

Calculations of Static Distortion of a MgO Crystal in the Presence of Paramagnetic Impurities

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Using the shell-model results for MgO, the static distortions of this crystal due to the substitution of paramagnetic impurities have been calculated in the ionic approximation. The static and dynamic crystal field parameters for a number of paramagnetic ions in a distorted MgO crystal are evaluated. The agreement between the theoretical and experimental values improves if the static distortions are taken into consideration.

I. INTRODUCTION

A CONSIDERABLE amount of work has been done with paramagnetic ions substituted in diamagnetic host crystals.¹ In many cases the paramagnetic ions go into lattice positions, without altering the point symmetry around the ions, and the host crystal is usually assumed to remain unchanged owing to the substitution of these ions. But in reality there may be two substitutional effects even when the site symmetry is not altered: (i) The force constants associated with the interaction between the impurity ion and its neighbors may be different from those between the host cation and the anions, and consequently the neighbors may be displaced from their original equilibrium positions: (ii) The mass of the paramagnetic ion being different from that of the host ion, the vibrations of the lattice around the paramagnetic ion may be altered. One or both of these effects may be important enough in certain cases to alter the magnetic and other properties of the crystal. In the present paper we intend to study the displacements of the ions due to the substitution of paramagnetic impurities in a MgO crystal.

Optical-absorption and electron-paramagnetic-resonance (EPR) measurements have been made for a number of iron transition-group and rare-earth ions in MgO.² Analysis of these data gives the magnitude of cubic crystalline field splitting as well as the strength of the spin-phonon coupling parameters. Assuming a point-charge model for the ligand O^{2-} ions around the paramagnetic ions, it is possible to derive theoretical expressions for the cubic field-splitting parameter Dq ,¹ the spin-phonon coupling parameters G_{11} and G_{44} for the single-phonon process,³ and for the C_2 coefficients of the

two-phonon process.⁴ To explain the experimental values of these parameters, it is necessary to take Z , the effective value of the charge for O^{2-} ions, to be very different from the ionic value of -2 . Moreover, in many cases the same value of Z cannot explain the static and dynamical parameters simultaneously. All these discrepancies are usually attributed to the overlap and covalency of the magnetic electronic functions with the ligand functions. Besides these effects, it is worthwhile to investigate whether the static distortion of the crystal due to the substitution of paramagnetic ion is important and can explain the experimental result in a more satisfactory way.

The questions of static distortion of alkali-halide crystals due to the substitution of monovalent impurities and the effects of this distortion on the nuclear quadrupole line shape were treated by Fukai.⁵ But a proper theory for the lattice deformations was first developed by Dick and Das⁶ within the limits of the ionic approximation. The displacements of the ions occur because of the difference of ionic radii for the case of monovalent impurities in alkali-halide crystals. In most cases, the impurity ion is at a cubic site, and consequently, the neighbors around the impurity ion move radially. The total change of energy in this displaced configuration of the lattice is calculated as a function of the displacements of the neighboring ions ξ_i and the induced dipoles μ_i . The Born-Mayer form of the repulsive potential⁷ was used in the calculations. The magnitudes of ξ_i and μ_i are then obtained by minimizing the total change in energy with respect to both ξ_i and μ_i . Das⁸ later applied this method to calculating the distortions in alkaline-earth oxides due to the substitution of the paramagnetic ions. For trivalent impurities, the interaction due to the extra charge of the paramagnetic ions was also considered and this interaction gave very large distortions for Cr^{3+} and Fe^{3+} ions in CaO. The shell model, the effect of the relative motion of the shells and ionic charges, was later incorporated properly in

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¹ W. Low, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1960), Suppl. 2; W. Low and E. L. Offenbacher, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1965), Vol. 17.

² B. Henderson and J. E. Wertz, *Advan. Phys.* **17**, 749 (1968).

³ N. S. Shiren, in *Proceedings of Eleventh Colloque Ampere, Eindhoven, 1962* (North-Holland, Amsterdam, 1963), p. 114.

⁴ D. K. Ray, T. Ray, and M. J. L. Sangster (unpublished).

⁵ Y. Fukai, *J. Phys. Soc. Japan* **18**, 1413 (1963); **18**, 1580 (1963); **19**, 175 (1964).

⁶ B. G. Dick and T. P. Das, *Phys. Rev.* **127**, 1053 (1962).

⁷ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, England, 1968).

⁸ T. P. Das, *Phys. Rev.* **140**, A1957 (1965).

the theory of Dick and Das by Dick.⁹ The magnitudes of the displacements ξ_i and the induced dipoles μ_i were modified to some extent when the shell model was used.

Peckham¹⁰ has recently made neutron-scattering experiments on MgO and has given the values of charges for the shells and cores for both O^{2-} and Mg^{2+} ions.¹¹ It will be worthwhile to investigate whether the magnitudes of the ion displacements, particularly for the substitution of trivalent paramagnetic ions for which displacements are expected to be large, are altered significantly if one uses the shell-model results of Peckham. One can then calculate the change in the static crystal-field splitting and the spin-phonon coupling parameters due to the deformation of the crystal. This has been done in the present paper where the recent compressibility data for MgO,¹² NiO¹³, MnO,¹⁴ and EuO¹⁵ crystals were used to calculate the Born-Mayer parameters required in the calculations.

