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ESR Investigations of Nearest-Neighbor Cr^{3+}-Cr^{3+} Interactions in Cr-Doped Spinel $MgAl_2O_4$

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The ESR spectrum of nearest-neighbor (nn) Cr^{3+} pairs in a synthetic single crystal of $MgAl_2O_4$ has been studied at $\nu = 9.85$ GHz (X band). Transitions within the spin multiplets $\Sigma = 2$ and $\Sigma = 3$ are observed. The coefficients of the bilinear (J) and biquadratic (j) exchange are determined from the temperature dependence of the intensities as: $J/k = -(41 \pm 3)\,°\mathrm{K}$, $j/k = -(3 \pm 1)\,°\mathrm{K}$. It is found that the accomodation of a nn Cr^{3+} pair in the lattice is accompanied with a local lattice distortion. This is borne out by the fact that the zero-field-splitting parameters of the pair $D_p = +1.042 \pm 0.005$ cm^{-1}, $E_p = -0.038 \pm 0.002$ cm^{-1} differ appreciably from those of the single ion $D = +0.910 \pm 0.002$ cm^{-1}, $E = 0$ cm^{-1}. Moreover, the anisotropic (traceless) part of the spin-spin coupling tensor is orthorhombic: $\mathcal{J}_{PP} = +0.1015 \pm 0.0025\,\mathrm{cm}^{-1}$, $\mathcal{J}_{QQ} = +0.0535 \pm 0.0025\,\mathrm{cm}^{-1}$, and $\mathcal{J}_{RR} = -0.1550 \pm 0.0010$ cm^{-1}, with principal axes along $P = [001]$, $Q = [1\bar{1}0]$, $R = [110]$ for a Cr-Cr pair along the R axis.

I. INTRODUCTION

In previous publications[1-3] the 90° exchange interactions within pairs of nearest-neighbor (nn) Cr^{3+} ions in the spinel $ZnGa_2O_4$ have been studied in detail by means of electron-spin resonance[1,2] as well as by optical techniques.[3] Some of the most salient results are (a) the absence of any detectable local lattice distortion due to the $Cr \rightarrow Ga$ substitution; (b) the large negative value of the coefficient of biquadratic exchange ($j/k = -2.4\,°\mathrm{K}$). An explanation of the latter fact was given in terms of Kittel's exchange-striction mechanism,[4] which leads to the estimate

$$j \simeq -\tfrac{1}{2}(J'^2/c r_T)\,, \qquad (1)$$

where c is the elastic stiffness component along the pair axis, r_T is the equilibrium Cr-Cr distance, and J' is the derivative of the Heisenberg exchange parameter with respect to the Cr-Cr distance.

From a list of asymptotic Curie temperatures[5] of chromites with 90° interaction it is found that J is practically a linear function of r_T, for $2.88 < r_T < 3.04$ Å. We therefore expect that j takes roughly the same value for these crystals, provided c and r_T are not too different. In order to verify this point, we have extended the investigations to chromium-doped $MgAl_2O_4$.

The lattice parameter of $MgAl_2O_4$ ($a = 8.080$ Å) is somewhat smaller than that of $ZnGa_2O_4$ ($a = 8.330$ Å), whereas the u parameters are identical within the experimental limits: $u = 0.38675 \pm 0.00005$ for $ZnGa_2O_4$[6] versus $u = 0.387 \pm 0.001$ for $MgAl_2O_4$.[7] The ionic radii[8] of Al^{3+} (0.51 Å) and Cr^{3+} (0.63 Å), however, differ appreciably so that distortions can be expected when Cr^{3+} is substituted for Al^{3+}.

The occurrence of structural distortions in the spinel series $MgCr_xAl_{2-x}O_4$ has been suggested by Grimes and Collett[9,10] and by Lou and Ballentyne,[11] albeit in our opinion on insufficient grounds. In the model proposed by these authors[9-11] the chromium ions would no longer be at a center of inversion symmetry but would be shifted away along their local trigonal $\langle 111 \rangle$ axis. The point group of Cr then would be C_{3v} instead of D_{3d}. Unfortunately, it is impossible to decide between these two alternatives from the ordinary ESR spectrum of isolated Cr^{3+} ions since the constraints imposed on the spin-Hamiltonian of a $S = \frac{3}{2}$ system are identical for D_{3d} and C_{3v} symmetries.[12] The magnitude of the zero-field-splitting parameter D cannot be used in favor of either one of these alternatives, because of the lack of a quantitative theory. The most direct experiment to establish the point symmetry would be the observation (or nonobservation) of the electric-field-induced splitting of the resonance lines.[13] This experiment has not yet been carried out.

