

Temperature-Dependent Crystal Field and Hyperfine Interactions*

WALTER M. WALSH, JR.

Bell Telephone Laboratories, Murray Hill, New Jersey

AND

JEAN JEENER† AND N. BLOEMBERGEN

Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts

(Received 18 March 1965)

The effects of temperature variation on the spin-Hamiltonian parameters of several paramagnetic ions bound in simple crystals have been measured by magnetic-resonance techniques. Whenever possible the data have been analyzed for implicit (thermal-expansion) and explicit (lattice-vibration) temperature dependences using isothermal volume dependences determined in earlier hydrostatic-pressure experiments. In MgO the g shifts of two F -state ions, V^{2+} and Cr^{3+} , increase and the cubic-field splittings of two S -state ions, Mn^{2+} and Fe^{3+} , decrease with increasing temperature almost exactly as would be expected from thermal expansion alone. The axial crystalline-field splitting of locally compensated Cr^{3+} ions also increases with temperature at a rate attributable primarily to thermal expansion. The absence of appreciable explicit temperature dependence of crystalline-field parameters in MgO is consistent with an effective point-charge model for the source of the lattice potential and cubically symmetric lattice vibrations. In zinc blende, however, the cubic-field splitting of Mn^{2+} decreases more rapidly with rising temperature than may be accounted for by thermal expansion alone, presumably because of failure of the point-charge approximation. The hyperfine couplings of $(V^{51})^{2+}$ and $(Mn^{55})^{2+}$ in MgO decrease with increasing temperature, whereas a much smaller increase would be expected due to thermal expansion. Similar explicit variations of the $(Mn^{55})^{2+}$ hyperfine interaction are found in ZnS, ZnO, CdTe, and $KMgF_3$. The effect may be approximately represented by a power law of the form $A(T) = A(0)(1 - CT^n)$ where $n \sim \frac{3}{2}$. The significance of this result for nuclear-magnetic-resonance studies of concentrated magnetic materials is indicated. The general nature of the explicit temperature dependence is discussed but no detailed theoretical analysis is possible at this time.

I. INTRODUCTION

THIS article deals with the effects of temperature variation on the paramagnetic resonance spectra of several iron-group ions present as dilute impurities in simple cubic crystals, principally magnesium oxide. In many ways the MgO lattice is an ideal host for these ions, as was recognized by Low,¹ since it has the simple NaCl structure (octahedral coordination) and the interionic spacing of 2.1 Å is a close match to those of the concentrated iron-group oxides. Further indications of its "model" character became apparent in the course of hydrostatic pressure experiments on many of these same spectra:² The local compressibility in the vicinity of the foreign cations appeared to be nearly identical to that of the bulk lattice, despite size, mass and even valence discrepancies. Another remarkable result of the pressure experiments from the purely empirical point of view was the success of an *effective point charge* (EPC) model for the crystalline potential in accounting within ~20% for the observed functional dependence of crystal-field splittings on interionic distance.³

Though attempts have been made to justify the EPC approximation using pseudopotential methods⁴ more recent molecular-orbital calculations⁵⁻⁸ do not exhibit any such simplification. In fact, the principal result of these recent analyses is to make clear the importance of delocalization of wave functions in determining the observed properties of magnetic ions bound in nominally ionic crystals. Despite its lack of theoretical foundation the EPC model provides a simple, if purely empirical, basis for estimating crystal potential variations in an idealized ionic limit. It is therefore of interest to examine the effects of dynamic strains on crystal-field splittings in an ion-host system where such an empirical law appears to hold.

The influence of lattice vibrations on magnetic-resonance spectra, as distinguished from linewidth and relaxation phenomena, were first examined in nuclear quadrupole resonance.⁹ Attempts to treat the axial-field splittings of Ni^{2+} in nickel fluosilicate and Cr^{3+} in chrome-aluminum alum and chromi-cobaltcyanide in a similar fashion¹⁰ proved unsuccessful owing to the

* The experiments reported in this article were initiated at Harvard University with Joint Services support and were completed at Bell Telephone Laboratories.

† Present address: Université Libre de Bruxelles, Bruxelles, Belgium.

¹ W. Low, Proc. Phys. Soc. (London) **B69**, 1169 (1956); Phys. Rev. **101**, 1827 (1956); **105**, 793 (1957); **105**, 807 (1957).

² W. M. Walsh, Jr., Phys. Rev. **122**, 762 (1961). This paper will be referred to as I.

³ This result was also found by S. Minomura and H. G. Drickamer [J. Chem. Phys. **35**, 903 (1961)] who measured the pressure dependence of the optical spectra of several iron-groups ions in

MgO and Al_2O_3 . The EPC model has also served to represent uniaxial strain induced optical splittings of Cr^{3+} and V^{2+} ions in MgO: A. L. Schawlow, A. H. Piksis, and S. Sugano, Phys. Rev. **122**, 1469 (1961); M. D. Sturge, *ibid.* **131**, 1456 (1963).

⁴ J. C. Phillips, J. Phys. Chem. Solids **11**, 226 (1959).

⁵ S. Sugano and R. G. Shulman, Phys. Rev. **130**, 517 (1963).

⁶ R. E. Watson and A. J. Freeman, Phys. Rev. **134**, A1526 (1963).

⁷ E. Simanek and Z. Sroubek, Phys. Stat. Solidi **4**, 251 (1964).

⁸ S. Sugano and Y. Tanabe, Phys. Rev. (to be published).

⁹ T. Kushida, G. B. Benedek, and N. Bloembergen, Phys. Rev. **104**, 1099 (1956).

¹⁰ W. M. Walsh, Jr., Phys. Rev. **114**, 1473, 1485 (1959).

inhomogeneous elastic properties of the complex unit cells of these hosts. In order to minimize such complications attention was then directed to the paramagnetic resonance (PMR) spectra of Cr^{3+} , Mn^{2+} , Fe^{3+} , and Ni^{2+} trace impurities in MgO and of Mn^{2+} in zinc blende (cubic ZnS, tetrahedral coordination) as functions of hydrostatic pressure.² The temperature dependences of these spectra as well as those of V^{2+} and a Cr^{3+} -compensation complex in MgO will be presented below. In addition, it has proved of interest to measure the effect of temperature on the hyperfine interaction of $(\text{Mn}^{55})^{2+}$ in three other hosts: KMgF_3 , ZnO, and CdTe.

The temperature data will be discussed in terms of implicit or thermal-expansion effects and explicit or lattice-vibration effects. Let G be any observable which is uniquely specified by the volume V and the temperature T of a cubic lattice held at constant pressure P . The change in G produced by a change in temperature may be written

$$\left(\frac{\partial G}{\partial T}\right)_P = \left(\frac{\partial G}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial G}{\partial T}\right)_V. \quad (1)$$

The first term on the right of Eq. (1), the implicit term, may be evaluated if the isothermal pressure dependence of G and the compressibility and thermal-expansion coefficients are known:

$$\left(\frac{\partial G}{\partial V}\right)_T = \left(\frac{\partial G}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T. \quad (2)$$

One may then evaluate $(\partial G/\partial T)_V$, the explicit temperature dependence. While such an analysis may always be formally performed, it is physically meaningful only if the local elastic and thermal-expansion properties in the vicinity of the impurity ions are essentially unchanged from those of the host crystal. It is assumed that such is the case in the present experiments. The assumption is justified, *a posteriori*, by the internal consistency of the data for various ions.

Similar investigations of crystalline fields in other ion-host systems have been reported and will be discussed in relation to our results. Benedek, Englman, and Armstrong¹¹ have examined the crystalline-field splitting of three diamagnetic Co^{3+} complexes via the chemical shift of the Co^{59} nuclear resonance. Though the pressure and temperature dependences were measured in liquid solutions, their analysis is valid in principle for solids. Rimai, Deutsch, and Silverman¹² studied the PMR spectra of several ions bound in strontium titanate versus both pressure and temperature. Recently Marshall, Hodges, and Serway¹³ have reported

¹¹ G. B. Benedek, R. Englman, and J. A. Armstrong, *J. Chem. Phys.* **39**, 3349 (1963).

¹² L. Rimai, T. Deutsch, and B. D. Silverman, *Phys. Rev.* **133**, A1123 (1964).

¹³ S. A. Marshall, J. A. Hodges, and R. A. Serway, *Phys. Rev.* **136**, A1024 (1964).

on the temperature dependence of the axial-field splitting of charge compensated Cr^{3+} ions in MgO. Our measurements of this parameter extend over a wider temperature range and are interpreted differently.

It should also be emphasized that the influence of lattice vibrations on the optical spectra of magnetic ions bound in crystals has been extensively studied.^{14,15} The phenomena are intrinsically similar but differ superficially owing to relative strengths of the vibrational perturbations in the two frequency regimes.

