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Electron Paramagnetic Resonance of Tetravalent Manganese Ions at Tetragonal and Octahedral Sites in MgO*

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A paramagnetic resonance spectrum of tetragonal symmetry due to Mn^{4+} ions in MgO has been observed. The spin-Hamiltonian parameters are $g_{\parallel}=1.9931\pm0.0002$, $g_{\perp}=1.9940\pm0.0002$, $A_{\parallel}=(-71.1\pm0.2)\times10^{-4}$ cm^{-1}, $A_{\perp}=(-70.6\pm0.1)\times10^{-4}$ cm^{-1}, and $D=(-528.7\pm0.7)\times10^{-4}$ cm^{-1}. The departure from octahedral symmetry is attributed to the presence of a positive-ion vacancy at the first cation site on the tetragonal axis, thus forming the arrangement 0-Mn^{2+}-0-[=], where only deviations from the normal lattice charge are shown. The spectrum from octahedrally coordinated Mn^{4+} ions has been observed in a powder sample of MgO; here the spin-Hamiltonian parameters are $g=1.9941\pm0.0002$ and $A=-(70.82\pm0.10)\times10^{-4}$ cm^{-1}. The hyperfine fields at the nuclei of the $3d^3$ ions V^{2+}, Cr^{3+}, and Mn^{4+} in MgO are found to be almost identical.

I. INTRODUCTION

MANGANESE is found as an impurity in most samples of magnesium oxide. Though the ion is usually observed in the divalent state, its occasional presence in tetravalent form has been established by several authors.[1] Electron spin resonance experiments have shown cubic spectra due to Mn^{4+} ions in octahedral surroundings. In addition, Henderson and Hall[1] have recently observed a spectrum of tetragonal symmetry, and have proposed that the center concerned is one in which a monovalent lithium ion occupies a cation site adjacent to the Mn^{4+} ion, in an [001] direction [Fig. 1(b)]. We report in this paper a different Mn^{4+} tetragonal center, which we believe to be analogous to the tetragonal centers observed in crystals containing the isoelectronic ion, Cr^{3+}, indicated in Fig. 1(a).[2] In such centers, the departure from octahedral symmetry is caused by a positive ion vacancy at the nearest cation site along an ⟨001⟩ axis.

II. EXPERIMENTAL DETAILS

The ESR spectra were taken at room temperature at X band. The octahedrally coordinated Mn^{4+} ions were observed in a powder sample doped with LiCl. The tetragonal spectrum was observed in crystals obtained from the Philips Research Laboratories, Eindhoven, and from the Norton Company. To produce Mn^{4+} ions in tetragonal symmetry, the crystals were first heated for several hours at 600°C, then cooled by placing on a metal plate at room temperature. This was followed by 70-kV x irradiation for one hour. The concentration of tetragonal Mn^{4+} was then about 1/500 of that of the octahedral Mn^{2+}. Heating for several hours at 400°C or above destroys the tetragonal spectra, which reappear on subsequent x irradiation. Some of the experimental results were obtained by Peteris Auzins, now deceased.

III. Mn^{4+} IONS AT OCTAHEDRAL SITES IN MgO

The Mn^{4+} ground state in an octahedral crystal field is a $(3d^3)^4A_2$ orbital singlet, with fourfold spin degeneracy (we use the notation of Mulliken, as described by Griffith[3]). The approximately 100% abundant isotope ^{55}Mn has nuclear spin $I=\frac{5}{2}$, and the spin Hamiltonian is

$$\hat{\mathcal{H}}=g\beta\mathbf{H}\cdot\hat{\mathbf{S}}+A\hat{\mathbf{S}}\cdot\hat{\mathbf{I}}. \tag{1}$$

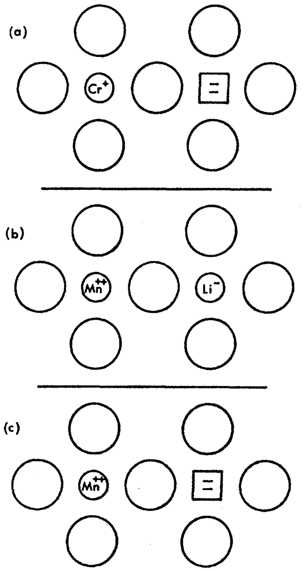

FIG. 1. $3d^3$ tetragonal centers in MgO: (a) Cr^{3+} tetragonal center (Ref. 2); (b) Mn^{4+} center observed by Henderson and Hall (Ref. 1); (c) proposed structure of the Mn^{4+} center reported here. Only deviations from the normal lattice charge are shown. Large circles represent oxygen ions and squares represent magnesium vacancies.