It will be shown in this paper, that some information about local distortions can be obtained by comparing ESR spectra of nearest-neighbor Cr pairs in $MgAl_2O_4$ and $ZnGa_2O_4$. It should be stressed that these distortions are specific for the pair situation and the experiments described here do not give information about eventual distortions around single chromium ions in the lattice.

A further difficulty with $MgAl_2O_4$ as a host lattice is the fact that it is partly inverse. For electron-spin-resonance work this has two consequences. First of all, the random distribution of cations among the A and B sites introduces internal strains, which in turn give rise to line broadening.[14,15] This broadening is more serious for synthetic than for natural spinels.[14] Second, in Cr-doped crystals additional Cr centers with lower than axial symmetry are to be expected. Indeed, Cr centers of orthorhombic symmetry have recently been reported.[16,17] The presence of these additional Cr centers complicates the study of the pair spectrum, since the intensities are sometimes of the same order as those of the pair lines.

II. EXPERIMENTAL DETAILS

The Cr-doped $MgAl_2O_4$ single crystals were grown from a PbF_2 flux.[18] The Cr concentration was determined both by spectrochemical analysis as well as photometrically after disclosure of the sample in HCl, and amounts to 0.06–0.10 g atom Cr/g mole $MgAl_2O_4$. Other magnetic impurities are of minor importance; their concentrations are listed in Ref. 17. A few small crystals with lower (not measured) Cr concentration were also available.

The methods of determining exchange parameters from ESR and optical spectra of isolated pairs have been reviewed recently.[19] Here we restrict ourselves to the ESR method. Results of optical measurements will be published in the near future. By analogy with $ZnGa_2O_4$: Cr we expect that J will be much larger than $g\mu_B H$, so that with a conventional ESR spectrometer transitions *within* the distinct spin multiplets ($\Sigma = 1, 2, 3$) will be observed. The values of the bilinear (J) and biquadratic (j) exchange parameters then follow from the temperature dependence of the signal intensities, whereas the sign of J is found from the spin value of the lowest state.

The requirements to be imposed upon the spectrometer in order to perform this experiment are briefly discussed in Ref. 2. Anisotropic spin-spin interactions are obtained from the angular dependence of the spectra.

III. EXPERIMENTAL RESULTS

A. Single-Ion Spectrum

Since Cr^{3+} has a strong preference for octahedral surroundings it is quite natural to expect that it will substitute for Al^{3+} (B sites). This is borne out by many experimental facts. In particular, the ESR spectra, reported by several authors[20–23] are described by an axial spin-Hamiltonian ($S_i = \frac{3}{2}$),

$$\mathcal{H}_i = g_{\parallel}\mu_B H_{Z\,i} S_{Z\,i} + g_{\perp}\mu_B (H_{X\,i} S_{X\,i} + H_{Y\,i} S_{Y\,i}) + D[S_{Z\,i}^2 - \tfrac{1}{3}S_i(S_i+1)] , \quad (2)$$

with center axes Z_i along the four $\langle 111\rangle$ axes in accordance with the trigonal symmetry of the B site. The parameters are $g_{\parallel} = 1.986 \pm 0.001$, $g_{\perp} = 1.980 \pm 0.001$, $D = +0.910 \pm 0.002\ \text{cm}^{-1}$. The g values are close to 2, as expected for an orbital singlet ground state (octahedral site). The value of D seems to vary slightly from crystal to crystal; the value quoted here refers to the single crystal which has been used in the major part of this work. The D value reported by Stahl-Brada and Low[23] is apparently an error since it differs by approximately a factor 2 from the values reported by other authors.[20–22] The value of $2D = 300 \pm 10\ \text{cm}^{-1}$ quoted by Lou and Ballentyne[11] clearly indicates that their interpretation of the optical spectrum is incorrect.