II. APPARATUS AND SAMPLES

In examining the effects of temperature on crystals, it is desirable to span the range from near absolute zero, where only the zero-point lattice vibrations are excited, up to the Debye temperature Θ_D , where even the highest energy optical modes are appreciably excited. This presents little difficulty in the case of a crystal such as zinc blende ($\Theta_D=326^\circ\text{K}$)¹⁶ but MgO has a Debye temperature in the range 760 to 950°K .^{16,17} We therefore require a reasonably efficient furnace capable of $\sim 1000^\circ\text{K}$ and consistent with the usual PMR requirements.

Many of the experiments were performed with a 10-kMc/sec homodyne spectrometer using low-frequency field modulation and bolometer detection. The entire cavity was heated by a noninductively wound Nichrome element powered by a Variac. The thermal inertia of the system was such that temperature fluctuations due to line-voltage variations rarely exceeded 5°K even at the maximum temperature ($\sim 1000^\circ\text{K}$). A water-cooled outer jacket prevented heating of the magnet pole pieces. Temperatures were monitored with platinum versus 90% platinum - 10% rhodium thermocouples. The accuracy of certain measurements (g shifts of V^{2+} and Cr^{3+}) was improved by operating at 30 kMc/sec. The indirectly heated cavity assembly shown in Fig. 1 was used for these experiments. The higher frequency microwaves were obtained by third-harmonic generation from 10 kMc/sec using a GaAs point-contact diode.^{18,19}

Samples of MgO lightly doped with a variety of iron-group ions were provided by the Norton and General Electric Companies. Professor C. Kikuchi kindly made available a natural crystal of cubic ZnS containing traces of divalent manganese. R. C. Linares, Jr., Dr. K. Knox, and Dr. R. E. Dietz, respectively, provided the Mn-doped ZnO, KMgF_3 , and CdTe crystals.

¹⁴ D. E. McCumber and M. D. Sturge, *J. Appl. Phys.* **34**, 1682 (1963).

¹⁵ G. F. Imbusch, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, *Phys. Rev.* **133**, A1029 (1964).

¹⁶ M. Blackman, *Proc. Roy. Soc. (London)* **164**, 62 (1938).

¹⁷ T. H. K. Barron, W. T. Berg, and J. A. Morrison, *ibid.* **A250**, 70 (1959).

¹⁸ W. M. Sharpless, *Bell System Tech. J.* **38**, 259 (1959).

¹⁹ L. W. Rupp, Jr. (unpublished).

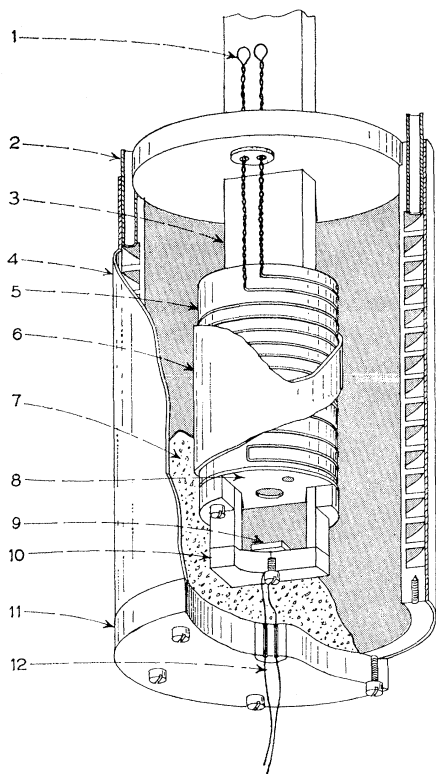


FIG. 1. Heated cavity assembly used at 30 kMc/sec: (1) Nichrome heater wire; (2) cooling water inlet; (3) stainless steel RG-96/U waveguide; (4) water-cooled outer jacket; (5) copper heat sink with asbestos insulation; (6) Johns-Manville No. 20 refractory cement; (7) Johns-Manville Sil-O-Cel C-3 insulation; (8) copper coupling iris; (9) sample crystal; (10) half-wavelength cavity; (11) OFHC copper cap; and (12) platinum-(90% platinum, 10% rhodium) thermocouple.

III. EXPERIMENTAL RESULTS

In view of the existing wealth of books and journal articles devoted to paramagnetic resonance and crystal-field theory, only a cursory description will be given of the physical origin of the various spin-Hamiltonian coefficients. The methods of evaluating them from the spectra will not be discussed at all. Rather than treat each ion in turn it is desirable to group the results according to the parameter measured. In most cases the same parameter has been examined for two distinct ions.

A. g Shifts

The ions $V^{2+}(d^3)$, $Cr^{3+}(d^3)$ and $Ni^{2+}(d^8)$ resemble each other closely in that their free-ion ground multiplets are orbital septets (F states) which are decomposed into two excited triplets (T_1 and T_2) and a lowest singlet (A_2) by an octahedral cubic electric field. This isolated orbital level would exhibit "spin-only" magnetism were it not for spin-orbit interaction which mixes into the ground state a small amount of

the orbital moment of the first excited triplet (T_2). The admixture produces a deviation of the measured g value from that of the free electron:

$$g - g_0 = -4\lambda g_0 / \Delta. \quad (3)$$

Here g is the isotropic spectroscopic splitting factor required in the spin-Hamiltonian description of the ground spin energy levels, $\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S}$, $g_0 = 2.0023$ is the free-electron splitting factor, λ is the spin-orbit coupling, Δ is the singlet-to-first-triplet ($E_{T_2} - E_{A_2}$) energy separation (often referred to as $10D_q$), β is the Bohr magneton, \mathbf{H} the applied magnetic field and \mathbf{S} the effective spin operator of multiplicity equal to that of the ground spin levels ($S = \frac{3}{2}$ for V^{2+} and Cr^{3+} , $S = 1$ for Ni^{2+}). The energy denominator Δ is sensitive to variations in the surroundings of the magnetic ion since it is a measure of the cubic (hexadecapole) moment of the crystalline potential at the magnetic ion. The pressure experiments on Cr^{3+} and Ni^{2+} reported in I were interpreted assuming the spin-orbit coupling to be insensitive to volume and, within an error of $\sim 10\%$, yielded $\Delta \propto r^{-6}$, where r is the interionic spacing. This result agrees with optical measurements of Δ versus pressure³ and is close to the r^{-5} dependence expected in the effective point-charge model.²

The results of three temperature runs at 30 kMc/sec on Cr^{3+} ions in sites of cubic symmetry in MgO are shown in Fig. 2. The implicit temperature dependence of the g shift based on the hydrostatic pressure experiments²

$$\left[\frac{\partial(g - g_0)}{\partial T} \right]_{\text{implicit}} = \left[\frac{\partial(g - g_0)}{\partial P} \right]_T \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \quad (4)$$

is indicated in the figure by a dashed curve (r^6) with a shaded error band. We use the thermal-expansion

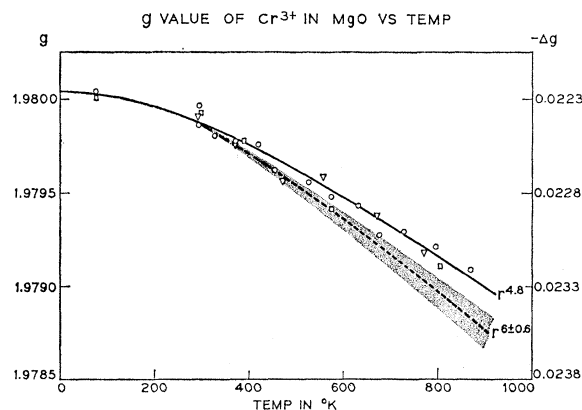


FIG. 2. Temperature dependence of the g value of Cr^{3+} ions in cubic sites in MgO. The solid curve is considered to be the best fit to the data from three runs. The dashed curve and associated shaded error band represents the implicit effect expected due to thermal expansion.

measurements of Durand.²⁰ The solid curve in Fig. 2 appears to best represent the data and corresponds to $(g-g_0)\alpha r^{4.8+1.0-0.5}$ assuming no explicit temperature variation of the shift. The assumption is at least crudely correct in that any real difference between our data and the implicit, thermal-expansion effect constitutes less than 20% of the total change and may in fact be zero within the accumulated errors.

A comparison of the g -value variations of Cr^{3+} and the isoelectronic V^{2+} ion, both in MgO , is shown in Fig. 3. The relatively weaker temperature dependence of the chromium splitting factor suggests that the local thermal expansion in the immediate vicinity of the trivalent ion may be reduced relative to the bulk value. Such a reduction could occur due to the excess charge, relative to Mg^{2+} , which presumably leads to increased binding of the nearest-neighbor anions. However the excess charge should also polarize these neighboring O^{2-} ions and lead to a slightly stronger dependence of the cubic potential on local interionic distances. The latter effect has been estimated² to cause $(g-g_0)$ to be proportional to $r^{5.5}$ but it is difficult to make any quantitative estimate of the change in local thermal expansion.