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[1] W. D. Hershberger and H. N. Leifer, Phys. Rev. **88**, 714 (1952); J. S. Prener, J. Chem. Phys. **21**, 160 (1953); M. Nakada, K. Awazu, S. Ibaki, Y. Miyako, and M. Date, J. Phys. Soc. Japan **19**, 781 (1964); J. E. Wertz, J. W. Orton, and P. Auzins, J. Appl. Phys. (Suppl.) **33**, 322 (1962); B. Henderson and T. P. P. Hall, Proc. Phys. Soc. (London) **90**, 511 (1967).

[2] J. E. Wertz and P. Auzins, Phys. Rev. **106**, 484 (1957).

[3] J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge University Press, London, 1961), p. 158.

Here, $S=\frac{3}{2}$. Higher-order terms[4] are found unnecessary. Since the spectrum has been reported by several authors,[1] our results will not be described in detail. We find that the positions of the six intense lines ($M_s=\frac{1}{2}\leftrightarrow-\frac{1}{2}$, $\Delta M_I=0$) can be fitted to within 0.1 G by the spin-Hamiltonian of Eq. (1), with the values

$$g=1.9941\pm0.0002\,,\quad A=(-70.82\pm0.10)\times10^{-4}\ \text{cm}^{-1}.$$

These compare with $g=1.9938\pm0.0003$ and $A=(70.85\pm0.5)\times10^{-4}$ cm^{-1}, obtained by Henderson and Hall.[1] The sign of A was not determined directly, but is expected to be negative by analogy with the hyperfine constants of V^{2+} [5,6] and Mn^{2+} [7] in this lattice. The hyperfine interaction is discussed more fully in Sec. VII.

IV. TETRAGONAL Mn^{4+} SPECTRUM

The tetragonal spectrum can be described by the following spin Hamiltonian:

$$\mathcal{H}=g_{\parallel}\beta H_z\hat{S}_z+g_{\perp}\beta(H_x\hat{S}_x+H_y\hat{S}_y)+D[\hat{S}_z^2-\tfrac{1}{3}S(S+1)]+A_{\parallel}\hat{S}_z\hat{I}_z+A_{\perp}(\hat{S}_x\hat{I}_x+\hat{S}_y\hat{I}_y)\,. \quad (2)$$

The tetragonal or z axes of the centers lie along [001] type directions, parallel to a cube edge. With the magnetic field along a cube edge one therefore has effectively two orientations of the center; in one, the field is along the z axis, and, in the other, is perpendicular to it. For each case there are three sets ($M_S=\frac{3}{2}\leftrightarrow\frac{1}{2}$, $\frac{1}{2}\leftrightarrow-\frac{1}{2}$, $-\frac{1}{2}\leftrightarrow-\frac{3}{2}$) of six lines, though a large number are obscured by lines from other impurities. For the field in the z direction, the line positions for the transition $M_S\leftrightarrow(M_S-1)$, $\Delta M_I=0$ are given by the following expression:

$$\begin{aligned}g_{\parallel}\beta H&=h\nu-A_{\parallel}M_I-D(2M_S-1)\\&-\tfrac{1}{4}A_{\perp}^2\left\{\frac{2[S(S+1)-M_S^2+M_S][I(I+1)-M_I^2]}{h\nu}\right.\\&-\frac{[S(S+1)-M_S^2-M_S][I(I+1)-M_I^2+M_I]}{h\nu+2D}\\&\left.-\frac{[S(S+1)-M_S^2+3M_S-2][I(I+1)-M_I^2-M_I]}{h\nu-2D}\right\}.\end{aligned}\quad (3)$$

$h\nu$ represents the microwave energy quantum. The accuracy of the experimental measurements does not justify the inclusion of terms of order $A^3/(h\nu)^2$, but it is necessary, for a good fit, to include the terms involving D in the denominators. This is of importance, since it allows a determination of the relative signs of $A_{\parallel}$ and D. We find these quantities to be of the same sign, and take them to be negative; the sign of $A_{\parallel}$ is then the same as that of comparable ions.