B. Pair Spin Hamiltonian

The spin Hamiltonian of a Cr-Cr pair may be written as the sum of two single-ion spin Hamiltonians and an interaction term

$$\mathcal{H}_p = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{\text{int}} . \quad (3)$$

It should be borne in mind, however, that the single-ion terms $\mathcal{H}_1$, $\mathcal{H}_2$ need not be identical with Eq. (2) since the formation of a pair lowers the symmetry of the individual ion-sites. In addition, there may be a real local lattice distortion around the Cr-Cr pair. It will be shown in Sec. III C that the extension of $\mathcal{H}_1$ and $\mathcal{H}_2$ with an orthorhombic term $E_p(S_X^2 - S_Y^2)$ suffices to describe the experimental results adequately. The g anisotropy is very small and will be neglected in the description of the pair spectra. Hence, we write $\mathcal{H}_1$ and $\mathcal{H}_2$ as

$$\begin{aligned} \mathcal{H}_1 &= g\mu_B \vec{H}\cdot\vec{S}_1 + D_p[S_{Z1}^2 - \tfrac{1}{3}S_1(S_1+1)] + E_p(S_{X1}^2 - S_{Y1}^2) , \\ \mathcal{H}_2 &= g\mu_B \vec{H}\cdot\vec{S}_2 + D_p[S_{\zeta 2}^2 - \tfrac{1}{3}S_2(S_2+1)] + E_p(S_{\xi 2}^2 - S_{\eta 2}^2) . \end{aligned} \quad (4)$$

Here, Z and ζ represent the local center axes of ions 1 and 2, respectively (see Fig. 1).

The dominant term in the interaction Hamiltonian $\mathcal{H}_{\text{int}}$ is the bilinear ("Heisenberg") exchange $-J\vec{S}_1 \cdot \vec{S}_2$. An additional biquadratic term, however, proves to be indispensable for a correct description of the multiplet energies. Finally, an anisotropic spin-spin coupling is present which is described by a traceless tensor $\overleftrightarrow{\mathcal{J}}$. Since the point group of M, the point midway between the two Cr ions, is C_{2v},

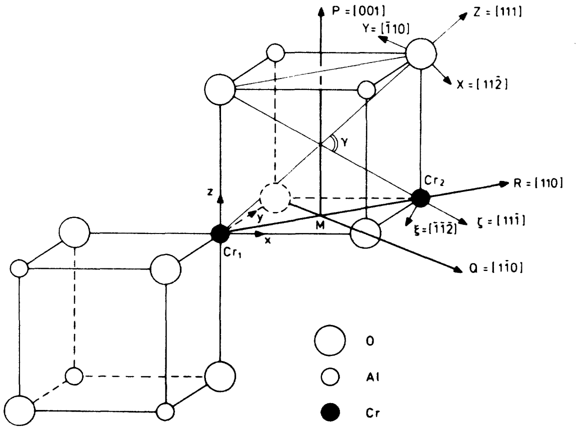

FIG. 1. Geometry of nn pairs in spinel and definition of coordinate systems.

an orthorhombic form of $\overleftrightarrow{\mathcal{J}}$ is symmetry allowed (Fig. 1). In the system $ZnGa_2O_4$: Cr the tensor $\overleftrightarrow{\mathcal{J}}$ could be approximated (within the experimental accuracy) by an axial dyad, with principal axis along R (Fig. 1). As we will see in Sec. III C, this approximation no longer holds for $MgAl_2O_4$: Cr. Finally, an antisymmetric anisotropic exchange term $\vec{\mathfrak{D}}\cdot(\vec{S}_1\times\vec{S}_2)$ is allowed in C_{2v} symmetry. However, since we find no experimental evidence for such a term, it will be skipped in what follows.

Summing up, we find for $\mathcal{H}_{int}$:

$$\mathcal{H}_{int} = -J\vec{S}_1\cdot\vec{S}_2 + j(\vec{S}_1\cdot\vec{S}_2)^2 + \mathcal{J}_{PP}S_{1P}S_{2P} + \mathcal{J}_{QQ}S_{1Q}S_{2Q} + \mathcal{J}_{RR}S_{1R}S_{2R}\,, \qquad (5)$$

with

$$\mathcal{J}_{PP} + \mathcal{J}_{QQ} + \mathcal{J}_{RR} = 0\ .$$

Using the definitions

$$A = -\tfrac{1}{2}\mathcal{J}_{RR}, \quad e = \tfrac{1}{8}(\mathcal{J}_{PP} - \mathcal{J}_{QQ}) \qquad (6)$$

we may rewrite $\mathcal{H}_{int}$ as

$$\mathcal{H}_{int} = -J\vec{S}_1\cdot\vec{S}_2 + j(\vec{S}_1\cdot\vec{S}_2)^2 - A[3S_{1R}S_{2R} - (\vec{S}_1\cdot\vec{S}_2)] + 4e(S_{1P}S_{2P} - S_{1Q}S_{2Q})\ . \qquad (7)$$

The coefficient A has the same meaning as in Ref. 2.