Rather than emphasize the modest differences between the thermal response of the two ions which may arise from a number of subtle effects, it is probably wiser to note their gross similarity. If no explicit temperature dependence exists for V^{2+} the data of Fig. 3 indicate $(g-g_0)\alpha r^7$ for this ion. No pressure data are available to allow a test of the assumption in this case. At most, any explicit temperature dependence constitutes less than 40% of the thermal-expansion effect and adds to it whereas for Cr^{3+} the explicit effect, if real, subtracts about 20% from the implicit contribution. These results are summarized in Table I.

Unsuccessful attempts were made to measure the temperature dependence of the g shift of Ni^{2+} in MgO . Despite its large value ($g-g_0=0.217$ at room temperature) which should facilitate measuring any changes, the experiment failed due to excessive linewidth. The resonance line is quite broad (150-G peak-to-peak) at

TABLE I. g shift data.^a

Ion and host	V^{2+} in MgO	Cr^{3+} in MgO
$\delta g \equiv g - g_0$	-0.0222	-0.0224
$(\partial \ln \delta g / \partial T)_P \times 10^6 (\text{°K})^{-1}$	7.0 ± 1	$4.8 - 0.6 \pm 1.0$
$(\partial \ln \delta g / \partial \ln V)_T (\partial \ln V / \partial T)_P \times 10^6 (\text{°K})^{-1b}$		6.1 ± 1
$(\partial \ln \delta g / \partial T)_V \times 10^6 (\text{°K})^{-1}$		$-1.6 - 1.1 \pm 2$

^a Evaluated at 295°K.

^b References 2 and 20.

²⁰ M. A. Durand, *Physics* **7**, 297 (1936). The thermal expansion of MgO has also been measured over a smaller temperature range by S. S. Sharma [*Proc. Indian Acad. Sci.* **A32**, 268 (1950)]. The two determinations are in reasonable agreement save below room temperature. Recent measurements due to McCammon and Carr confirm and extend Durand's work [G. K. White (private communication)].

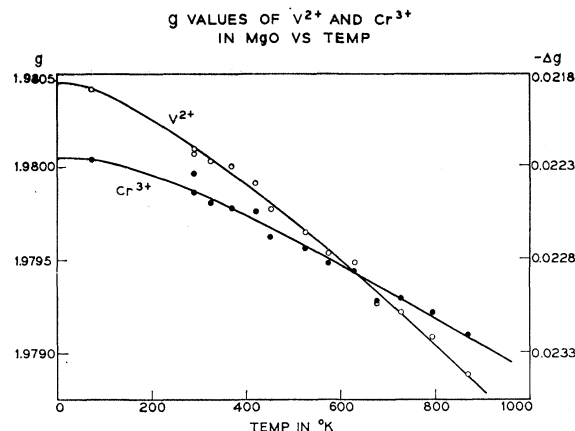


Fig. 3. Comparison of the temperature dependence of the g values of V^{2+} and Cr^{3+} in MgO .

room temperature and below and increases in width rapidly above 300°K presumably due to rapid spin-lattice relaxation.

B. Cubic Crystalline-Field Splittings

Both Mn^{2+} and Fe^{3+} are d^5 ions which, having half-filled d shells, are in S ground states and are therefore relatively insensitive to perturbation by the crystalline potential. This is reflected in their g shifts which are considerably smaller than those of V^{2+} and Cr^{3+} and prove to be quite insensitive to pressure and temperature. However, their high spin values ($S = \frac{5}{2}$) permit a splitting of the ground spin energy levels in a cubic electric potential which is usually represented by a spin-Hamiltonian term, $\mathcal{H}_{\text{cubic}} = (a/6)(S_x^4 + S_y^4 + S_z^4)$ whose coefficient a is a measure of the cubic moment of the crystalline potential. The relationship between a and the potential at the ion's position is extremely complex since a number of high-order perturbations connect the orbitally nondegenerate ground state with excited configurations. Calculations by Gabriel, Johnston, and Powell²¹ are at least qualitatively consistent with the results of pressure experiments² which indicated $a \propto r^{-21.24}$ for both Mn^{2+} and Fe^{3+} in MgO . Thus $a \propto (\text{cubic potential})^n$ with $n \sim 3.5 - 4.25$ depending on one's assumptions concerning the cubic potential itself. While a is certainly more complex in origin than the g shifts of the F -state ions, it is a very sensitive monitor of the cubic-lattice potential. The temperature dependence of $a' \equiv a/g\beta$ for both d^5 ions in MgO are shown in Fig. 4 along with the variation expected due to thermal expansion based on the pressure data. There is essentially no explicit temperature dependence above room temperature when the accumulated experimental errors

²¹ J. R. Gabriel, D. F. Johnston, and M. J. D. Powell, *Proc. Roy. Soc. (London)* **A264**, 503 (1961). See also the experiments of A. J. Shuskus [*Phys. Rev.* **127**, 1529 (1962)].

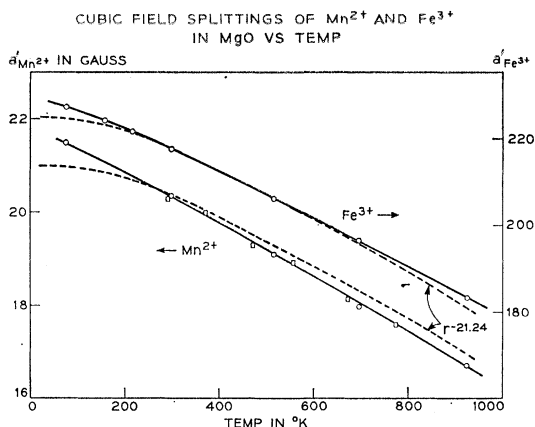


FIG. 4. The cubic-field splittings of Mn^{2+} and Fe^{3+} in MgO versus temperature. The solid lines are visual fits to the data. The dashed curves show the variations expected from thermal expansion.

are considered (see Table II).²² The experimental variation of a below room temperature is somewhat larger than would be expected due to thermal expansion alone.

An interesting contrast to the data taken with MgO as host occurs in the case of Mn^{2+} bound in cubic ZnS . As shown in Fig. 5 and summarized numerically in Table II, a clearcut explicit temperature dependence of a is observed over the entire temperature range if we

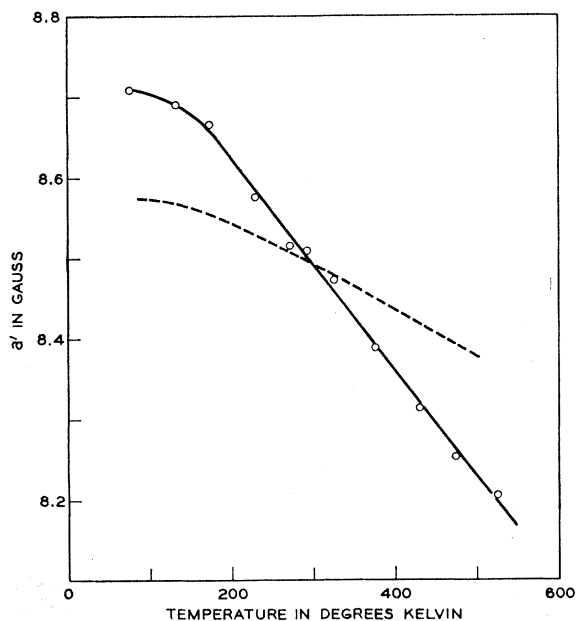


FIG. 5. The cubic field splitting of Mn^{2+} in cubic ZnS versus temperature. The dashed curve is the implicit effect expected due to thermal expansion. The difference between the solid and dashed curves represents a clearcut explicit temperature dependence, i.e., $(\partial a'/\partial T)_V \neq 0$.

²² This result was reported earlier by W. M. Walsh, Jr. [Phys. Rev. Letters 4, 507 (1960)] but was incorrectly interpreted at that time.

use the pressure data obtained earlier² and the thermal-expansion measurements of Benoit and Adenstedt as tabulated by Krishnan.²³

C. Axial Crystalline-Field Splitting

A small percentage of the Cr^{3+} ions present in MgO have charge-compensating centers localized sufficiently near them that the site symmetry becomes observably less than cubic. Most readily observed are ion-compensation complexes having $\langle 100 \rangle$ -oriented axial symmetry.²⁴ As a result of the decreased symmetry the spin-Hamiltonian of these ions contains an additional axial-field splitting term, $\mathcal{H}_{\text{axial}} = D_{\langle 100 \rangle} S^2_{\langle 100 \rangle}$. The temperature dependence of $D'_{\langle 100 \rangle} \equiv D_{\langle 100 \rangle}/g\beta$ is indicated in Fig. 6. Our own data cover the range from 880°K down to room temperature while the measurements of Marshall, Hodges, and Serway,¹³ also shown, extend from 340°K down to 4.2°K. No pressure data are available for this parameter. In view of the g shift and cubic-field splitting information just presented we have attempted to fit the data of Fig. 6 using thermal expansion alone whereas Marshall *et al.* assumed the

TABLE II. Cubic-field-splitting data.^a

Ion and host	Mn^{2+} in MgO	Fe^{3+} in MgO	Mn^{2+} in ZnS
$a \times 10^4, \text{cm}^{-1}$	19.01	203.8	7.97
$(\partial \ln a)/\partial T)_P \times 10^4, (\text{°K})^{-1}$	-2.66 ± 0.3	-2.26 ± 0.1	-1.50 ± 0.2
$(\partial \ln a/\partial \ln V)_P (\partial \ln V/\partial T)_P \times 10^4, (\text{°K})^{-1b}$	-2.15 ± 0.5	-2.15 ± 0.2	-0.62 ± 0.4
$(\partial \ln a/\partial T)_V \times 10^4, (\text{°K})^{-1}$	-0.51 ± 0.8	-0.11 ± 0.3	-0.88 ± 0.6

^a Evaluated at 295°K.