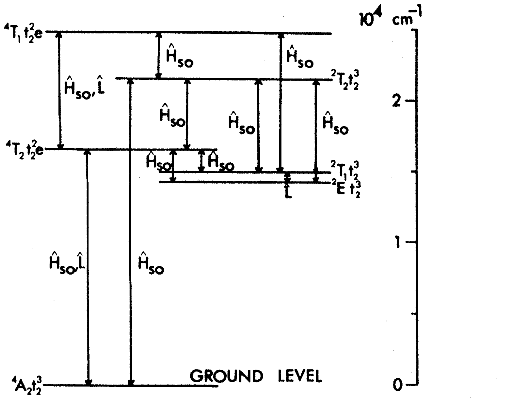

FIG. 2. Lowest-energy levels of a $3d^3$ ion in an octahedral field. The spacings are those appropriate to Cr^{3+}:MgO, where $\Delta=16\,600$ cm^{-1}, $B=688$ cm^{-1}, and $C=3095$ cm^{-1} (Ref. 19). The vertical arrows indicate nonvanishing matrix elements of the spin-orbit coupling ($\mathbf{H}_{SO}$) and the orbital angular momentum ($\mathbf{L}$) operators (Ref. 10).

The line positions for the field along an x or y axis are given by

$$g_{\perp}\beta H=h\nu\pm D\mp\frac{3D^3}{8(h\nu)^2}+\text{hyperfine terms}\,,\quad (4)$$

for $M_S=\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$, and by

$$g_{\perp}\beta H=h\nu-\frac{3D^2}{4(h\nu)}+\text{hyperfine terms}\,,\quad (5)$$

for $M_S=\frac{1}{2}\leftrightarrow-\frac{1}{2}$. Terms of order $D^4/(h\nu)^3$ and higher have been neglected. The hyperfine terms are as in Eq. (3), but with $A_{\parallel}$ replaced by $A_{\perp}$, $A_{\perp}$ by $\frac{1}{2}(A_{\parallel}+A_{\perp})$ and D by $-\frac{1}{2}D$ in the denominators.

Since many of the lines were obscured by lines from other impurities, only the outer components of each set were measured accurately. Using Eqs. (3)-(5) we find the following parameters:

$$\begin{aligned}g_{\parallel}&=1.9931\pm0.0002;\\A_{\parallel}&=(-71.1\pm0.2)\times10^{-4}\ \text{cm}^{-1},\\g_{\perp}&=1.9940\pm0.0002;\\A_{\perp}&=(-70.6\pm0.1)\times10^{-4}\ \text{cm}^{-1},\\(g_{\parallel}-g_{\perp})&=-0.0009\pm0.0002;\\(A_{\parallel}-A_{\perp})&=(-0.5\pm0.3)\times10^{-4}\ \text{cm}^{-1},\\D&=(-528.7\pm0.7)\times10^{-4}\ \text{cm}^{-1}.\end{aligned}$$

Henderson and Hall[1] found the corresponding parameters for the manganese-lithium center to be

$$g=1.995\pm0.001\,,\quad |A|=(70.8\pm0.5)\times10^{-4}\ \text{cm}^{-1},\quad |D|=(280\pm20)\times10^{-4}\ \text{cm}^{-1}.$$

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[4] B. Bleaney, Proc. Phys. Soc. (London) **A73**, 939 (1959).

[5] W. Low, Phys. Rev. **101**, 1827 (1956).

[6] J. S. van Wieringen and J. G. Rensen, in *Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1962), Vol. 1, p. 105.

[7] W. Low, Phys. Rev. **105**, 793 (1957).

It should be noted that the centers reported here have a much larger zero-field splitting.

