2}(\mathrm{F}_5LM)[B_{l_2,M,m_2}(0)B_{2,M,m_2}(0)+B_{l_2,M,m_2}(-\pi)B_{2,M,m_2}(-\pi)],$$
$$P_{L,l_2}{}^{(2)M,m_2}(l') = 4B_{l_2,M,m_2}(-\tfrac{1}{2}\pi)B_{2,M,m_2}(-\tfrac{1}{2}\pi)[M_{3d,2}{}^{L,M}(\mathrm{F}_1)+\gamma^{L,M}(\mathrm{F}_1)]h_{d,l_2}{}^{l'-1,l'+2}(\mathrm{F}_1LM)$$
$$+[M_{3d,2}{}^{L,M}(\mathrm{F}_5)+\gamma^{L,M}(\mathrm{F}_5)]h_{d,l_2}{}^{l'-1,l'+2}(\mathrm{F}_5LM)[B_{l_2,M,m_2}(0)B_{2,M,m_2}(0)+B_{l_2,M,m_2}(-\pi)B_{2,M,m_2}(-\pi)]. \quad (53)$$

$$R_{l_2,M}{}^{l'}(1) = \sum_{m_2} B_{l_2,M,m_2}(-\tfrac{1}{2}\pi)B_{2,M,m_2}(-\tfrac{1}{2}\pi)N_{l_2,m_2}{}^{l'}(1),$$
$$R_{l_2,M}{}^{l'}(2) = \sum_{m_2} B_{l_2,M,m_2}(-\tfrac{1}{2}\pi)B_{2,M,m_2}(-\tfrac{1}{2}\pi)N_{l_2,m_2}{}^{l'}(2). \quad (54)$$

$$R_{l_2,M}{}^{l'}(3) = \sum_{m_2} N_{l_2,m_2}{}^{l'}(1)\,(B_{l_2,M,m_2}(0)B_{2,M,m_2}(0)+B_{l_2,M,m_2}(-\pi)B_{2,M,m_2}(-\pi)),$$
$$R_{l_2,M}{}^{l'}(4) = \sum_{m_2} N_{l_2,m_2}{}^{l'}(2)\,(B_{l_2,M,m_2}(0)B_{2,M,m_2}(0)+B_{l_2,M,m_2}(-\pi)B_{2,M,m_2}(-\pi)). \quad (55)$$

$$D_{\mathrm{ss}}{}^{\mathrm{nl}} = -D_0[4\sum_{L,M}(M_{3d,2}{}^{L,M}(\mathrm{F}_1)+\gamma^{L,M}(\mathrm{F}_1))\sum_{\substack{l'=1,3,5\\ l_2=0,2,4}}\{g_{3d,l_2}{}^{l'-1,l'+2}(\mathrm{F}_1LM)R_{l_2,M}{}^{l'}(1)$$
$$+h_{3d,l_2}{}^{l'-1,l'+2}(\mathrm{F}_1LM)R_{l_2,M}{}^{l'}(2)\}+\sum_{L,M}(M_{3d,2}{}^{L,M}(\mathrm{F}_5)+\gamma^{L,M}(\mathrm{F}_5))$$
$$\times\sum_{\substack{l'=1,3,5\\ l_2=0,2,4}}\{g_{3d,l_2}{}^{l'-1,l'+2}(\mathrm{F}_5LM)R_{l_2,M}{}^{l'}(3)+h_{3d,l_2}{}^{l'-1,l'+2}(\mathrm{F}_5LM)R_{l_2,M}{}^{l'}(4)\}]. \quad (56)$$