Recently, Dienes, Hatcher, Smoluchowski, and Wilson¹⁶ treated the problem of Li^+ impurity in KCl and KBr crystals and have calculated the electric field \mathcal{E}_i at the ionic sites i in terms of ξ_i . The change in energy ΔE due to the substitution was then minimized numerically with respect to ξ_i parameters. If we expand \mathcal{E}_i at each site in terms of ξ_i and μ_i , we get self-consistent relations of μ_i in terms of ξ_i . It is then possible to obtain an algebraic expression for ΔE in terms of ξ_i only, which can be minimized algebraically with respect to ξ_i . We have followed this method for the case of paramagnetic impurities in MgO. This method of approach can be shown to be equivalent to the method of Dick and Das. Details of the calculations for ξ_i and μ_i for both rigid-ion and shell model for Mg^{2+} and O^{2-} ions are given in Sec. II. The results indicate that the ξ_i change enormously when the shell model is used—particularly for the trivalent paramagnetic ions. This result together with the large dependence of ξ_i on the Born-Mayer parameters makes it necessary to undertake calculations using a proper covalent model for the interaction between the paramagnetic ions and the six nearest O^{2-} ions. In Sec. III the modifications to the static crystal-field parameters Dq and the spin-phonon coupling coefficients for a number of ions in MgO are calculated.

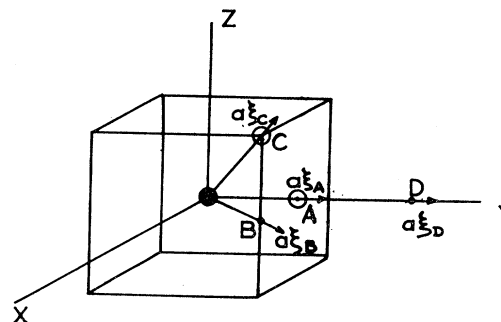


FIG. 1. The displacements of four different types of ions around the paramagnetic impurity.

II. CALCULATIONS OF DISPLACEMENTS OF IONS AROUND PARAMAGNETIC IMPURITIES IN A MgO CRYSTAL

The displacements of each of the ion types around the substituted paramagnetic ion are shown in Fig. 1. The displacements have been written as $a\xi_A$, $a\xi_B$, $a\xi_C$, and $a\xi_D$, where a is the cation-anion distance of the perfect crystal. In the present calculations, we are principally interested in knowing the displacements of type-A ions and, consequently, the calculations are expected to be fairly accurate if we consider four types of ions. When the ions are displaced from their equilibrium positions, electric dipole moments are induced on these ions and these are denoted by $2ea\mu_A$, $2ea\mu_B$, $2ea\mu_C$, and $2ea\mu_D$ for A, B, C, and D types of ions, respectively. Hence, μ_i denotes the amount of the relative displacement between the positive and negative charge of the i th displaced ion.

Following Dick and Das, the total change in energy due to the substitution can be written as

$$\Delta E = \Delta E_R + \Delta E_e + \Delta E_{\text{self}} + \Delta E_{\text{ex}}, \quad (1)$$

where ΔE_R is the change in short-range repulsive interaction, ΔE_e is the change in electrostatic interaction, ΔE_{self} is the self-energy of the dipoles, and ΔE_{ex} is the interaction due to the extra charge for trivalent paramagnetic ions. We write below the expressions for the

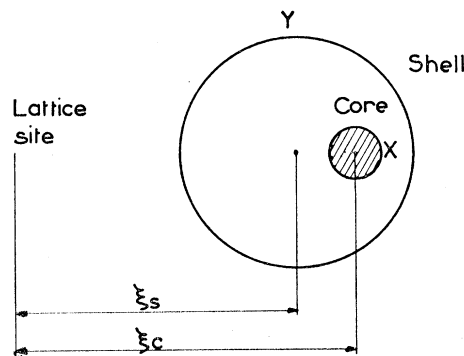


FIG. 2. Displacements of the cores and shells from the cubic lattice sites.

⁹ B. G. Dick, Phys. Rev. **145**, 609 (1966).

¹⁰ G. Peckham, Proc. Phys. Soc. (London) **90**, 657 (1967).

¹¹ M. J. L. Sangster, thesis, University of Reading, 1968 (unpublished).

¹² O. L. Anderson and P. Andreatch, Jr., J. Am. Ceram. Soc. **49**, 404 (1966).

¹³ I. Wakabayashi, H. Kobayashi, H. Nagasaki, and S. Minomura, J. Phys. Soc. Japan **25**, 227 (1968).

¹⁴ H. G. Drickamer, R. W. Lynch, R. L. Clendenen, and E. A. Perez-Albuerne, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic New York, 1966), Vol. 19, p. 157.