V. g VALUES AND ZERO-FIELD SPLITTING

The low-lying states of a $3d^3$ ion in an octahedral field are shown in Fig. 2. The symbols in parentheses represent the strong-field electron configuration.[8] In this approximation the low-lying $^2T_2$ state is composed of three electrons in t_{2g} orbitals. The $3d^3$ configuration also gives rise to four other $^2T_2$ states, formed from $t_{2g}^2e_g$ and $t_{2g}e_g^2$. These lie at higher energies, but are mixed with the low-lying states of the same symmetry by the hitherto neglected interelectronic electrostatic interactions (configuration mixing).[9] Similar mixing occurs for the other doublets, and for the $^4T_1$ state.

The spin-orbit coupling operator has non-zero matrix elements between the states of Fig. 2, where indicated.[10] Spin-orbit admixtures to the $|^4A_2\rangle$ ground state cause g shifts and a zero-field splitting. The g shifts arise through the combined effect of the spin-orbit coupling and the orbital part of the Zeeman operator. The only state connected to $|^4A_2\rangle$ by the orbital angular momentum is $|^4T_2\rangle$, so that admixtures of this state give the only first-order contribution to the g shift.

To this approximation the octahedral g value is given by

$$g=2.0023-8\zeta_0/3\Delta_1.$$

ζ_0 is the spin-orbit coupling constant for a single d electron, and Δ is the energy of the $|^4T_2\rangle$ state relative to $|^4A_2\rangle$. Covalency and charge transfer considerably modify this expression. Lacroix and Emch[11] have considered the effects in detail and find, for Mn^{4+} with oxygen neighbors, that the deviation of g from 2.0023 is reduced to 0.416 of the ionic value by covalency; charge transfer effects are found to give a contribution of -0.226 of the ionic value. Thus

$$\Delta g(\mathrm{expt})=0.190\Delta g(\mathrm{ionic})=0.190(8\zeta_0/\Delta).$$

Use of $\zeta_0=402$ cm^{-1} [12] and the experimental g value of 1.9941 now leads to $\Delta\approx 28\,600$ cm^{-1}. Our single-crystal samples contained insufficient Mn^{4+} for an optical determination of this quantity. For Mn^{4+}:$\alpha-Al_2O_3$, Δ is found to be 21 000 cm^{-1},[13] so that the value estimated above is probably a little large.

To consider the effects of a tetragonal perturbation, we return to the ionic approximation. Under such a perturbation, $|^4T_2\rangle$ splits into a component $|^4T_2\zeta\rangle$ at Δ_1, and components $|^4T_2\xi\rangle$ and $|^4T_2\eta\rangle$ at Δ_2. Δ_1 and Δ_2 will be considered measured relative to $|^4A_2\rangle$. The resulting g values are

$$g_\parallel=2.0023-8\zeta_0/3\Delta_1, \tag{6a}$$

$$g_\perp=2.0023-8\zeta_0/3\Delta_2. \tag{6b}$$

Spin-orbit coupling admixtures of $|^4T_2\rangle$ to $|^4A_2\rangle$ also produce spin-dependent energy shifts. These are described by the inclusion of a zero-field splitting term $D_1[\hat{S}_z^2-\frac{1}{3}S(S+1)]$ in the spin Hamiltonian, where

$$D_1=-\frac{4}{9}\zeta_0^2\left[\frac{1}{\Delta_1}-\frac{1}{\Delta_2}\right]. \tag{7}$$

Using Eqs. (6a) and (6b), one obtains

$$D_1=\tfrac{1}{6}\zeta_0[g_\parallel-g_\perp]. \tag{8}$$

For Mn^{4+}, use of the experimental g values and the free ion value of ζ_0 leads to D_1 in the range -469×10^{-4} cm^{-1} to -837×10^{-4} cm^{-1}. This is close to the experimental value of $D=-528.7\times10^{-4}$ cm^{-1}. Covalency should affect Eq. (7), but its effects will tend to cancel in Eq. (8). Charge transfer contributions to D are difficult to calculate, since this requires the tetragonal field at the ligands; we shall assume these contributions to be smaller than those from the $^4T_2$ admixtures. In deriving Eq. (8) it was implicitly assumed that the anisotropy in the g tensor is due to $^4T_2$ admixtures alone.