$$D_{\mathrm{ss}}{}^{\mathrm{nl}}(L=0,\,M=0) = -4D_0\{[S_s(\mathrm{F}_1)+\gamma_s(\mathrm{F}_1)][-1.7889h_{d,0}{}^{0,3}(\mathrm{F}_1,s)+2.6833g_{d,0}{}^{2,5}(\mathrm{F}_1,s)$$
$$+0.2857g_{d,2}{}^{0,3}(\mathrm{F}_1,s)-1.1429h_{d,2}{}^{0,3}(\mathrm{F}_1,s)+0.4898(g_{d,2}{}^{2,5}(\mathrm{F}_1,s)+h_{d,2}{}^{2,5}(\mathrm{F}_1,s))$$
$$-1.5333h_{d,4}{}^{0,3}(\mathrm{F}_1,s)+0.0183g_{d,4}{}^{2,5}(\mathrm{F}_1,s)+0.9127h_{d,4}{}^{2,5}(\mathrm{F}_1,s)+3.1944h_{d,4}{}^{4,7}(\mathrm{F}_1,s)]$$
$$-[S_s(\mathrm{F}_5)+\gamma_s(\mathrm{F}_5)][-1.7889h_{d,0}{}^{0,3}(\mathrm{F}_5,s)+2.6833g_{d,0}{}^{2,5}(\mathrm{F}_5,s)+0.2857g_{d,2}{}^{0,3}(\mathrm{F}_5,s)$$
$$-1.1429h_{d,2}{}^{0,3}(\mathrm{F}_5,s)+0.4898(g_{d,2}{}^{2,5}(\mathrm{F}_5,s)+h_{d,2}{}^{2,5}(\mathrm{F}_5,s))-1.5333h_{d,4}{}^{0,3}(\mathrm{F}_5,s)$$
$$+0.0183g_{d,4}{}^{2,5}(\mathrm{F}_5,s)+0.9127h_{d,4}{}^{2,5}(\mathrm{F}_5,s)+3.1944h_{d,4}{}^{4,7}(\mathrm{F}_5,s)]\}. \quad (58a)$$

$$D_{\mathrm{ss}}{}^{\mathrm{nl}}(L=1,\,M=0) = -4D_0\{[S_\sigma(\mathrm{F}_1)+\gamma_\sigma(\mathrm{F}_1)][-1.7889h_{d,0}{}^{0,3}(\mathrm{F}_1,\sigma)+2.6833g_{d,0}{}^{2,5}(\mathrm{F}_1,\sigma)$$
$$+0.2857g_{d,2}{}^{0,3}(\mathrm{F}_1,\sigma)-1.1429h_{d,2}{}^{0,3}(\mathrm{F}_1,\sigma)+0.4898(g_{d,2}{}^{2,5}(\mathrm{F}_1,\sigma)+h_{d,2}{}^{2,5}(\mathrm{F}_1,\sigma))$$
$$-1.5333h_{d,4}{}^{0,3}(\mathrm{F}_1,\sigma)+0.0183g_{d,4}{}^{2,5}(\mathrm{F}_1,\sigma)+0.9127h_{d,4}{}^{2,5}(\mathrm{F}_1,\sigma)+3.1944h_{d,4}{}^{4,7}(\mathrm{F}_1,\sigma)]$$
$$-[S_\sigma(\mathrm{F}_5)+\gamma_\sigma(\mathrm{F}_5)][-1.7889h_{d,0}{}^{0,3}(\mathrm{F}_5,\sigma)+2.6833g_{d,0}{}^{2,5}(\mathrm{F}_5,\sigma)+0.2857g_{d,2}{}^{0,3}(\mathrm{F}_5,\sigma)$$
$$-1.1429h_{d,2}{}^{0,3}(\mathrm{F}_5,\sigma)+0.4898(g_{d,2}{}^{2,5}(\mathrm{F}_5,\sigma)+h_{d,2}{}^{2,5}(\mathrm{F}_5,\sigma))-1.5333h_{d,4}{}^{0,3}(\mathrm{F}_5,\sigma)$$
$$+0.0183g_{d,4}{}^{2,5}(\mathrm{F}_5,\sigma)+0.9127h_{d,4}{}^{2,5}(\mathrm{F}_5,\sigma)+3.1944h_{d,4}{}^{4,7}(\mathrm{F}_5,\sigma)]\}. \quad (58b)$$