In evaluating the eigenvalues of $\mathcal{H}_p$ it is convenient to introduce the total spin $\vec{\Sigma} = \vec{S}_1 + \vec{S}_2$, which is a good quantum number because the interaction between the multiplets $\Sigma = 0, 1, 2$, and 3 proves to be negligible. The theory is given in detail in Ref. 2 and will not be repeated here. The only additional data we need here are the matrix elements of the orthorhombic spin-spin coupling, which may be rewritten

$$4e(S_{1P}S_{2P} - S_{1Q}S_{2Q}) = 2e[(1-\cos\gamma)S_{1Z}S_{2Z} + (1+\cos\gamma)S_{1X}S_{2X} - 2S_{1Y}S_{2Y} - \sin\gamma(S_{1Z}S_{2X} + S_{1X}S_{2Z})] \qquad (8)$$

in the coordinate system (X, Y, Z) used in Ref. 2 (see Fig. 1). The matrix elements are given in Table I.

C. Pair Spectra

Identification of pair lines has been done in a rough way by comparing ESR spectra of heavily and lightly doped crystals. Nearest-neighbor lines are easily distinguished from pairs at a greater distance and from orthorhombic Cr^{3+} centers[16,17] since their ESR lines disappear at liquid-helium temperatures. We have found two classes of nearest-neighbor-pair lines with intensity maxima at $T \simeq 80$ °K and $T \simeq 150$–180 °K; they are attributed to transitions within the multiplets $\Sigma = 2$ and $\Sigma = 3$, respectively. Transitions within $\Sigma = 1$ cannot be observed at X-band frequencies ($\nu = 8$–10 GHz) since the zero-field splitting ($\simeq 1\ cm^{-1}$) cannot be bridged by the microwave quantum.

TABLE I. Nonvanishing matrix elements of orthorhombic spin-spin coupling $4e(S_{1P}S_{2P} - S_{1Q}S_{2Q})$ within the basis $|\Sigma M\rangle$, defined in Table I of Ref. 2.

Σ	M	M'	$\langle M \vert 4e(S_{1P}S_{2P} - S_{1Q}S_{2Q}) \vert M'\rangle$
1	1	1	$+1.7\,(1-\cos\gamma)e$
	0	0	$-3.4(1-\cos\gamma)e$
	-1	-1	$+1.7(1-\cos\gamma)e$
	1	0	$-1.7\sqrt{2}\sin\gamma\ e$
	0	-1	$+1.7\sqrt{2}\sin\gamma\ e$
	-1	1	$(+5.1+1.7\cos\gamma)e$
2	2	2	$+3(1-\cos\gamma)e$
	1	1	$-1.5(1-\cos\gamma)e$
	0	0	$-3(1-\cos\gamma)e$
	-1	-1	$-1.5(1-\cos\gamma)e$
	-2	-2	$+3(1-\cos\gamma)e$
	2	1	$-3\sin\gamma\ e$
	1	0	$-0.5\sqrt{6}\sin\gamma\ e$
	0	-1	$+0.5\sqrt{6}\sin\gamma\ e$
	-1	-2	$+3\sin\gamma\ e$
	2	0	$(+1.5\sqrt{6}+0.5\sqrt{6}\cos\gamma)e$
	1	-1	$(4.5+1.5\cos\gamma)e$
	0	-2	$(+1.5\sqrt{6}+0.5\sqrt{6}\cos\gamma)e$
3	3	3	$+4.5(1-\cos\gamma)e$
	2	2	0
	1	1	$-2.7(1-\cos\gamma)e$
	0	0	$-3.6(1-\cos\gamma)e$
	-1	-1	$-2.7(1-\cos\gamma)e$
	-2	-2	0
	-3	-3	$+4.5(1-\cos\gamma)e$
	3	2	$-3\sqrt{1.5}\sin\gamma\ e$
	2	1	$-0.9\sqrt{10}\sin\gamma\ e$
	1	0	$-0.6\sqrt{3}\sin\gamma\ e$
	0	-1	$+0.6\sqrt{3}\sin\gamma\ e$
	-1	-2	$+0.9\sqrt{10}\sin\gamma\ e$
	-2	-3	$+3\sqrt{1.5}\sin\gamma\ e$
	3	1	$+1.5\sqrt{0.6}\,(3+\cos\gamma)e$
	2	0	$+3\sqrt{0.3}\,(3+\cos\gamma)e$
	1	-1	$+1.8\,(3+\cos\gamma)e$
	0	-2	$+3\sqrt{0.3}\,(3+\cos\gamma)e$
	-1	-3	$+1.5\sqrt{0.6}\,(3+\cos\gamma)e$