For the Cr^{3+}:MgO tetragonal center of Fig. 1(a), the agreement between D_1 and D(expt) is not so close, though the order of magnitude and sign are correct. For this center, $g_\parallel-g_\perp=0.0032$ [14] and $\zeta_0=273$ cm^{-1}.[12] Equation (8) gives $D_1=-1450\times10^{-4}$ cm^{-1}, compared with $D=-819.2\times10^{-4}$ cm^{-1}, obtained experimentally.[2]

There are further contributions to D from spin-orbit coupling admixtures of $|^2T_2\rangle$ states to the $|^4A_2\rangle$ ground state. For Mn^{4+}:MgO, we have insufficient information to estimate these effects, but for the tetragonal Cr^{3+} center in MgO [Fig. 1(a)] the ^2E splitting, measured directly by fluorescence techniques,[15] may be combined with the ground-state g values[14] to obtain an estimate of the tetragonal field parameter. The splittings of the $|^2T_2\rangle$ states may then be calculated to obtain the $^2T_2$ contribution to the zero-field splitting of the ground state. We estimate this contribution to be $\sim+80\times10^{-4}$ cm^{-1}. This is much smaller than the contribution from the $|^4T_2\rangle$ state, and we shall assume the same to be true for Mn^{4+}.

The fact that Eq. (8) is fairly well satisfied indicates that $|^4T_2\rangle$ admixtures give at least a major contribution to the zero-field splitting. For this reason, and for simplicity, we shall assume that effects such as spin-spin coupling[16] are small. On this basis, it will be shown in Sec. VI that the spin-resonance parameters are not

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[8] Reference 3, p. 226.

[9] See, for example, S. Sugano and M. Peter, Phys. Rev. **122**, 381 (1961).

[10] S. Sugano and Y. Tanabe, J. Phys. Soc. Japan **13**, 880 (1958).

[11] R. Lacroix and G. Emch, Helv. Phys. Acta **35**, 592 (1962).

[12] Reference 3, p. 437.

[13] S. Geschwind, P. Kisliuk, M. P. Klein, J. P. Remeika, and D. L. Wood, Phys. Rev. **126**, 1684 (1962).

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

[15] G. F. Imbusch, A. L. Schawlow, A. D. May, and S. Sugano, Phys. Rev. **140**, A830 (1965).

[16] Reference 3, p. 330.

inconsistent with the structure of Mn^{4+} center in Fig. 1(c).

VI. NATURE OF Mn^{4+} CENTER

The similarity between the g values and the hyperfine constants of the cubic and tetragonal centers, and the relatively small magnitude of the zero-field splitting, indicate that the crystal field in the tetragonal center is predominantly octahedral. It is therefore reasonable to suppose that the source of the superimposed tetragonal field is a point defect along the z axis. In the center proposed by Henderson and Hall,[1] this was presumed to take the form of a monovalent lithium ion at the first cation site along the tetragonal axis [Fig. 1(b)]. In this case, the sample had been doped with 1% LiF. The samples in which the present Mn^{4+} tetragonal centers were observed have not been doped, and are in fact fairly low in (magnetic) impurity content. It therefore seems unlikely that a second impurity species is responsible for the tetragonal field. The remaining possibility is that of a positive ion vacancy at the first axial cation site. The effective charge of such a combination would be zero, so that the center would be expected to be stable. It therefore seems likely that this is in fact the configuration of the center we are reporting.

As evidence that their center was not the Mn^{4+} analog of the Cr^{3+} center of Fig. 1(a), Henderson and Hall[1] pointed to the fact that their Cr^{3+} zero-field splitting was much larger. Since the Cr^{3+} D term is also larger than the D term of the center reported here, a discussion of the tetragonal field is of interest. For simplicity, it will be assumed that the D term arises solely from $|{}^4T_2\rangle$ admixtures. That this is reasonable was shown in the previous section.