^b References 2, 20, and 23.

effect to be entirely explicit. The curve shown in the figure was drawn assuming $D \propto r^n$ and was normalized at 273°K. The optimum exponent proved to be $n = 8.65$. The fit is very good save below 200°K when the experimental data vary less rapidly than the computed curve. It should be noted that it is in this low-temperature range that Marshall *et al.*¹³ found an isotope effect on the magnitude of $D_{\langle 100 \rangle}$. No such effect should be seen if local thermal expansion equal to that of the host were the sole mechanism operative. It is also in the temperature range below room temperature that some explicit temperature dependence of the cubic-field splittings was observed. The assumption of negligible explicit temperature dependence is therefore incorrect in this range.

Despite our inability to fit the data below 200°K it is interesting to observe that the value of the exponent n appropriate over most of the range covered is not unreasonable. In the pure EPC model the dominant

²³ R. S. Krishnan, *Progress in Crystal Physics I* (Viswanathan, Madras, India, 1958).

²⁴ J. E. Wertz and P. Auzins, Phys. Rev. 106, 484 (1957).

contribution to D is expected to have the form

$$D\alpha \frac{\text{axial potential}}{(\text{cubic potential})^2} \propto r^7.$$

If we use the observed variation of the cubic potential (r^{-6}) rather than the EPC value (r^{-5}) we might expect $D\alpha r \sim 9$ in close agreement with our data.

It is clear that only a pressure experiment can determine the validity of our tentative conclusion that most of the temperature dependence of D is due to thermal expansion of the host crystal rather than changes in lattice-vibration amplitudes at constant volume.

D. Hyperfine Splittings

The unpaired d electrons of the iron-group ions produce large effective magnetic fields H_N at their nuclei. In cubic symmetry the interaction may be represented by a simple, isotropic term, $A\mathbf{I}\cdot\mathbf{S}$, in the spin Hamiltonian. The hyperfine coupling coefficient A is a measure of the field produced by the electronic spin S of the ion (expectation value $\langle S_z \rangle$) at the nucleus of spin I and moment μ_N

$$\mathbf{H}_N = (AI/\mu_N)\langle \mathbf{S}_z \rangle. \quad (5)$$

In cubic symmetry and in the absence of appreciable orbital angular momentum the dominant contribution to A arises from exchange polarization of the magnetic ion's shells by the unpaired d electrons. An extensive

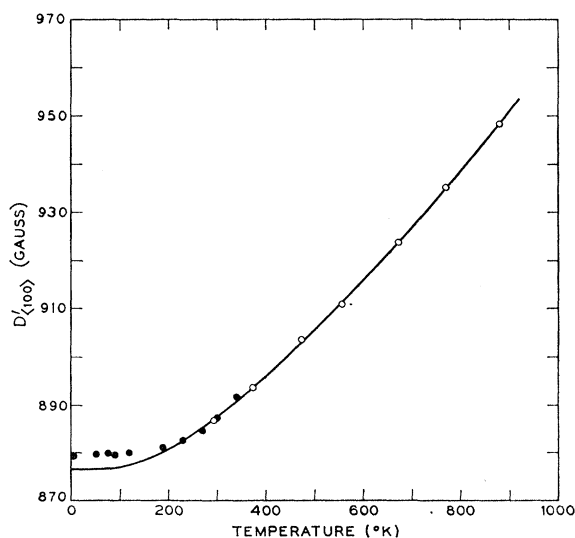


FIG. 6. Temperature dependence of the axial field splitting of Cr^{3+} ions in MgO whose charge compensation is localized nearby in $\langle 100 \rangle$ directions. The closed circles show the measurements of Marshall, Hodges, and Serway (Ref. 13). The open circles are our own data. The solid curve represents the contribution of thermal expansion assuming $D\alpha r^{3.65}$ and normalizing at 273°K.

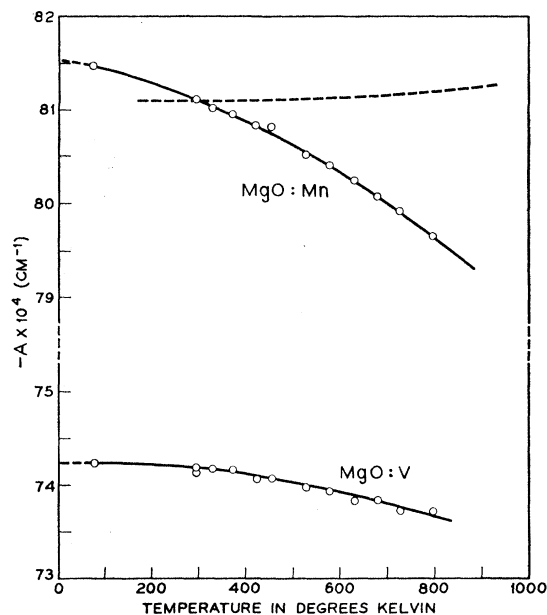


FIG. 7. The variation with temperature of the hyperfine coupling of Mn^{2+} and V^{2+} in MgO. The solid curves are visual fits to the data. The dashed curve is the implicit effect expected for Mn^{2+} on the basis of pressure experiments. The explicit (phonon) effect is clearly dominant.

review of this problem has been presented by Watson and Freeman.²⁵

It is generally found that the electron-nuclear interaction, though intrinsically a property of the ion itself, is sensitive to the ion's environment in that the magnitude of A for a given paramagnetic ion may change by several percent in going from one host crystal to another. Much less easily observed are variations of A with interionic distance in a given ion-host complex. Modest effects of hydrostatic pressure on the hyperfine coupling of $(\text{Mn}^{55})^{2+}$ in MgO ($A \propto r^{0.02}$) and cubic ZnS ($A \propto r^{0.12}$) have been reported in I. The present experiments indicate that quite appreciable explicit variations of A are produced by thermal lattice vibrations. This is in contrast to the bulk of the crystalline-field data where thermal expansion played the dominant role.

The well-resolved hyperfine splittings of the PMR spectra of $(\text{V}^{51})^{2+}$ and $(\text{Mn}^{55})^{2+}$, both bound in MgO,²⁶ have been measured from 77 to 800°K as illustrated in Fig. 7. The most noteworthy aspect of these data is the decrease of $|A|$ with increasing temperature. Since $(\partial \ln A / \partial \ln r)_T$ was found to be positive for Mn^{55} in the pressure experiments² the effect of thermal expansion

²⁵ R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1957).

²⁶ Hyperfine splitting of the PMR spectra of several other ions commonly found in MgO are also observed. These have not proved measurably temperature-dependent in our experiments either due to poor resolution, i.e., small $|A|$ values [$(\text{Cr}^{53})^{3+}$, $(\text{Fe}^{57})^{3+}$, $(\text{Ni}^{61})^{2+}$], or a restricted temperature range of observation due to spin-lattice relaxation broadening [$(\text{Co}^{59})^{2+}$, $(\text{Ni}^{61})^{2+}$].

is more than overcome by an explicit temperature dependence. The small implicit contribution to the variation of $|A|$ is shown as a dashed curve in Fig. 7. In the absence of pressure data for V^{2+} in MgO no such comparison may be made but the qualitative similarity to the manganese data suggests that thermal expansion is much less important than the explicit lattice-vibration effects in this case also.