The definite assignment to the multiplets $\Sigma = 2$ and 3 has been made on account of the angular dependence of the lines for $\vec{H}$ rotating in a $(1\bar{1}0)$ plane. The results are shown in Figs. 2 and 3. For the sake of clarity we restrict our presentation to the specific pair Cr_1-Cr_2 (see Fig. 1) although the other geometrical types of nn pairs are present in the actual spectra. As expected for the pair Cr_1-Cr_2, extrema in the angular diagrams are found along the $P = [001]$ and $R = [110]$ directions.

From Table II in Ref. 2 it is seen that the matrix elements of the E_p and D_p terms (single-ion anisotropies) vanish within the $\Sigma = 2$ multiplet. Therefore, the positions of the $\Sigma = 2$ lines can be used to determine the coefficients A and e of the

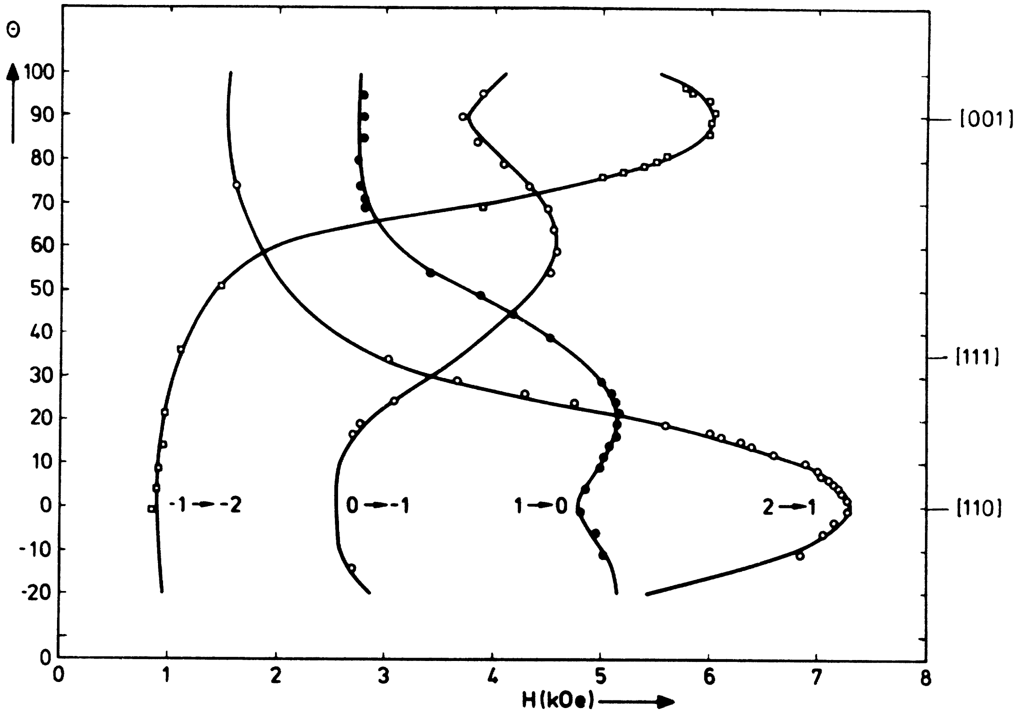

FIG. 2. Angular dependence of $\Sigma=2$ transitions for $\vec{H}$ rotating in the $(1\bar{1}0)$ plane; $\nu=9851$ MHz. $T=77\,^{\circ}$K. The solid lines are calculated with $g=1.9800$, $A=+0.0775$ cm^{-1}, and $e=+0.0060$ cm^{-1}. Only transitions of the specific pair $\mathrm{Cr}_1-\mathrm{Cr}_2$ are shown.