Apart from a constant term affecting all levels equally, the departure from octahedral symmetry can be described by two parameters, and can be written in the form[17]

$$\hat{V}_{\text{tetragonal}}=\gamma_{20}r^2Y_{20}(\theta,\phi)+\gamma_{40}r^4Y_{40}(\theta,\phi)\,.$$

The γ's characterize the field, and the Y's are spherical harmonics. The coordinates r, θ, and ϕ refer to the metal ion orbitals. We find the splitting of the components of $|{}^4T_2\rangle$ arising from this operator to be given by $\Delta_1-\Delta_2=\alpha\langle r^4\rangle$, where $\alpha=-5\gamma_{40}(4\sqrt{4\pi})^{-1}$. Roughly speaking, $\langle r^4\rangle$ is a property of the metal ion, and α is a property of the environment.

The further assumption that $\Delta_1-\Delta_2\ll\Delta_1$, Δ_2 leads to $D=-4/9(\alpha\langle r^4\rangle/\Delta^2)\zeta_0^2$. The quantity $D\cdot\Delta^2/(\zeta_0^2\langle r^4\rangle)$ is therefore a measure of the tetragonal field caused by the presence of the second defect. The experimental D terms can be used in this expression to compare the values of α for the Cr^{3+} center and the present Mn^{4+} center. For a rough estimate we use $\langle r^4\rangle_{Cr}=4.3$ a.u.,[18] $\langle r^4\rangle_{Mn}\approx 2.0$ a.u. (estimated), $\Delta(Cr^{3+})=16\,600$ cm^{-1},[19] $\Delta(Mn^{4+})\approx 21\,000$ cm^{-1},[13] and the free ion values $\zeta_0(Mn^{4+})=404$ cm^{-1} and $\zeta_0(Cr^{3+})=273$ cm^{-1}.[12] (In taking the ratio, the effects of covalency will tend to cancel.) We then obtain

$$\alpha(Cr^{3+})/\alpha(Mn^{4+})\approx 0.98\,.$$

Had the ratio of $(g_{\parallel}-g_{\perp})$ for the two ions been used in place of the ratio of zero-field splittings, we would have obtained $\alpha(Cr^{3+}):\alpha(Mn^{4+})\approx 1.5$. The exact value of the ratio is unimportant, especially in view of the many approximations made. It is only of importance to note that the ratio is of the order of unity, so that the impurity ions are in similar environments. It follows that the identification of the Mn^{4+} center as that of Fig. 1(c) is quite reasonable.

TABLE I. Hyperfine fields, in kG per electron, at the nuclei of some $3d^3$ ions in oxide surroundings.

Ion	MgO	CaO
Mn^{4+}	98[a]	101[b]
Cr^{3+}	97[c]	99[d]
V^{2+}	96[e]	96[f]
Ti^{+}		66[g]

[a] Reference 1 and this paper.
[b] Reference 21.
[c] References 6 and 21.
[d] W. Low and R. S. Rubins, in *Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), Vol. I, p. 79.
[e] References 5 and 6.
[f] See footnote d above, and W. Low and R. S. Rubins, Phys. Letters 1, 316 (1962).
[g] Reference 22.

VII. HYPERFINE STRUCTURE

The Abragam-Pryce[20] operator for the magnetic hyperfine interaction for d electrons is

$$\hat{\mathcal{H}}_{AP}=P\sum_i\{\mathbf{l}_i\cdot\hat{\mathbf{I}}+1/7[4\hat{\mathbf{s}}_i\cdot\hat{\mathbf{I}}-(\hat{\mathbf{l}}_i\cdot\hat{\mathbf{s}}_i)(\hat{\mathbf{l}}_i\cdot\hat{\mathbf{I}}) \\ -(\hat{\mathbf{l}}_i\cdot\hat{\mathbf{I}})(\hat{\mathbf{l}}_i\cdot\hat{\mathbf{s}}_i)]-\kappa\hat{\mathbf{s}}_i\cdot\hat{\mathbf{I}}\}\,,$$

where $P=2g_n\beta\beta_n\langle r^{-3}\rangle$ and the term in κ represents the contact interaction with the Mn^{4+} nucleus due to core polarization of the s orbitals. Working to first order in spin-orbit coupling admixtures, one finds the following expressions for the hyperfine parameters:

$$A_{\parallel}=-P\left(\kappa+\frac{8}{3}\frac{\zeta_0}{\Delta_1}\right), \tag{9a}$$

$$A_{\perp}=-P\left(\kappa+\frac{8}{3}\frac{\zeta_0}{\Delta_2}\right). \tag{9b}$$