$$D_{\mathrm{ss}}{}^{\mathrm{nl}}(L=1,\,M=1) = -2D_0\{[S_\pi(\mathrm{F}_1)+\gamma_\pi(\mathrm{F}_1)][0.2857g_{d,2}{}^{0,3}(\mathrm{F}_1,\pi)-1.1429h_{d,2}{}^{0,3}(\mathrm{F}_1,\pi)$$
$$+0.4898(g_{d,2}{}^{2,5}(\mathrm{F}_1,\pi)+h_{d,2}{}^{2,5}(\mathrm{F}_1,\pi))-2.7994h_{d,4}{}^{0,3}(\mathrm{F}_1,\pi)+0.0333g_{d,4}{}^{2,5}(\mathrm{F}_1,\pi)$$
$$+1.6663h_{d,4}{}^{2,5}(\mathrm{F}_1,\pi)+5.8321h_{d,4}{}^{4,7}(\mathrm{F}_1,\pi)]-[S_\pi(\mathrm{F}_5)+\gamma_\pi(\mathrm{F}_5)][0.2857g_{d,2}{}^{0,3}(\mathrm{F}_5,\pi)$$
$$-1.1429h_{d,2}{}^{0,3}(\mathrm{F}_5,\pi)+0.4898(g_{d,2}{}^{2,5}(\mathrm{F}_5,\pi)+h_{d,2}{}^{2,5}(\mathrm{F}_5,\pi))-2.7994h_{d,4}{}^{0,3}(\mathrm{F}_5,\pi)$$
$$+0.0333g_{d,4}{}^{2,5}(\mathrm{F}_5,\pi)+1.6663h_{d,4}{}^{2,5}(\mathrm{F}_5,\pi)+5.8321h_{d,4}{}^{4,7}(\mathrm{F}_5,\pi)]\}. \quad (58c)$$

$$D_{\mathrm{ss}}{}^{\mathrm{nl}}(L=0,\ M=0)=-1.21\times10^{-4}\ \mathrm{cm}^{-1},$$

$$D_{\mathrm{ss}}{}^{\mathrm{nl}}(L=1,\ M=0)=-3.39\times10^{-4}\ \mathrm{cm}^{-1},$$

$$D_{\mathrm{ss}}{}^{\mathrm{nl}}(L=1,\ M=\pm1)=+0.024\times10^{-4}\ \mathrm{cm}^{-1}. \tag{59}$$

$$D_{\mathrm{ss}}{}^{\mathrm{nl}}=-4.55\times10^{-4}\ \mathrm{cm}^{-1}. \tag{60}$$

$$E_{\mathrm{ss}}{}^{\mathrm{nl}}=-\tfrac{1}{2}E_0\sum_{\mathrm{F}LMl_2m_2} b_{l,M,m_2}(\mathrm{F})\{E_{L,l_2}{}^{(1)M,m_2}(\mathrm{F})\lambda_{L,M,m_2-2}{}^{\mathrm{F}}+E_{L,l_2}{}^{(2)M,m_2}(\mathrm{F})\lambda_{L,M,m_2+2}{}^{\mathrm{F}}\}. \tag{62}$$

$$E_{L,l_2}{}^{(1)M,m_2}(\mathrm{F})=\sum_{l'}\{g_{d,l_2}{}^{l'-1,l'+2}(\mathrm{F}LM)G_{l_2,m_2}{}^{l'}(1)+h_{d,l_2}{}^{l'-1,l'+2}(\mathrm{F}LM)G_{l_2,m_2}{}^{l'}(2)\},$$

$$E_{L,l_2}{}^{(2)M,m_2}(\mathrm{F})=\sum_{l'}\{g_{d,l_2}{}^{l'-1,l'+2}(\mathrm{F}LM)G_{l_2,m_2}{}^{l'}(3)+h_{d,l_2}{}^{l'-1,l'+2}(\mathrm{F}LM)G_{l_2,m_2}{}^{l'}(4)\}. \tag{63}$$