anisotropic spin-spin coupling. Figure 2 shows that a good fit is obtained with $A=+0.0775\pm0.0005$ cm^{-1} and $e=+0.0060\pm0.0005$ cm^{-1}. From Eq. 6 we then find

$$\mathcal{J}_{PP}=+0.1015\pm0.0025\ \mathrm{cm}^{-1}\ ,$$

$$\mathcal{J}_{QQ}=+0.0535\pm0.0025\ \mathrm{cm}^{-1}\ ,$$

$$\mathcal{J}_{RR}=-0.1550\pm0.0010\ \mathrm{cm}^{-1}\ .$$

Under the assumption that the values of A and e are independent of Σ, the angular dependence of the $\Sigma=3$ transitions can be used to determine D_p and E_p. The best fit, shown as solid lines in Fig. 3, is obtained with $D_p=+1.042\pm0.005$ cm^{-1} and $E_p=-0.038\pm0.002$ cm^{-1}. The assumption, mentioned above, may not be completely justified, since A and e may vary slightly with Σ as a consequence of exchange striction.[24] This is a tiny effect, however, of the order of $\Delta A=A(\Sigma=3)-A(\Sigma=2)=-0.002$ cm^{-1}, $\Delta e=-0.0002$ cm^{-1} and the scanty data on the $\Sigma=3$ multiplet are insufficient to establish its importance.

The $\Sigma=3$ lines are very hard to find, since they are an order less intense than the $\Sigma=2$ transitions. We had the same experience with the system $\mathrm{ZnGa_2O_4}:\mathrm{Cr}$.[2] An impression of the relative intensities of the $\Sigma=2$, $\Sigma=3$ and single-ion lines can be obtained from Fig. 4. The reason for the absence of any experimental points on the $-2\to-3$ branch in Fig. 3 is rather trivial: The spectrometer sensitivity is reduced for $H>6$ KOe as a consequence of a spurious bias signal.

The linewidths depend on the specific transition and vary from 30–150 Oe. The smallest width (30 Oe) is found for the high-field ($\Sigma=3$; $1\to0$) transition near $\vec{H}\parallel[110]$, whereas the transition ($\Sigma=3$; $0\to-1$) exhibits the largest width of about 150 Oe. The widths of all $\Sigma=2$ lines are of the order of 70 Oe. No temperature dependence of the linewidths has been observed in the range $30<T<300\,^{\circ}$K.

The values of the exchange parameters J and j are determined from the temperature dependence of the line heights:

$$\mathcal{J}_{\Sigma}\propto h\nu/kT\,\mathfrak{z}^{-1}e^{(-W_{\Sigma}/kT)}\ , \tag{9}$$

with

$$\mathfrak{z}=1+3e^{(-W_1/kT)}+5e^{(-W_2/kT)}+7e^{(-W_3/kT)} \tag{10}$$

and

$$\begin{aligned} W_1&=-J-\tfrac{13}{2}j\ ,\\ W_2&=-3J-\tfrac{27}{2}j\ ,\\ W_3&=-6J-9j\ . \end{aligned} \tag{11}$$

Typical curves of signal height versus temperature are shown in Figs. 5 and 6, for $\Sigma=2$ and $\Sigma=3$, re-