The measured values of $A_{\parallel}$ and $A_{\perp}$ are not sufficiently accurate to permit any useful estimate of P. No value of $\langle r^{-3}\rangle$ appears available for Mn^{4+}, though from Watson's results[18] one can estimate that it is of the order of 5 a.u. Use of this value in the spin-orbit

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[17] Reference 3, Chap. 8.

[18] A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, p. 290.

[19] W. A. Runciman and K. A. Schroeder, Proc. Roy. Soc. (London) **A265**, 489 (1962).

[20] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

coupling correction terms of Eqs. (9a) and (9b), together with the experimental g value and hyperfine constant, leads to $P_K = 69 \times 10^{-4}$ cm^{-1}. This corresponds to a hyperfine field at the Mn^{4+} nucleus of $-P_K/(2g_n\beta_n) = -98$ kG/electron, which is close to the value[13] of -97 kG/electron for α-Al$_2$O$_3$:Mn^{4+} and to the value of -101 kG/electron for CaO:Mn^{4+}.[21] The hyperfine fields are compared with those of other $3d^3$ ions in Table I; apart from Ti$^+$:CaO,[22] they are seen to be remarkably constant. This is surprising when one considers the marked changes in radial functions and covalency which must accompany changes in nuclear charge. For a discussion of the hyperfine fields due to core polarization, the reader is referred to the review of Freeman and Watson.[23]

VIII. SUMMARY

A hitherto unobserved Mn^{4+} spectrum of tetragonal symmetry has been reported. The departure of the crystal field from octahedral symmetry is attributed to the presence of a positive ion vacancy at the first cation site on the tetragonal axis, as indicated in Fig. 1(c). The value of the zero-field splitting constant D was shown to be consistent with this interpretation. The hyperfine field at the Mn^{4+} nucleus due to core polarization was found to be almost identical with the fields at Cr^{3+} and V^{2+} nuclei in the same lattice.

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[21] P. Auzins, J. W. Orton, and J. E. Wertz, in *Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), Vol. I, p. 90.

[22] B. Henderson (private communication).

[23] A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, p. 167.

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Correlations in Light from a Laser at Threshold*

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In this study, we measured the temporal correlations in the electromagnetic field radiated by a laser in the threshold region of oscillation, from $\frac{1}{10}$ to 10 times threshold intensity. The experimental results are compared with theoretical predictions based on solutions of a Fokker-Planck equation. We stabilized the intensity of a He-Ne cw gas laser by means of a long-time-constant servo system which controlled the cavity length. Using a fast photomultiplier as detector, we recorded the photoelectron count distribution within a short counting time (3 μsec) while the photomultiplier was exposed to the laser light. From the photoelectron count distribution measurement, we calculated second, third, and fourth normalized cumulants of the intensity probability density function of the light field. The normalized cumulant is a measure of "pure" correlations among photons because the contributions from lower-order correlations are removed. The statistics of the photoelectron count distribution shows that the intensity fluctuations at about $\frac{1}{10}$ threshold are nearly those of a Gaussian field, and continuously approach those of a constant-amplitude field as the intensity is raised to about 10 times threshold. The normalized second, third, and fourth cumulants of the intensity probability density function of the laser light were also measured at 17 and 42% of threshold intensity as the counting time was increased from 3 to 1000 μsec. The results agree with predictions computed under the assumption that the dependence of the correlation functions on the time variables is the same as for Gaussian light.

I. INTRODUCTION

SINCE the invention of the laser, intensity fluctuation phenomena in laser radiation have been of great interest. It is well known that if the photocount technique is employed in the measurement, the statistics of photoelectron counting reveals information about the statistics of the light intensity fluctuations. The advantage of the photocount technique is the relative simplicity of the measurement of higher-order correlations. In fact, remarkable work has been done with this

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