Equation (64) should be omitted.

$$G_{l_2,m_2}{}^{l'}(1)=-\sum_{\beta}C_{l',\beta-m_2+1}{}'\mathrm{F}_{2,2}{}^{-m_2+2,\beta}(l'+1)\,\mathrm{F}_{2,l_2}{}^{-\beta,m_2}(l'-1),$$

$$G_{l_2,m_2}{}^{l'}(2)=C_{l',1}{}'(-)^{m_2}\mathrm{F}_{2,l_2}{}^{2-m_2,m_2}(l'+1)[5/(4\pi)^{1/2}]\delta_{l',1}-\sum_{\beta}C_{l',m_2-\beta-1}{}'\mathrm{F}_{2,2}{}^{2-m_2,\beta}(l'-1)\,\mathrm{F}_{2,l_2}{}^{-\beta,m_2}(l'+1). \tag{65a}$$

$$G_{l_2,m_2}{}^{l'}(3)=-\sum_{\beta}C_{l',m_2-\beta+1}{}'\mathrm{F}_{2,2}{}^{-m_2-2,\beta}(l'+1)F_{2,l_2}{}^{-\beta,m_2}(l'-1),$$

$$G_{l_2,m_2}{}^{l'}(4)=C_{l',1}{}'(-)^{m_2}\mathrm{F}_{2,l_2}{}^{-2-m_2,m_2}(l'+1)[5/(4\pi)^{1/2}\delta_{l',1}-\sum_{\beta}C_{l',\beta-m_2-1}{}'\mathrm{F}_{2,2}{}^{-m_2-2,\beta}(l'-1)\,\mathrm{F}_{2,l_2}{}^{-\beta,m_2}(l'-1). \tag{65b}$$

$$E_{\mathrm{ss}}{}^{\mathrm{nl}}=-2E_0\cos2p\sum_{L,M}[M_{3d,2}{}^{LM,}(\mathrm{F}_1)+\gamma^{L,M}(\mathrm{F}_1)]\{H_{l_2,M}{}^{l'}(1)\,g_{d,l_2}{}^{l'-1,l'+2}(\mathrm{F}_1LM)+H_{l_2,M}{}^{l'}(2)\,h_{d,l_2}{}^{l'-1,l'+2}(\mathrm{F}_1LM)\}. \tag{66}$$

$$H_{l_2,M}{}^{l'}(1)=\sum_{m_2}B_{l_2,M,m_2}(-\tfrac{1}{2}\pi)\{B_{2,M,m_2+2}(-\tfrac{1}{2}\pi)G_{l_2,m_2}{}^{l'}(3)+B_{2,M,m_2-2}(-\tfrac{1}{2}\pi)G_{l_2,m_2}{}^{l'}(1)\},$$

$$H_{l_2,M}{}^{l'}(2)=\sum_{m_2}B_{l_2,M,m_2}(-\tfrac{1}{2}\pi)\{B_{2,M,m_2+2}(-\tfrac{1}{2}\pi)G_{l_2,m_2}{}^{l'}(4)+B_{2,M,m_2-2}(-\tfrac{1}{2}\pi)G_{l_2,m_2}{}^{l'}(2)\}. \tag{67}$$