¹⁵ D. B. McWhan, P. C. Souers, and G. Jura, Phys. Rev. **143**, 385 (1966).

¹⁶ G. J. Dienes, R. D. Hatcher, R. Smoluchowski, and W. Wilson, Phys. Rev. Letters **16**, 25 (1966); Phys. Rev. **161**, 888 (1967).

different contributions to ΔE :

$$\begin{aligned} \Delta E_R = & 6(Be^{-a/\sigma} - Ae^{-a/\rho}) + 6\left(-\frac{A}{\rho}e^{-a/\rho} - \frac{B}{\sigma}e^{-a/\sigma}\right)\xi_A + 6\left[\left(\frac{a^2}{2\rho^2} - \frac{2a}{\rho}\right)Ae^{-a/\rho} + \frac{a^2}{2\sigma^2}Be^{-a/\sigma}\right]\xi_A^2 \\ & + 6\left(\frac{a^2}{\rho^2} - \frac{2a}{\rho}\right)Ae^{-a/\rho}(2\xi_B^2 + \xi_D^2) + 12\sqrt{2}\frac{a}{\rho}Ae^{-a/\rho}\xi_A\xi_B - 6\frac{a^2}{\rho^2}Ae^{-a/\rho}\xi_A\xi_D \\ & + 8\left(\frac{a^2}{\rho^2} - \frac{2a}{\rho}\right)e^{-a/\rho}\xi_C^2 + 8\sqrt{(6)}\frac{a}{\rho}Ae^{-a/\rho}\xi_B\xi_C, \quad (2) \end{aligned}$$

$$\begin{aligned} \frac{\Delta E_e}{3e^2/a} = & 9.484\xi_A'^2 + 21.66\xi_B'^2 + 4.102\xi_C'^2 + 1.186\xi_D'^2 - 36.406\xi_A'\xi_B' + 11.97\xi_A'\xi_D' \\ & + 10.30\xi_A'\xi_C' - 36.80\xi_B'\xi_C' + 12.91\xi_B'\xi_D' - 8.676\xi_C'\xi_D', \quad (3) \end{aligned}$$

$$\frac{\Delta E_{\text{self}}}{3e^2/a} = 4\frac{a^3}{\alpha_A}\mu_A^2 + 8\frac{a^3}{\alpha_B}\mu_B^2 + \frac{16}{3}\frac{a^3}{\alpha_C}\mu_C^2 + 4\frac{a^3}{\alpha_D}\mu_D^2, \quad (4)$$

$$\begin{aligned} \frac{\Delta E_{\text{ex}}}{3e^2/a} = & -0.5775 + 4\xi_A - 4\xi_B + 1.778\xi_C - \xi_D - 4\mu_A - 4\mu_B - 1.778\mu_C - \mu_D - 4\xi_A^2 + 2.828\xi_B^2 - 1.026\xi_C^2 \\ & + 0.5\xi_D^2 + 8\mu_A\xi_A + 5.657\mu_B\xi_B + 2.053\mu_C\xi_C + \mu_D\xi_D + 4\mu_A^2 + 2.828\mu_B^2 + 1.026\mu_C^2 + 0.5\mu_D^2, \quad (5) \end{aligned}$$

where

$$\begin{aligned} \xi_A' &= \xi_A - \mu_A, \\ \xi_B' &= \xi_B + \mu_B, \\ \xi_C' &= \xi_C - \mu_C, \\ \xi_D' &= \xi_D + \mu_D. \end{aligned} \quad (6)$$

Here, A , ρ and B , σ are the Born-Mayer parameters for Mg^{2+} - O^{2-} ions and the impurity- O^{2-} ions, respectively. The α_i 's are the ionic polarizability factors. For the reasons mentioned by Dick,⁹ we have not included the van der Waals interactions in our calculations. If one takes the Dick and Das model to be correct, it is possible now to minimize ΔE with respect to all ξ_i and μ_i and evaluate the values of ξ_i and μ_i for which ΔE is at a minimum. But as Peckham's analysis indicated a large departure from the rigid-ion model for the phonon dispersion relations in MgO , we introduce the shell model in the deformation calculations in the same way as was done by Dick and then compare the numerical results with those obtained from the Dick and Das (DD) model.