In order to determine the generality of this finding the hyperfine splittings of $(Mn^{55})^{2+}$ in a variety of

other host crystals were also examined. The most precise data were obtained for cubic ZnS:Mn as shown in Fig. 8. The atmospheric pressure data were corrected to constant volume (that of the lattice at room temperature) using the isothermal volume dependence measured earlier.² The small difference between the two curves again reflects the dominant contribution of lattice-vibration amplitudes to the thermal changes of A . Similar, though less extensive, data were also taken on the systems ZnO:Mn (wurzite structure), CdTe:Mn (zinc-blende structure) and $KMgF_3$:Mn (perovskite, Mn^{2+} surrounded by a regular octahedron of fluorine ions.) Corrections to constant volume could not be made in these cases as the hydrostatic-pressure experi-

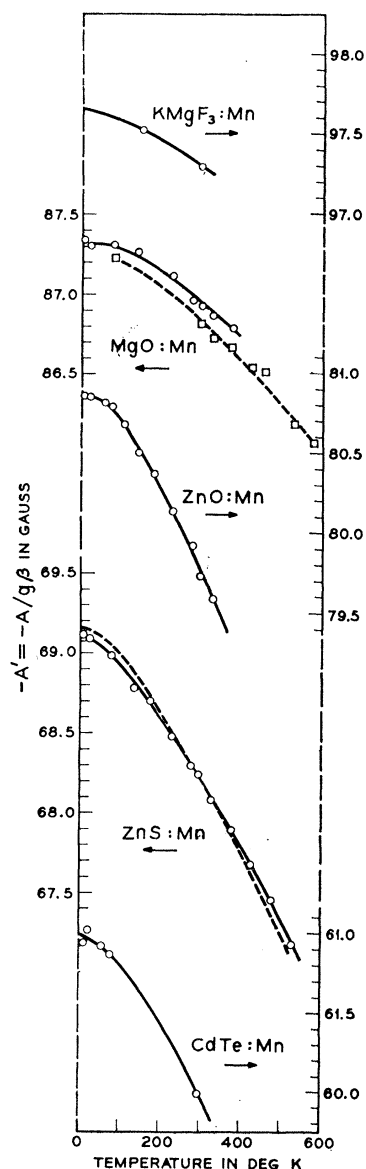


FIG. 8. Hyperfine coupling versus temperature for Mn^{2+} in various host crystals. Solid curves are visual fits to the data. The dashed curve lying just below the MgO solid curve represent the less precise, higher temperature data. The interrupted curve running nearly parallel to the solid ZnS curve was obtained by correcting the solid curve to constant, room-temperature volume, i.e., constitutes the true explicit temperature dependence.

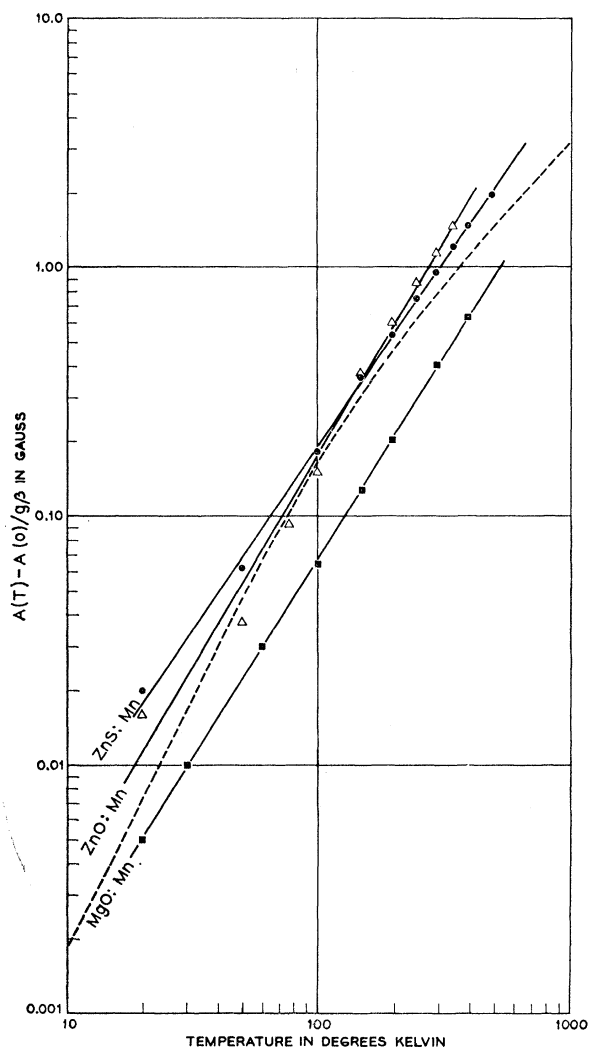


FIG. 9. Deviations of certain hyperfine couplings from their $0^\circ K$ values plotted versus $\ln T$ in order to emphasize the approximately T^{-3} behavior actually observed. The dashed curve represents *qualitatively* the variation which might be expected if the coupling parameter depended simply on $\langle \delta r^2 \rangle$, the mean-square lattice-vibration amplitude, for a lattice having a Debye temperature of $300^\circ K$.

TABLE III. Hyperfine-coupling data fitted to $A(T) = A(0)(1 - CT^n)$.

Host and nucleus	MgO:V ⁵¹	MgO:Mn ⁵⁵		KMgF ₃ :Mn ⁵⁵	ZnO:Mn ⁵⁵	ZnS:Mn ⁵⁵		CdTe:Mn ⁵⁵
		a	b			a	b	
$-A(0^\circ\text{K}) \times 10^4 \text{ cm}^{-1}$	74.26	81.55	81.59	91.27	75.56	64.58	64.62	57.15
C	2.2×10^{-8}	2.96×10^{-7}	8.8×10^{-7}	0.72×10^{-8}	1.00×10^{-6}	6.7×10^{-6}	2.88×10^{-6}	2.97×10^{-6}
n	1.92	1.68	1.60	1.5	1.67	1.35	1.48	1.53

^a Constant-atmospheric-pressure data.

^b Data corrected to constant, room-temperature volume (Refs. 2, 20, and 23).

^c Exponent taken as 1.5 in this case owing to insufficient data.

ments have not been performed but the corrections are likely to be quite small. In all cases $|A|$ decreases with increasing temperature and the curves are qualitatively similar to those obtained for MgO and ZnS.

An empirical representation of the data has been made using a simple power-law expression of the form

$$A(T) = A(0)(1 - CT^n) \quad (6)$$

which lends itself to comparison with theoretical analyses of lattice-vibration effects (see Sec. IV). That such an expression is appropriate in those cases where sufficient data are available is most clearly seen in Fig. 9, a log-log plot of $[A(T) - A(0)]/g\beta$ versus T . The coefficients and exponents for the various hosts are given in Table III as are the 0°K values of the hyperfine coupling coefficients themselves. The errors are of the order of $\pm 0.03 \times 10^{-4}$ or $\pm 0.05\%$ in A , ± 0.1 or $\pm 6\%$ in n , and since C depends very sensitively on the chosen value of n , it is usually not meaningful to better than a factor of 2. It is of interest that while the magnitude of C in Table III ranges over several decades as a function of the host lattice the exponent n is consistently near 1.5 for Mn^{2+} and is only slightly larger for V^{2+} .

The explicit temperature dependence of the hyperfine coupling parameter of Mn^{55} is of some significance in the analysis of nuclear resonance experiments in concentrated magnetic materials such as manganese ferrite. The NMR frequency is given by

$$h\nu_{\text{NMR}} = A \langle S_z \rangle, \quad (7)$$

where $\langle S_z \rangle$ is the thermal average value of the ion's spin and is directly related to the sublattice magnetization M_s

$$\langle S_z \rangle / S = M_s(T) / M_s(0). \quad (8)$$

It is usually assumed in experiments of this kind that A is a constant and that the temperature dependence of ν_{NMR} therefore accurately reflects that of the sublattice magnetization. This is certainly true as a first approximation but in fact A itself does depend on temperature.

In the case of manganese ferrite where the Mn^{2+} ions preferentially occupy sites with tetrahedral oxygen coordination the value of A implied by the low-temperature NMR frequency, 585 Mc/sec,²⁷ is $78 \times 10^{-4} \text{ cm}^{-1}$,

quite comparable to that observed in ZnO:Mn. One would therefore expect a contribution to the temperature dependence of ν_{NMR} proportional to $T^{3/2}$ with a fractional coefficient of the order of 1×10^{-6} (see Table III). The observed temperature variation of ν_{NMR} , primarily due to spin waves, is proportional to $T^{3/2}$ up to $\sim 150^\circ\text{K}$ with a fractional coefficient of 1.2×10^{-5} . Thus, the explicit variation of A with temperature contributes roughly 8% to the NMR frequency variation in the low-temperature region. Similar effects may occur in the case of other magnetic ions, and other crystal lattices, e.g., Fe^{3+} in yttrium iron garnet.

IV. DISCUSSION

The experiments described in the preceding section yield two qualitatively clear results:

(1) Spin-Hamiltonian coefficients which depend directly on the crystalline electric field vary with temperature very nearly as if only the *average* interionic distance is important. Any explicit temperature dependences constitute less than $\sim 20\%$ of the thermal-expansion effect. This conclusion holds for several different ions bound in MgO but fails in the case of ZnS:Mn.

(2) The magnitude of the hyperfine coupling of $(\text{Mn}^{55})^{2+}$ bound in a variety of crystals decreases with increasing temperature whereas thermal expansion would produce a much smaller effect of opposite sign. Evidently vibration amplitudes rather than average interionic separations are important for this interaction.