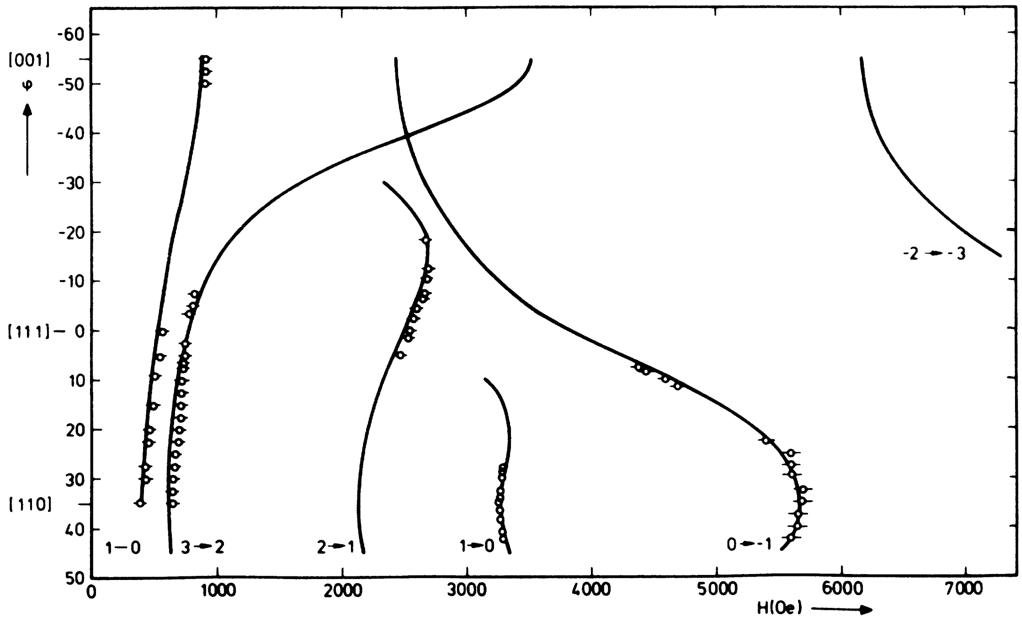

FIG. 3. Angular dependence of Σ = 3 lines for $\vec{H}$ rotating in the $(1\bar{1}0)$ plane; $\nu = 9846$ MHz, $T = 293$ °K. The solid lines are calculated with $D_p = +1.042$ cm^{-1}, $E_p = -0.038$ cm^{-1}, $A = +0.0775$ cm^{-1}, $e = +0.0060$, and $g = 1.9800$. Only transitions of the specific pair $Cr_1 - Cr_2$ are shown.

spectively. The best fit (solid lines) is obtained for

$$J/k = -(41 \pm 2)\,°\mathrm{K}\ ,\quad j/k = -(3 \pm 1)\,°\mathrm{K}.$$

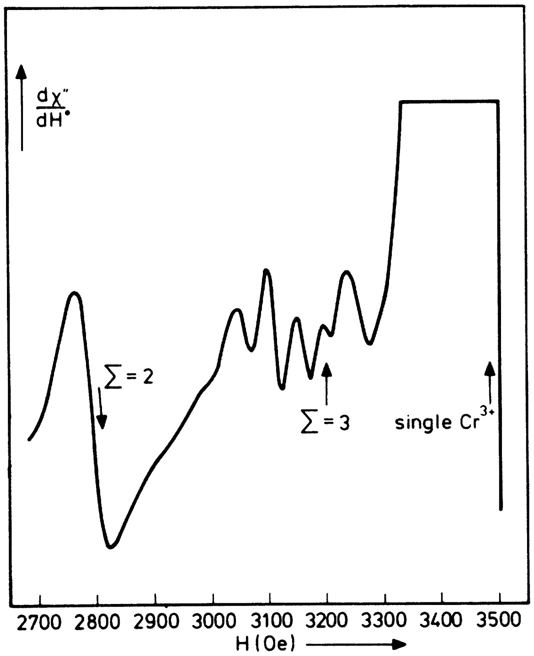

FIG. 4. Part of ESR spectrum of $MgAl_2O_4:Cr^{3+}$ for $\vec{H} \parallel [111]$, showing Σ = 2 and Σ = 3 transitions of nn Cr pairs together with a single-ion line $(-\frac{1}{2} \rightarrow +\frac{1}{2})$. $T = 77$ °K, $\nu = 9827$ MHz.

The assumption that the exchange parameters are independent of temperature is implicit in Eqs. (9)-(11). The good agreement between theoretical and experimental $\mathscr{I}_\Sigma$-T profiles seems to justify this assumption.

IV. DISCUSSION

A. Isotropic Exchange

The antiferromagnetic character of the interaction follows unambiguously from the fact that Σ = 3 is an excited multiplet. The magnitude of the bilinear exchange ($J/k = -41$ °K) is roughly in agreement with the asymptotic Curie temperature $\Theta = -350$ °K of $MgCr_2O_4$,[25] which leads to an estimated nearest-neighbor interaction $J/k \simeq -47$ °K if the approximation $3k\Theta = 6S(S+1)J$ is made.

It is also interesting to compare the J values of Cr-Cr interactions in $MgAl_2O_4$ and $ZnGa_2O_4$. Qualitatively, the larger absolute value of J/k in $MgAl_2O_4:Cr^{3+}$ (−41 °K) as compared with $ZnGa_2O_4:Cr^{3+}$ (−32 °K) is in agreement with the smaller lattice parameter of $MgAl_2O_4$ (8.080 Å vs 8.330 Å). More quantitatively, we may use Motida and Miyahara's[5] Θ data to arrive at a prediction of the difference $\Delta(J/k) = J/k(MgAl_2O_4) - J/k(ZnGa_2O_4)$. From a plot of Θ vs R (see Fig. 10 in Ref. 2) we obtain $(1/k)dJ/dR = (460 \pm 70)$° K/Å. With $R(ZnGa_2O_4) = 2.94$ Å and $R(MgAl_2O_4) = 2.86$ Å, the expected change in bilinear exchange parameters is $\Delta(J/k) = -37$ °K. Experimentally we find $\Delta(J/k) = -(9 \pm 4)$ °K. The discrepancy may be lifted by allowing the Cr-