Following the shell model, we assume that the ionic core of charge X and a massless shell of charge Y do not move in the same way. But the total charge $X+Y$ must be equal to Z , the ionic charge. The displacements of the cores and shells from the cubic sites are indicated in Fig. 2. The dipole moment due to the displacements of shell and core is given by

$$M = X\xi_c + Y\xi_s = Z\xi_c + \mu_c = Z\xi_s + \mu_s, \quad (7)$$

where ξ_c and ξ_s are the displacements of the core and shell of an ion from its equilibrium position and μ_c and μ_s

are the core-centered and shell-centered induced dipoles. The Born-Mayer repulsive interaction acts between the shells and consequently the ξ_i in Eq. (2) should be shell centered. ΔE_R contains a term linear in ξ_A . So if we use core-centered displacements for ΔE_R , it should then involve terms linear in $\xi_A - d$, where d is the relative displacement between the shell and core. As d is proportional to μ_A , then ΔE_R would involve a term linear in μ_A . Terms up to second order are kept in the expression for ΔE_R , and this would require μ_A to be expanded up to terms quadratic in ξ_i . On the other hand, if we use shell-centered ξ_i in ΔE_R , then no term linear in μ_A appears in ΔE for divalent paramagnetic ions, and it will be sufficient to expand μ_i up to terms linear in ξ_i . On the basis of these considerations, we use shell-centered ξ_i in all energy expressions. Using this convention about the choice of the ξ_i parameters, ΔE_R remains unaltered. The other ΔE_i can also be expressed in terms of the displacements of the shells ξ_i and $(\mu_s)_i$. ΔE_e has the same form as in Eq. (3) but the definitions of ξ_i' are modified as follows:

$$\begin{aligned} \xi_A' &= \bar{\xi}_A - \bar{\mu}_A, \\ \xi_B' &= \bar{\xi}_B + \bar{\mu}_B, \\ \xi_C' &= \bar{\xi}_C - \bar{\mu}_C, \\ \xi_D' &= \bar{\xi}_D + \bar{\mu}_D, \end{aligned} \quad (8)$$

where $\bar{\xi}_i = |\frac{1}{2}Z|\xi_i$ and $\bar{\mu}_i = \frac{1}{2}X\mu_i$, ξ_i are the displacements of the shells, and μ_i are the shell-centered dipole moments expressed in units of $2ea$.

In the expression for ΔE_{self} , all ξ_i and μ_i are to be replaced by $\bar{\xi}_i$ and $\bar{\mu}_i$. For ΔE_{self} we require values for the shell-centered polarizability α_i . It has been shown by

Dick⁹ that these polarizability factors are related to core-centered polarizability factors α_i by the relation

$$\bar{\alpha}_i = [(Y-Z)/Y]^2 \alpha_i. \quad (9)$$

For the case of Mg^{2+} and O^{2-} ions in a MgO crystal, the following values of Y and Z are given by Sangster¹¹: For Mg^{2+} ,

$$Y = -2, \\ Z = 1.897;$$

for O^{2-} ,

$$Y = -2.875, \\ Z = -1.897.$$

Using values of α for Mg^{2+} and O^{2-} ions of 0.103 and 2.0 Å³, respectively, and the above values of Y and Z , we get α for Mg^{2+} and O^{2-} ions to be 0.39 and 0.23 Å³, respectively. Thus there is an order-of-magnitude reduction of the polarizability factor for the O^{2-} ion and we get $\bar{\alpha}_{\text{Mg}^{2+}} > \bar{\alpha}_{\text{O}^{2-}}$. We shall see that this change in the values α modifies the magnitudes of displacements enormously.

The electric field is now calculated at the centers of the shells and the following self-consistent expressions are obtained for the induced moments in which expansions up to first order in ξ_i have been made:

$$\begin{aligned} (a^3/\bar{\alpha}_A + 2.371)\bar{\mu}_A &= b_A + 2.371\bar{\xi}_A - 4.551(\bar{\xi}_B + \bar{\mu}_B) \\ &\quad + 1.288(\bar{\xi}_C - \bar{\mu}_C) + 1.497(\bar{\xi}_D + \bar{\mu}_D), \\ (a^3/\bar{\alpha}_B + 2.708)\bar{\mu}_B &= b_B + 2.275(\bar{\xi}_A - \bar{\mu}_A) - 2.708\bar{\xi}_B \\ &\quad + 2.300(\bar{\xi}_C - \bar{\mu}_C) - 0.8087(\bar{\xi}_D + \bar{\mu}_D), \\ (a^3/\bar{\alpha}_C + 0.7691)\bar{\mu}_C &= b_C + 0.9659(\bar{\xi}_A - \bar{\mu}_A) \\ &\quad - 3.450(\bar{\xi}_B + \bar{\mu}_B) + 0.7691\bar{\xi}_C - 0.8134(\bar{\xi}_D + \bar{\mu}_D), \\ (a^3/\bar{\alpha}_D + 0.2964)\bar{\mu}_D &= b_D - 1.697(\bar{\xi}_A - \bar{\mu}_A) \\ &\quad - 1.614(\bar{\xi}_B + \bar{\mu}_B) + 1.085(\bar{\xi}_C - \bar{\mu}_C) - 0.2964\bar{\xi}_D, \end{aligned} \quad (10)$$

where $\bar{\alpha}_A$, $\bar{\alpha}_B$, $\bar{\alpha}_C$, and $\bar{\alpha}_D$ are the shell-centered polarizability factors for the ions A , B , C , and D , respectively, and b_A , b_B , b_C , and b_D are the contributions to the induced moments from the extra charge at the paramagnetic ion site if it is present. For divalent ions, these are zero. For a single extra charge we get

$$\begin{aligned} b_A &= 0.5 - (2/|z|)\bar{\xi}_A, \\ b_B &= 0.25 - 0.3536(2/|z|)\bar{\xi}_B, \\ b_C &= 0.1667 - 0.1925(2/|z|)\bar{\xi}_C, \\ b_D &= 0.125 - 0.125(2/|z|)\bar{\xi}_D. \end{aligned} \quad (11)$$

Solutions of the coupled equations for $\bar{\mu}_i$ given in Eq. (10) in terms of $\bar{\xi}_i$ can be found in a straightforward manner and are given below.