These results may be understood in terms of the simple physical description which follows.

A complete analysis of the effect of thermal motion of the surrounding ions on the spin-Hamiltonian parameters of a paramagnetic ion should be derived from the many-electron ion-crystal Hamiltonian including a quantized phonon field. Such an undertaking is impractical in view of the complexities which arise in such a fundamental calculation, even in the static limit.⁴⁻⁸ An alternative conceptual approach, which is consistent in spirit with the use of a spin Hamiltonian, consists in determining, at least in principle, the changes in the observable spin energy-level splittings produced by small, arbitrary and *static* displacements of the neighboring ions from their ideal, equilibrium positions.

²⁷ A. J. Heeger and T. Houston, J. Appl. Phys. 35, 836 (1964); Phys. Rev. 135, A661 (1964).

The point symmetry of the paramagnetic ion's site is thus reduced. The spin Hamiltonian appropriate to this distorted situation contains a number of low-symmetry crystalline field and hyperfine terms as well as modified values of the higher symmetry parameters appropriate to the static, unstrained geometry. The actual attainment of a completely general configuration is severely restricted in practice by the symmetry properties of those homogeneous strain fields which may be experimentally generated. For example, lattice vibrations can destroy local inversion symmetry but homogeneous stress cannot. If, however, an empirical representation such as the EPC model appears to correctly describe the results of those deformation experiments which are possible one might place some trust in a computation of the crystal-field effects which inhomogeneous deformations should produce. In the case of hyperfine interactions there appears to be no such simplifying expedient.

The next step would be to consider the displacements from equilibrium positions as time-dependent, coupled variables which are specified by the amplitudes and polarizations of the normal-vibrational modes of the crystal. Local-mode modifications of the host vibrational spectrum due to the impurity nature of the paramagnetic species should also be included. Neglect of this detail, while perhaps not justified, would be consistent with our earlier assumption that local quasistatic-elastic properties are unaffected by substitution of iron-group ions for the host cation. Anharmonic coupling of the normal modes may also be neglected for practical purposes if the isobaric data are corrected to constant volume as we have done wherever the appropriate data were available. Thus we will only discuss *explicit* temperature dependences in what follows.

The time dependence introduced into the "instantaneous" spin Hamiltonian via the normal-mode coordinates is averaged in the magnetic-resonance experiment. The nature of the averaging procedure is the real point of this discussion. Since the bulk of the phonon density of states lies in the energy range below about 500 cm^{-1} whereas the energy-level separations pertinent to crystal field and hyperfine effects of interest to us are at least several thousand cm^{-1} , the electronic wave functions respond to thermal disturbances as if they were static deformations (adiabatic approximation). One can therefore estimate the order of magnitude of the maximum instantaneous variations of the spin-Hamiltonian parameters which may be generated thermally by comparing the magnitudes of thermal interionic displacements from equilibrium with the static deviations from cubicity found in lower symmetry host crystals (or produced by stress). The mean-square amplitude of lattice vibrations of a monatomic

lattice in the Debye approximation is given²⁸ by

$$\langle \delta r^2 \rangle_t = \frac{9\hbar}{Mk\Theta_D} \left(\frac{1}{4} + \frac{1}{y^2} \int_0^y \frac{xdx}{e^x - 1} \right), \quad (9)$$

where δr is the deviation in cm of an ion from its equilibrium position, M is the atomic mass, k is Boltzmann's constant, Θ_D is the Debye temperature and $y \equiv \Theta_D/T$. At low temperatures ($y \gtrsim 5$) the limiting behavior is

$$\langle \delta r^2 \rangle_t \simeq \frac{9\hbar^2}{Mk\Theta_D} \left(\frac{1}{4} + 1.642 \frac{T^2}{\Theta_D^2} \right), \quad (10)$$

which leads to a mean-square zero-point vibration amplitude of $\sim 7 \times 10^{-3} \text{ \AA}^2$ for the O^{2-} ions of MgO . Even at 0°K the root-mean-square deviation from equilibrium positions amounts to $\sim 4\%$ of the interionic distance. This value roughly doubles as the temperature is raised to the Debye temperature since, for $y \lesssim 0.5$, Eq. (9) reduces to

$$\langle \delta r^2 \rangle_t \simeq 9\hbar^2 T / Mk\Theta_D^2. \quad (11)$$

Static deviations from cubic site symmetry of comparable magnitude (2–10% in linear dimensions) are found in various host crystals. The principal effect of the decreased symmetry for the ions of present interest is to introduce a crystal-field gradient spin-Hamiltonian term of the form $\mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$ where typical values of the tensor components D_{ij} rarely exceed on cm^{-1} . Appreciable percentage anisotropies are also introduced in the g factors and hyperfine couplings as well as low-symmetry fourth-order terms for spins ≥ 2 . Thus if the ions of our cubic host crystal could be immobilized in their instantaneous positions the resultant PMR spectra would be smeared out over a frequency (or magnetic field) range comparable to typical observation frequencies (fields) even if the crystal had been at 0°K before the hypothetical immobilization. The fact that observed spectra reflect only the *average* site symmetry is a result of motional narrowing.^{29–31}

In a crystalline solid the dynamic perturbations which affect electromagnetic spectra are simply periodic rather than completely random in character as in Brownian motion in liquids²⁹ or exchange effects in concentrated magnetic systems.³⁰ A frequency-modulation description is therefore particularly appropriate. Detailed treatments of narrow-line optical spectra from this point of view have recently been presented.^{32,33} Under the conditions that the shift $\delta\nu$ of the "carrier"

²⁸ R. W. James, *The Optical Principles of the Diffraction of X-rays* (G. Bell and Sons, Ltd., London, 1948).

²⁹ N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).

³⁰ P. W. Anderson, *J. Phys. Soc. Japan* **9**, 316 (1954).

³¹ J. H. Van Vleck, *Nuovo Cimento* **6**, 993 (1957).

³² R. H. Silsbee, *Phys. Rev.* **128**, 1726 (1962).

³³ D. E. McCumber, *Phys. Rev.* **133**, A163 (1964); **135**, A1676 (1964).

frequency ν_0 produced by phonons of frequency ν_p is such that $\delta\nu \sim \nu_p$ (strong coupling optical case) one observes both the original carrier or no-phonon line and phonon sidebands of appreciable intensity. In the case of microwave spectroscopy the frequency-deviation ratio $\delta\nu/\nu_p$ is $\lesssim 0.01$ which leads to essentially all the line intensity remaining in the carrier with extremely weak side bands being displaced by multiples of phonon frequencies, i.e., well out of our range of observation. We see only the no-phonon spectrum.

Static disturbances, such as strain gradients around dislocations, are not averaged. They create a distribution of ν_0 values about each of which the local dynamic shifts are averaged. This mechanism is the dominant source of linewidth in our experiments though some thermal broadening is observed at high temperatures. The thermal broadening may result both from spin-lattice relaxation and nearly secular shifts due to low-frequency phonons or to multiple-phonon disturbances whose "beat" frequencies are comparable to the shifts produced.^{14,15,32,33} Though all these phenomena are intimately related²⁹ we are here concerned only with the shift in the center of gravity of the no-phonon line, ignoring higher moments.

Low-frequency (acoustic-mode) vibrations such that $\nu_p \sim \nu_0$ might be expected to be important in the radio- and microwave-frequency experiments. Their influence is minor, however, since the number of modes decreases as ν_p^2 at the low-frequency end of the vibration spectrum. Also their long-wavelength character makes these phonons relatively ineffective in changing *local* interionic distances and, a fortiori, such short-range interactions as crystal potential moments. The principal role played by the low-frequency vibrations is in single-quantum spin-lattice relaxation.

The experiments of Rimai *et al.*¹² on paramagnetic ions bound in ferroelectric strontium titanate show that spin-Hamiltonian parameters may also be sensitive to temperature via the host dielectric constant. The slight difference in the behavior of the g shifts of V^{2+} and Cr^{3+} in MgO suggests such an effect, as mentioned earlier. However the absence of significant difference between the a -versus- T variations of Mn^{2+} and Fe^{3+} in the same host does not support such an interpretation.

Thus, for present purposes, the net effect of the thermal vibrations is to "condense" the PMR spectrum into a time-averaged pattern which may be described by a spin Hamiltonian having the site symmetry. It is, therefore, identical in form to the original spin Hamiltonian appropriate to the static lattice. Each coefficient of the "real" Hamiltonian is however the average of a distribution which has been motionally narrowed and is not, in general, equal to the corresponding parameter in the static Hamiltonian.