$$\begin{aligned}E_{\mathrm{ss}}{}^{\mathrm{nl}}(L=0,\ M=0)=&-4E_0\cos2p[S_s(\mathrm{F}_1)+\gamma_s(\mathrm{F}_1)][5.3666h_{d,0}{}^{0,3}(\mathrm{F}_1,\ s)-8.0498g_{d,0}{}^{2,5}(\mathrm{F}_1,\ s)\\&-0.8571g_{d,2}{}^{0,3}(\mathrm{F}_1,\ s)+3.4286h_{d,2}{}^{0,3}(\mathrm{F}_1,\ s)-1.4694(g_{d,2}{}^{2,5}(\mathrm{F}_1,\ s)+h_{d,2}{}^{2,5}(\mathrm{F}_1,\ s))\\&+4.5999h_{d,4}{}^{0,3}(\mathrm{F}_1,\ s)-0.0548g_{d,4}{}^{2,5}(\mathrm{F}_1,\ s)-2.7380h_{d,4}{}^{2,5}(\mathrm{F}_1,\ s)-9.5831h_{d,4}{}^{4,7}(\mathrm{F}_1,\ s)].\end{aligned} \tag{69a}$$

$$\begin{aligned}E_{\mathrm{ss}}{}^{\mathrm{nl}}(L=1,\ M=0)=&-4E_0\cos2p[S_\sigma(\mathrm{F}_1)+\gamma_\sigma(\mathrm{F}_1)][5.3666h_{d,0}{}^{0,3}(\mathrm{F}_1,\ \sigma)-8.0498g_{d,0}{}^{2,5}(\mathrm{F}_1,\ \sigma)\\&-0.8571g_{d,2}{}^{0,3}(\mathrm{F}_1,\ \sigma)+3.4286h_{d,2}{}^{0,3}(\mathrm{F}_1,\ \sigma)-1.4694(g_{d,2}{}^{2,5}(\mathrm{F}_1,\ \sigma)+h_{d,2}{}^{2,5}(\mathrm{F}_1,\ \sigma))\\&+4.5999h_{d,4}{}^{0,3}(\mathrm{F}_1,\ \sigma)-0.0548g_{d,4}{}^{2,5}(\mathrm{F}_1,\ \sigma)-2.7386h_{d,4}{}^{2,5}(\mathrm{F}_1,\ \sigma)-9.5831h_{d,4}{}^{4,7}(\mathrm{F}_1,\ \sigma)].\end{aligned} \tag{69b}$$

$$\begin{aligned}E_{\mathrm{ss}}{}^{\mathrm{nl}}(L=1,\ M=1)=E_{\mathrm{ss}}{}^{\mathrm{nl}}(L=1,\ M=-1)=&-2E_0\cos2p[S_\pi(\mathrm{F}_1)+\gamma_\pi(\mathrm{F}_1)][-0.8571g_{d,2}{}^{0,3}(\mathrm{F}_1,\ \pi)\\&+3.4286h_{d,2}{}^{0,3}(\mathrm{F}_1,\ \pi)-1.4694(g_{d,2}{}^{2,5}(\mathrm{F}_1,\ \pi)+h_{d,2}{}^{2,5}(\mathrm{F}_1,\ \pi))+8.3982h_{d,4}{}^{0,3}(\mathrm{F}_1,\ \pi)\\&-0.1000g_{d,4}{}^{2,5}(\mathrm{F}_1,\ \pi)-4.9990h_{d,4}{}^{2,5}(\mathrm{F}_1,\ \pi)-17.4964h_{d,4}{}^{4,7}(\mathrm{F}_1,\ \pi)].\end{aligned} \tag{69c}$$

$$E_{\mathrm{ss}}{}^{\mathrm{nl}}(L=0,\ M=0)=-4.57\times10^{-4}\ \mathrm{cm}^{-1},$$

$$E_{\mathrm{ss}}{}^{\mathrm{nl}}(L=1,\ M=0)=-22.44\times10^{-4}\ \mathrm{cm}^{-1},$$

$$E_{\mathrm{ss}}{}^{\mathrm{nl}}(L=1,\ M=\pm1)=+0.15\times10^{-4}\ \mathrm{cm}^{-1}. \tag{70}$$

$$E_{\mathrm{ss}}{}^{\mathrm{nl}}=-26.71\times10^{-4}\ \mathrm{cm}^{-1}. \tag{71}$$