For divalent paramagnetic ions,

$$\begin{aligned} \bar{\mu}_A &= 0.04382\bar{\xi}_A - 0.09814\bar{\xi}_B + 0.02240\bar{\xi}_C + 0.03886\bar{\xi}_D, \\ \bar{\mu}_B &= 0.08346\bar{\xi}_A - 0.08574\bar{\xi}_B + 0.08306\bar{\xi}_C - 0.03224\bar{\xi}_D, \\ \bar{\mu}_C &= 0.01680\bar{\xi}_A - 0.07327\bar{\xi}_B + 0.01043\bar{\xi}_C - 0.01789\bar{\xi}_D, \\ \bar{\mu}_D &= -0.06608\bar{\xi}_A - 0.06446\bar{\xi}_B + 0.04057\bar{\xi}_C - 0.00695\bar{\xi}_D. \end{aligned} \quad (12)$$

For trivalent paramagnetic ions,

$$\begin{aligned} \bar{\mu}_A &= 0.01095 + 0.02008\bar{\xi}_A - 0.09668\bar{\xi}_B \\ &\quad + 0.02251\bar{\xi}_C + 0.03866\bar{\xi}_D, \\ \bar{\mu}_B &= 0.00810 + 0.08553\bar{\xi}_A - 0.09941\bar{\xi}_B \\ &\quad + 0.08346\bar{\xi}_C - 0.03207\bar{\xi}_D, \\ \bar{\mu}_C &= 0.00302 + 0.01721\bar{\xi}_A - 0.07217\bar{\xi}_B \\ &\quad + 0.00570\bar{\xi}_C - 0.01779\bar{\xi}_D, \\ \bar{\mu}_D &= 0.00521 - 0.06772\bar{\xi}_A - 0.06350\bar{\xi}_B \\ &\quad + 0.04077\bar{\xi}_C - 0.01219\bar{\xi}_D. \end{aligned} \quad (13)$$

Thus for the cases of Ni^{2+} , Mn^{2+} , and Eu^{2+} we shall use Eq. (12), whereas for Cr^{3+} and Er^{3+} Eq. (13) will be used. These expressions for $\bar{\mu}_i$ are to be substituted in ΔE so as to obtain ΔE as a function of ξ_i only. ΔE is then to be minimized with respect to ξ_i which will give four linear equations for ξ_i . Solutions of these equations give the values of ξ_i as well as ΔE . It can easily be shown that the method of Dick and Das⁶ where ΔE is minimized independently with respect to ξ_i and μ_i and the method followed here are equivalent.¹⁷ This is due to the fact that the total electrostatic interaction (due also to the extra charge in the case of trivalent ions) can be written as $-2ea \sum_i \mathbf{u}_i \cdot \mathbf{E}_i$. Adding the self-energy for the dipoles to this energy, the part of ΔE depending on μ_i can be written as

$$\Delta E = - \sum_i 2ea \mathbf{u}_i \cdot \mathbf{E}_i + \frac{1}{2} \sum_i \frac{4e^2 a^2 \mu_i^2}{\alpha_i}.$$

Minimizing ΔE with respect to μ_i , we arrive at the consistency relations $2ea \mathbf{u}_i = \alpha_i \mathbf{E}_i$ which we have used to eliminate μ_i from the expression for ΔE . This will also be evident from the results obtained for ions such as Cr^{3+} in MgO. The expression for ΔE_R contains the short-range exchange parameters A and ρ for the MgO crystal and B and σ for the paramagnetic impurity. The experimental values of the compressibility for MgO,¹² NiO,¹³ MnO,¹⁴ and EuO¹⁵ crystals are given in Table I. The Born-Mayer parameters are calculated from these values of the compressibility and are also tabulated in Table I. For Ni^{2+} , Mn^{2+} , and Eu^{2+} in MgO we take the same functional form of the Born-Mayer interaction as in NiO, MnO, and EuO, respectively. In order to get the B and σ for Cr^{3+} and Er^{3+} , we use

¹⁷ We are indebted to Dr. T. P. Das for pointing out the equivalency of the two methods.

TABLE I. Born-Mayer parameters for different crystals.