Detailed calculations of such averages have been performed for the case of optical spectra, as indicated above, and also for the chemical shift of the Co^{3+}

nuclear magnetic resonance.¹¹ The latter parameter is inversely proportional to the cubic moment of the crystal potential and is therefore similar to the g shifts of the F -state ions in the present experiments. The general result of such calculations is that the position of a no-phonon line may depend explicitly on temperature via the mean-square amplitude of the lattice vibrations which must be individually weighted according to their effectiveness in changing the position of the spectral line. This result may be derived in a manner consistent with the spin-Hamiltonian description by expanding the parameter of interest, $G(\mathbf{r}_i - \mathbf{r}_0)$, in terms of the deviations $\delta_i \equiv \mathbf{r}_i - \delta\mathbf{r}_0$ of the magnetic ions Z effective neighbors located at \mathbf{r}_i ($i=1, 2, \dots, Z$) from their equilibrium positions $\Delta_i \equiv \mathbf{r}_i - \mathbf{r}_0$ relative to the ion at \mathbf{r}_0 . For simplicity G is considered to be a scalar though one is usually interested in tensors of second (g, A) or fourth (a) rank. Each component of such a tensor should, in principle, be treated separately.

To second order in the local coordinate deviations δ_i

$$G(\Delta_i) = G_0 + \sum_{i=1}^Z \left(\frac{\partial G}{\partial \Delta_i} \right)_0 \cdot \delta_i + \frac{1}{2} \sum_{i,j=1}^Z \delta_i \cdot \left(\frac{\partial^2 G}{\partial \Delta_i \partial \Delta_j} \right)_0 \cdot \delta_j, \quad (12)$$

where the notation is that of Ziman.³⁴ One may now introduce the lattice vibrations by expanding the δ_i in terms of the normal coordinates ξ_l , i.e.,

$$\delta_i = \sum_l C_{il} \xi_l, \quad (13)$$

where

$$\xi_l = l \xi_{l0} \cos[\omega_l t - \mathbf{k}_l \cdot \mathbf{r} + \alpha_l(t)]. \quad (14)$$

Equation (14) defines a traveling wave of amplitude ξ_{l0} , angular frequency ω_l , propagation vector \mathbf{k}_l , time-dependent phase α_l (due to finite phonon lifetimes) and unit polarization vector l . Since the δ_i are *local* coordinate changes the coefficient C_{il} weigh optical modes most heavily. However optical studies of magnetic ions in MgO ¹⁵ show that a wide range of phonon frequencies (200–500 cm^{-1}) are appreciably coupled to the foreign ion and that the effective density of states is complicated. It is therefore unlikely that the restriction of the phonon summation to the normal modes of the ion-nearest-neighbor complex (equivalent to summation over particular optical branches of the crystal) which has been employed by Van Vleck³⁵ and Benedek *et al.*,¹¹ is valid for the diatomic crystals of moderate cation-to-anion mass ratio which are of present interest.

Substituting expressions (13) and (14) into the expansion (12) and averaging over times long compared to phonon lifetimes (thus allowing the phases α_l to fluctuate

³⁴ J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960).

³⁵ J. H. Van Vleck, *Phys. Rev.* **57**, 426 (1940).

randomly) leads to

$$\langle G \rangle_t = G_0 + \frac{1}{4} \sum_{i,j=1}^Z \sum_l \dot{l} \cdot \left(\frac{\partial^2 G}{\partial \Delta_i \partial \Delta_j} \right) \cdot \dot{l} C_{il} C_{jl} \xi_{i0}^2. \quad (15)$$

Equation (15) has been left in mixed notation, containing both the Δ_i and the ξ_l coordinates, in order to emphasize that explicit temperature effects depend on the curvatures of the quantity G with respect to *local* interionic distances, that these coordinates are *coupled* whereas the normal modes contribute independently and that the various modes are weighted by their effectiveness in changing the local interionic distances. The equation may of course be written more simply but somewhat less informatively as

$$\langle G \rangle_t = G_0 + \frac{1}{4} \sum_l \left(\frac{\partial^2 G}{\partial \xi_l^2} \right)_0 \xi_{l0}^2. \quad (16)$$

The temperature dependence of $\langle G \rangle_t$ is determined by that of the normal-mode amplitudes. Equating the energy of a lattice vibration to that of a quantum-mechanical harmonic oscillator leads to

$$\begin{aligned} \xi_{l0}^2 &= \frac{2\hbar}{\omega_l} \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega_l/kT} - 1} \right) \\ &= \frac{\hbar}{\omega_l} \coth \frac{\hbar\omega_l}{2kT}. \end{aligned} \quad (17)$$

While the time averaging which leads to Eqs. (15) or (16) describes the purely secular shifts of interest in this article one can gain more insight into the motional narrowing aspect of the phenomenon using a classical, frequency-modulation formulation. If $G(t)$ is the instantaneous frequency of a wave (energy-level separation) then the corresponding Fourier spectrum is that of a rotating vector whose instantaneous angular position is

$$\Theta(t) = \int_0^t G(t') dt'. \quad (18)$$

Ignoring phase fluctuations due to phonon scattering Eq. (18) may be written

$$\Theta(t) = A + B + C + D, \quad (19)$$

where

$$A = \left[G_0 + \frac{1}{4} \sum_l \left(\frac{\partial^2 G}{\partial \xi_l^2} \right)_0 \xi_{l0}^2 \right] t = \langle G \rangle_t, \quad (19a)$$

$$B = \frac{1}{4} \sum_{l,l' \neq l} \left(\frac{\partial^2 G}{\partial \xi_l \partial \xi_{l'}} \right)_0 \xi_{l0} \xi_{l'0} \frac{\sin[(\omega_l - \omega_{l'})t - (\mathbf{k}_l - \mathbf{k}_{l'}) \cdot \mathbf{r}]}{\omega_l - \omega_{l'}} \quad (19b)$$

$$C = \sum_l \left(\frac{\partial G}{\partial \xi_l} \right)_0 \xi_{l0} \frac{\sin(\omega_l t - \mathbf{k}_l \cdot \mathbf{r})}{\omega_l}, \quad (19c)$$

$$D = \frac{1}{4} \sum_{l,l'} \left(\frac{\partial^2 G}{\partial \xi_l \partial \xi_{l'}} \right)_0 \xi_{l0} \xi_{l'0} \frac{\sin[(\omega_l + \omega_{l'})t - (\mathbf{k}_l + \mathbf{k}_{l'}) \cdot \mathbf{r}]}{\omega_l + \omega_{l'}}. \quad (19d)$$

Term A , linear in time, defines the carrier frequency $\langle G \rangle_t$. The shift from the static value G_0 results from zero-frequency "beats." These are particular components of the difference-frequency spectrum which is completed by term B . The latter, nearly zero beat frequencies can contribute to line broadening since their spectral density is peaked around the carrier frequency. Term C leads to sidebands removed from the carrier by integral multiples of phonon frequencies in first order. Taken to second and higher orders C can also generate sum and difference frequency components. Term D consists entirely of sum frequencies and therefore produces sidebands displaced from the carrier by even multiples of phonon frequencies. At microwave and lower carrier frequencies the frequency-deviation ratios, $\rho_i \equiv (\text{shift/modulation frequency})$, of the C and D components are small compared to unity and the intensity of the corresponding sidebands is very small. Only the difference-frequency components of B are likely to have appreciable intensity though in fact their contribution to the linewidth is less than that due to residual static strains in our sample crystals, except possibly at the upper temperature limit. Thus, the virtual width of the line, $\sim (\partial G / \partial \xi_l)_0 \xi_{l0} \sim G_0$ according to our earlier estimates, is motionally narrowed below the limits of observation. Only the secular shift contained in term A plays a significant role in the present experiments. In the optical-frequency regime, however, the situation is quite different since the ρ_i may be comparable to unity and all terms then contribute appreciably.^{22,33}

Despite the formal simplicity of Eq. (16) its evaluation is quite difficult in any specific case since experimentally one is usually not able to measure second derivatives with respect to interionic distance with any precision. Also, as indicated earlier, the effects of low symmetry deformations are generally not measurable via static strain experiments. Fortunately the qualitative results of Sec. III may be understood without evaluating all the coupling coefficients.