Substance	Compressibility (10^{-12} cm ² /dyn)	A (10^{-10} erg)	ρ (10^{-8} cm)
MgO	0.607 (Ref. 12)	6.05	0.377
NiO	0.500 (Ref. 13)	10.70	0.334
EuO	0.840 (Ref. 15)	33.42	0.329
Mn ²⁺ -O ²⁻	0.694 (Ref. 14)	7.654	0.375
Cr ³⁺ -O ²⁻		8.20	0.334
Er ³⁺ -O ²⁻		15.3	0.329

the Mayer relation as used earlier by Das⁸:

$$B_2 = B_1 e^{(a_2 - a_1)/\sigma_1},$$

$$\sigma_2 = \sigma_1,$$

where B_2 and σ_2 are the Born-Mayer parameters for Cr³⁺-O²⁻ or Er³⁺-O²⁻ pairs and B_1 and σ_1 denote the corresponding parameters for an ion pair which does not differ much from these pairs. The parameters a_1 and a_2 denote the cation-anion distance in the reference ion pair and the pair to be investigated. Thus for the case of Cr³⁺ in MgO we take the reference pair to be Ni²⁺-O²⁻ in NiO, and for Er³⁺ in MgO, the reference pair is Eu²⁺-O²⁻ in EuO.

Using the values of the Born-Mayer parameters given in Table I, ΔE is minimized with respect to ξ_i . The values of ξ_i thus obtained for different cases are given in Table II. The magnitudes of ξ_i fix the values of μ_i which are also given in the same table. The results indicate that the displacements of ions decrease as their distances from the paramagnetic ion increase except for ions of type D which have more displacements than ions of type C . Also, because of the neglect of ions beyond D , the ξ_D values obtained here may not be accurate. For the calculations of the change of static as well as dynamic crystalline potential we are more interested in knowing the displacements of nearest neighbors ξ_A . It follows from Table III that the value of ξ_A does not change as we increase the number of neighbors from three to four. Hence we have not considered more than four types of ions in the present paper.

The magnitudes of induced dipoles μ_i given in Table II are always small compared to the displacement dipoles. This is true even for the cases of Cr³⁺ and Er³⁺. This is principally due to the fact that the shell-centered polarizability factors are small both for Mg²⁺ and O²⁻ ions and the core charge of O²⁻ ions is small.

In order to compare the results obtained following the method used here with those obtainable from the method

TABLE III. Displacements ξ_i for the different combinations of ions.

Displaced ions	ξ_A	ξ_B	ξ_C	ξ_D
A	-0.18			
AB	-0.20	-0.020		
ABC	-0.210	-0.025	-0.0082	
ABD	-0.242	-0.044		0.057
$ABCD$	-0.244	-0.048	-0.0089	0.054

of Dick and Das, we give the results of displacements and induced moments for the case of Cr³⁺ in MgO:

$$\begin{aligned} \xi_A &= -0.236, & \mu_A &= +0.0247, \\ \xi_B &= -0.0459, & \mu_B &= -45.4 \times 10^{-4}, \\ \xi_C &= -0.0091, & \mu_C &= 27.3 \times 10^{-4}, \\ \xi_D &= +0.0530, & \mu_D &= 0.0113. \end{aligned} \quad (14)$$

The two sets of results are in full agreement, as is to be expected. The slight discrepancies between the values given in (14) and those given in Table II for Cr³⁺ is due to the fact that we have used in Eq. (10) expansion of μ_i up to the first order in ξ_i only. In order to see how much the shell-model polarizability factors influence the results, we calculate the displacements and induced moments for Cr³⁺ in MgO. Using core-centered polarizabilities and taking three types of neighbors, we obtain

$$\begin{aligned} \xi_A &= 10.01, & \mu_A &= -6.847, \\ \xi_B &= 9.259, & \mu_B &= 0.2211, \\ \xi_D &= -12.26, & \mu_D &= -0.3906. \end{aligned}$$

Thus we get completely divergent results with the DD model, particularly for the trivalent ions for which displacements are expected to be large. Use of the shell model profoundly affects the results in this case. For the divalent impurities the interaction due to the extra charge is absent and the magnitudes of the displacements are small. Consequently, shell-model parameters do not alter ξ_i profoundly. It is to be noted that the results for Ni²⁺ and Mn²⁺ in MgO were obtained earlier by Das using DD model. But his results cannot be compared with ours as we have used the Born-Mayer parameters obtained from more recent compressibility experiments.

TABLE II. Values of the displacements and the induced moments for different ions in a MgO crystal.

Substance	ξ_A	ξ_B	ξ_C	ξ_D	μ_A	μ_B	μ_C	μ_D
Ni ²⁺ :MgO	-0.00212	-0.00079	-0.000029	0.00027	-0.101×10^{-4}	-0.589×10^{-4}	0.337×10^{-4}	0.917×10^{-4}
Mn ²⁺ :MgO	0.0226	0.0085	0.00031	-0.0029	1.07×10^{-4}	6.24×10^{-4}	-3.59×10^{-4}	-9.78×10^{-4}
Eu ²⁺ :MgO	0.0838	0.0313	0.00116	-0.0107	3.98×10^{-4}	23.1×10^{-4}	-13.3×10^{-4}	-36.2×10^{-4}
Cr ³⁺ :MgO	-0.244	-0.0485	-0.0089	0.0543	0.0257	-48.7×10^{-4}	28.5×10^{-4}	0.0117
Er ³⁺ :MgO	-0.0892	0.00425	-0.0218	0.0351	0.0202	-8.31×10^{-4}	12.5×10^{-4}	0.00502

III. MODIFICATIONS TO CRYSTAL-FIELD-SPLITTING PARAMETER AND TO SPIN-PHONON COUPLING COEFFICIENTS

We shall now discuss the extent to which modifications are introduced in the static cubic field-splitting parameter Dq and the spin-phonon coupling coefficients for paramagnetic ions in a MgO crystal when the displacements of the nearest neighbors ξ_A are considered.

The static cubic crystalline field-splitting parameter Dq has been measured for a number of ions in MgO and are given in Table IV. On the basis of the effective-point-charge model and taking into account the nearest O^{2-} ions, one gets the following theoretical expression for Dq :

$$Dq = Ze^2 \langle r^4 \rangle / 6R^5, \quad (15)$$

where $\langle r^n \rangle$ is the expectation value of r^n over the wave function of paramagnetic electrons and Z is the effective charge of the nearest O^{2-} ions. If one takes the value for R corresponding to the undistorted MgO crystal 2.1 Å and equates the experimental values of Dq with its theoretical expression given in Eq. (15), we get the values of Z to be always much larger than the free ionic value of -2 . From Table IV it is evident that when one takes proper account of the distortion of the lattice the values of Z for the trivalent ions are closer to the free ionic value. As the values of the induced moments are small in all cases the contribution of the induced moments to the cubic field splitting will be negligibly small and have been neglected. The remaining discrepancies can perhaps be explained by overlap and covalency of the magnetic and ligand ionic functions. For the case of divalent iron group ions Ni^{2+} and Mn^{2+} in MgO the lattice distortion is not important and, consequently, overlap and covalency effects seem to be more important. Z is fairly close to the free ionic value for the case of the rare-earth ion Er^{3+} in MgO. Thus the effective-point-charge model with modified values of R can explain more satisfactorily the cubic field splitting for trivalent ions in MgO.

Next, we consider the change of the dynamic spin Hamiltonian parameters G_{11} and G_{44} ³ due to the dis-

TABLE V. Comparison of the theoretical values of the dynamical parameters G_{11} and G_{44} for Cr^{3+} , Ni^{2+} , and Er^{3+} in MgO with their experimental values.

Ion	Experiment		Theory	
	G_{11} (cm^{-1})	G_{44} (cm^{-1})	G_{11} (cm^{-1})	G_{44} (cm^{-1})
Cr^{3+}	0.6 ± 0.6 (Ref. 3)	4.2 (Ref. 3)	1.16	1.14
Ni^{2+}	57 (Ref. 3)	36 (Ref. 3)	46.4	88.5
Er^{3+}	153 ^a	120 ^a	29	105

^a See Ref. 18. G_{11} and G_{44} have been calculated from the experimental value of the relaxation times using $\nu_m = 6.4 \times 10^6$ cm/sec.

tortion of the crystal. The experimental values of G_{11} and G_{44} for a number of ions in MgO are given in Table V. For the cases of Cr^{3+} and Ni^{2+} , one can obtain the following expressions for G_{11} and G_{44} by third-order perturbation calculation on the Γ_2 orbital singlet state:

$$G_{11} = 4\lambda^2 R^5 / Ze^2 \langle r^4 \rangle = \frac{2}{3} \lambda^2 / Dq, \\ G_{44} = 2\lambda^2 R^5 / Ze^2 \langle r^4 \rangle [(114/175)(R^2 \langle r^2 \rangle / \langle r^4 \rangle) - (1/35)] \\ = \lambda^2 / 3Dq [(114/175)(R^2 \langle r^2 \rangle / \langle r^4 \rangle) - (1/35)], \quad (16)$$

where λ is the spin-orbit coupling parameter. G_{11} in the above equations is determined by the experimental values of λ and Dq , and R does not appear separately. But G_{44} contains both R^2 and the ratio $\langle r^2 \rangle / \langle r^4 \rangle$ separately. The values of G_{11} and G_{44} for Cr^{3+} and Ni^{2+} in MgO as obtained from the experimental values of Dq and λ are given in Table V. The experimental value of G_{11} for Cr^{3+} in MgO has large uncertainty and the theoretically calculated value lies within this region of uncertainty. But the theoretical value of G_{44} is smaller by a factor of 4 compared to the experimental one. In the case of Ni^{2+} , the two values of G_{11} are in fairly close agreement whereas the theoretical value of G_{44} is larger by a factor of 2.4 than the experimental one. This difference of results for G_{44} may be largely due to the ratio $\langle r^2 \rangle / \langle r^4 \rangle$. Overlap and covalency effects are expected to modify the $\langle r^4 \rangle$ integral as a result of which the ratio of $\langle r^2 \rangle / \langle r^4 \rangle$ will be changed. Moreover, there may be some shielding effect of the closed shells of electrons on the $\langle r^2 \rangle$ value. A proper molecular orbital treatment for the dynamical parameters is now necessary to explain the discrepancies between the existing theoretical and experimental values of G_{44} . For the case of Er^{3+} in MgO, measurements of the relaxation time¹⁸ have recently been done and from these G_{11} and G_{44} can be calculated. These values and the theoretically estimated ones taking account of the distortion of the lattice are given in Table V. The agreement for the case of G_{44} is good but not for G_{11} . Both G_{11} and G_{44} in this case involve contributions from the $l=2, 4$ and 6 terms of the orbit-lattice interaction. Overlap and covalency effects are expected to influence these terms differently and consequently both G_{11} and G_{44} are expected to be modified. It will be interesting to investigate how these