A. Crystal-Field Parameters

The spin-Hamiltonian parameters which are sensitive to the magnetic ion's environment primarily through the crystalline potential are most easily treated since the effective point-charge model may be used to estimate the changes produced by arbitrary crystal distortions. In fact, the absence of appreciable explicit temperature dependence of these parameters in MgO is easily understood in terms of this model. Consider the electrostatic potential φ at \mathbf{r}_0 produced by Z charges q_i

located at \mathbf{r}_i :

$$\varphi = \sum_{i=1}^Z \frac{q_i}{|\mathbf{r}_i - \mathbf{r}_0|}, \quad (20)$$

which may be rewritten in terms of the static interionic vectors Δ_i and their time-dependent variations δ_i as

$$\varphi = \sum_{i=1}^Z \frac{q_i}{|\Delta_i + \delta_i|}. \quad (20')$$

If the vectors δ_i are expressed in terms of normal modes ξ_l and Eq. (20') is expanded to second order in ξ_{l0}/Δ_i and averaged over time the result is

$$\langle \varphi \rangle_t \simeq \sum_{i=1}^Z \frac{q_i}{|\Delta_i|} \left[1 - \frac{1}{4\Delta_i^2} \sum_l C_{il}^2 \xi_{l0}^2 (1 - 3 \cos^2 \Theta_{il}) \right]. \quad (21)$$

In Eq. (21) the angles Θ_{il} are those made by the polarization vector \hat{l} with the static interionic vector Δ_i . In cubic symmetry, for any particular mode and value of Θ_{il} there are two other, equivalent (in the sense of weighting factors and amplitudes) and mutually orthogonal modes such that the subset sum of the $\cos^2 \Theta_{il}$ is $\frac{1}{3}$. As a result

$$\langle \varphi \rangle_t \simeq \varphi_{\text{static}} \quad (22)$$

through the third order in δ_i/Δ_i . This cancellation of explicit vibrational contributions to the potential is most easily described in terms of multipole moments: No change in the zeroth order or monopole term is produced by oscillations of the potential source. Odd-order terms corresponding to dipole, octupole, etc., moments vanish on the average due to their time dependence. In general, the second order or quadrupolar term will produce a nonvanishing contribution but the imposition of cubic symmetry eliminates this term since it produces a spherically symmetric charge distribution whose external potential does not depend on its radial structure. Thus the lowest effective order is sexdecipolar in cubic symmetry and is obviously related to the cubic anisotropy of the lattice-vibration amplitudes.

It is worth emphasizing that the cancellation of the quadrupolar terms is sensitive both to the symmetry and to the potential law. An appreciable deviation from a simple inverse distance dependence of the potential would lead to a second-order effect in even cubic symmetry since the radial structure of the source distribution does then affect the external potential.

The approximate equality (22) is the basic explanation of the observed lack of explicit temperature dependence of the crystalline field-dependent spin-Hamiltonian coefficients in MgO. However, there is a further degree of approximation involved since these parameters are not linear functions of the crystalline potential. For example the g shifts of the F -state ions depend on the inverse of the cubic moment of φ and the

a coefficients of the S -state ions vary roughly as that cubic moment to the fourth power. To the extent that the changes in φ produced by vibration are small, however, the cancellation holds for an arbitrary function $f(\varphi)$ since we may then write

$$\langle f(\varphi) \rangle_t \simeq f(\varphi_{\text{static}}) + (\partial f / \partial \varphi) \langle \varphi - \varphi_{\text{static}} \rangle_t \simeq f(\varphi_{\text{static}}). \quad (23)$$

The first-order approximation of Eq. (23) is equivalent to the second-order approximation of Eq. (22). If one should seek the sexdecipole corrections to Eq. (22) it would be necessary to push the expansion of $f(\varphi)$ to the second order.

The most sensitive test of Eqs. (22) and (23) is provided by the cubic-field splittings of Mn^{2+} and Fe^{3+} since these have been measured quite accurately versus both pressure and temperature. It is clear from Fig. 4 that essentially no explicit temperature dependence exists above room temperature. The magnitude of the cancellation of dynamic quadrupolar terms can be estimated by comparing the fractional effect of a pure "breathing" (A_{1g}) local-vibrational mode with the thermal-expansion effect. Near the Debye temperature of MgO we would have

$$\frac{1}{2a_0} \left(\frac{\partial^2 a}{\partial r^2} \right) \langle \delta r^2 \rangle \sim 5 \times 10^{-4} T, \quad (24)$$

which is comparable in magnitude but opposite in sign to the implicit contribution

$$\frac{1}{a_0} \left(\frac{\partial a}{\partial r} \right) \delta r(T) \sim -3 \times 10^{-4} T. \quad (25)$$

The quadrupolar terms cancel to within a few percent.

In view of its success in the high-temperature regime the model's apparent failure below room temperature in the case of the cubic field and, probably, axial-field splittings is surprising. One might have expected deviations to occur where large amplitude oscillations might produce appreciable sexdecipole distortions of the time-averaged neighboring charge distributions seen by the magnetic ions. Similarly a breakdown of the assumption of equal local and bulk thermal-expansion coefficients would seem more likely at high rather than at low temperatures. However the gross features of the experiments on crystalline-field parameters in MgO are "explained" by the EPC model and cubic symmetry of the vibration amplitudes. The clear-cut explicit temperature dependence of the cubic-field splitting of Mn^{2+} in cubic ZnS probably results from failure of the EPC model in a more covalent crystal since there is no reason to expect the vibrations to be less symmetric than in MgO nor to expect enhanced local thermal expansion.

B. Hyperfine Couplings

The overwhelming importance of explicit vibrational effects for the Mn⁵⁵ hyperfine coupling cannot be explained quantitatively since there is little hope of measuring or estimating the curvature coefficients required to evaluate Eq. (15) in this case. If, however, we accept the fact that appreciable coefficients exist, the general form of the observed temperature dependence, Eq. (6) with $n \approx 1.5$, is not unreasonable. The explicit temperature dependence of A will necessarily take the form,

$$\langle A_i \rangle = A_{\text{static}} + B \langle \delta r^2 \rangle_i$$

unless some very peculiar weighting factors enter the problem. Separating $\langle \delta r^2 \rangle_i$ into its zero-point and temperature-dependent contributions [see Eqs. (10) and (11)] we see that $\langle A_i \rangle \cong (A_{\text{static}} + \delta A_{\text{zero-point}}) \times (1 - CT^n)$ where $n=2$ for $T < \Theta_D/5$ decreasing to $n=1$ for $T > 2\Theta_D$. The measured exponents near 1.5 are thus reasonable. It is, however, somewhat surprising that no variation of n could be measured over the available temperature range for a given solid since, as shown in Fig. 9, [$\langle \delta r^2 \rangle_i - \delta r^2_{\text{zero-point}}$] does exhibit curvature on a log-log plot assuming a typical Debye temperature of 300°K. In the absence of detailed knowledge of the hyperfine coupling's sensitivity to lattice distortions of various symmetries it is not profitable to pursue the matter. In general, one would expect the greatest sensitivity to temperature to occur in crystals where appreciable delocalization of the d orbitals decreases the core polarization relative to the free ion. Thus the smaller the absolute value of the hyperfine coupling in a crystal the greater the temperature dependence expected. This is crudely borne out in practice (Table III). However, the relative amplitudes of the thermal vibrations must also be taken into account when making such comparisons: Recent measurements³⁶⁻³⁸ show that the temperature dependences of $|A|$ of Mn²⁺ in CaO and SrO are much larger than in MgO despite the increased interionic spacing and hence, presumably, more ionic binding. A careful intercom-

³⁶ A. J. Shuskus, Phys. Rev. **127**, 1529 (1962).

³⁷ W. Low and R. S. Rubins, *Proceedings of the First International Conference Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963).

³⁸ A. J. Shuskus, J. Chem. Phys. **41**, 1885 (1964).

parison of the temperature and pressure dependences of the manganese hyperfine coupling in these three cubic oxides might help to illuminate the nature of the reduction of $|A|$ which occurs in the solid state. Such clarification is particularly desirable in view of the use of A values inferred from PMR experiments in the interpretation of nuclear magnetic resonance and specific-heat studies of concentrated magnetic crystals. In particular, the deduced 0°K limiting values of the sublattice magnetizations of several antiferromagnetic manganous salts³⁹⁻⁴³ appear to be very close to the fully ordered (Néel ground state) values whereas spin-wave theory predicts significant reductions due to zero-point modes.

V. CONCLUSIONS

The dominance of thermal expansion in the temperature dependence of crystalline field parameters of iron-group ions in MgO has been shown to result from a cancellation of second-order lattice vibration terms. We use an effective-point-change model for the crystalline potential sources and assume cubic symmetry of the vibration amplitudes even in the immediate vicinity of the foreign ions. The EPC model fails in cubic ZnS.

The hyperfine coupling of (Mn⁵⁵)²⁺ in several host crystals depends on temperature primarily through the lattice vibration amplitudes. The observed $T^{-1.5}$ variation is crudely consistent with a Debye spectrum but no detailed analysis is possible at this time.

ACKNOWLEDGMENTS

One of us (W. M. W. Jr.) has benefited from discussions with S. Geschwind, D. E. McCumber, and R. G. Shulman. The technical assistance of L. W. Rupp, Jr. in the latter phases of the experimental work is appreciated.

³⁹ H. Montgomery, D. T. Teaney, and W. M. Walsh, Jr., Phys. Rev. **128**, 80 (1962).

⁴⁰ A. J. Heeger, A. M. Portis, and G. L. Witt, *Proceedings of the Eleventh Colloquium Ampere* (John Wiley & Sons, Inc., New York, 1963).

⁴¹ G. L. Witt and A. M. Portis, Phys. Rev. **135**, A1616 (1964).

⁴² E. D. Jones and K. B. Jefferts, Phys. Rev. **135**, A1277 (1964).

⁴³ E. D. Jones and M. E. Lines, Bull. Am. Phys. Soc. **10**, 33 (1965).