TABLE IV. Values of Z_{eff} for O^{2-} ion for various ions in MgO crystals as deduced from static crystal-field splitting.

Material	$\langle r^4 \rangle / a_0^4$	Dq cm^{-1} experimental	Z_{eff} without distortion	Z_{eff} with distortion
Ni^{2+} :MgO	3.003	860 ^a	-7.72	-7.64
Mn^{2+} :MgO	5.512	1000 ^b	-4.89	-5.47
Cr^{3+} :MgO	4.297	2270 ^c	-14.2	-3.60
Fe^{3+} :MgO	2.790	1700 ^d	-16.4	-4.16
Er^{3+} :MgO	1.126	168.5 ^e	-4.03	-2.53

^a W. Low, Phys. Rev. **109**, 247 (1958).

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

^c W. Low, Phys. Rev. **105**, 801 (1957).

^d Reference 19.

^e D. Descamps and Y. M. D'Aubigné, Phys. Letters **8**, 5 (1964).

¹⁸ M. Borg, R. Buisson, and C. Jacolin, Phys. Rev. (to be published).

effects can have more influence on some of the spin-phonon coupling parameters than on the static crystal-field parameter. For Fe^{3+} in MgO the dynamical parameters have recently been calculated by Sharma.¹⁹ G_{11} has come out to be an order of magnitude less than the experimental one, whereas G_{44} was less by a factor of 2 only. Preliminary calculation of these parameters taking into account the distortion of the lattice indicate that the values of both G_{11} and G_{44} are increased by a factor of 4. Thus the value of G_{11} comes closer to its experimental value, but G_{44} becomes larger by a factor of 2. Thus we find that the distortion of the MgO lattice, due to the substitution of a paramagnetic impurity, decreases the gap between the theoretical and experimental values of the dynamical spin Hamiltonian parameters in many cases. But discrepancies still exist between these parameters, and proper consideration of the overlap and covalency effects in the presence of distortion is necessary to resolve the discrepancies.

Because of the change of the site symmetry of the neighboring ions around the impurity from cubic to noncubic, there will now be a nonvanishing electric field gradient at these ions due to the lattice distortion. The magnitude of the electric field gradient would depend on the displacements calculated here. An O^{16} nucleus has no electric quadrupole moment, but in a MgO crystal enriched with O^{17} nuclei there would be nonvanishing electric quadrupole interaction at the O^{17} nucleus sites of types *A* and *C*. Similarly, a nonvanishing electric quadrupole interaction is also expected at the Mg site of types *B* and *D*. It is thus seen that within

the limitation of the Born-Mayer theory it is possible to calculate the displacements of neighbors around paramagnetic impurities—both for the iron group and rare-earth ions—in a MgO crystal. For divalent iron group ions the displacements of the neighbors are small. But for divalent rare-earth ions such as Eu^{2+} , the difference between the ionic radii of the impurities and that of the host Mg^{2+} ion is larger, and consequently the displacements of the neighbors are not negligible. For the case of trivalent impurities the extra charge has a large effect on the position of the neighbors. Meaningful results can only be obtained if the shell-model values of the polarizability factors are used. There is, in general, better agreement between the theoretical and experimental values of the static and dynamic crystal-field parameters if the static distortion is taken into consideration. But a large uncertainty still remains in the choice of the Born-Mayer parameters for these ions. Quigley and Das²⁰ have recently treated the problem of the Li^+ impurity in KCl and KBr crystals. They indicated the necessity of considering covalent bonding between the impurity ions and the nearest neighbors in the calculations of displacements of ions for the Li^+ impurity in KCl. One can then remove the uncertainties in the choice of Born-Mayer parameters. The analysis presented in this paper shows that such a covalent model is also necessary for the case of trivalent paramagnetic impurities in MgO. Such calculations will remove the uncertainties associated with the choice of Born-Mayer parameters and the polarizability factors.

¹⁹ R. R. Sharma, Phys. Rev. 176, 467 (1968).

²⁰ R. J. Quigley and T. P. Das, Phys. Rev. 164, 1185 (1967); 177, 630 (1969).