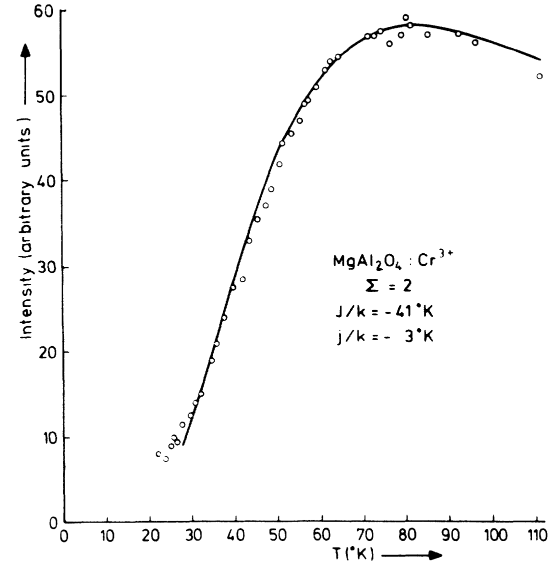

FIG. 5. Intensity vs temperature for a $\Sigma = 2$ transition. The solid line is the theoretical curve Eq. (9), with $J/k = -41\,°\mathrm{K}$ and $j/k = -3\,°\mathrm{K}$.

Cr separation to be 1–2% greater than the Al-Al separation in $MgAl_2O_4$.

The coefficients of biquadratic exchange are found to be practically identical in $MgAl_2O_4$ and $ZnGa_2O_4$. This accords with the expectation set forth in Sec. I and supports our view[1,2] that j is mainly determined by exchange-striction effects.

B. Anisotropic Spin-Spin Coupling

Although an orthorhombic spin-spin coupling is compatible with the C_{2v} symmetry of the nearest-neighbor pair, the physical origin of the orthorhombic term needs an explanation, the more since the coupling is perfectly axial (along the R axis) in the analogous system $ZnGa_2O_4{:}Cr^{3+}$. In that case the strength A of the anisotropic interaction can be fully accounted for by a magnetic point dipole-dipole calculation, based on unmodified lattice separations.[2]

In principle an orthorhombic term in the magnetic dipole-dipole interaction could arise through the anisotropy of the g tensor,[26] which would lead to an orthorhombicity ρ:

$$\rho = \left| \frac{\mathcal{J}_{PP} - \mathcal{J}_{QQ}}{\mathcal{J}_{RR}} \right| \lesssim \frac{g_{\parallel}^2 - g_{\perp}^2}{g_{\parallel}^2} = 0.005 \,. \tag{12}$$

This is two orders smaller than the experimental value $\rho = 0.3$.

A possible alternative is anisotropic exchange. In order to discuss this effect it is necessary first to subtract the magnetic dipole-dipole interaction from the experimental tensor $\overleftrightarrow{\mathcal{J}}$:

$$\overleftrightarrow{\mathcal{J}}(\mathrm{expt}) - \overleftrightarrow{\mathcal{J}}\,(d\text{-}d) = \overleftrightarrow{\mathcal{J}}(\mathrm{an\,exch}). \tag{13}$$

If the Cr-Cr separation is put equal to the Al-Al separation we obtain

$$\begin{bmatrix} +0.1015 & & \\ & +0.0535 & \\ & & -0.1550 \end{bmatrix} - \begin{bmatrix} +0.0720 & & \\ & +0.0720 & \\ & & -0.1440 \end{bmatrix} = \begin{bmatrix} +0.0295 & & \\ & -0.0185 & \\ & & -0.0110 \end{bmatrix}. \tag{14}$$

In the coordinate system (P, Q, R). In Sec. IV A, however, we have shown that R(Cr-Cr) is probably 1-2% greater than R(Al-Al). Using the probably more realistic estimate $R(\text{Cr-Cr}) = 2.91$ Å instead of 2.86 Å we find

$$\begin{bmatrix} +0.1015 & & \\ & +0.0535 & \\ & & -0.1550 \end{bmatrix} - \begin{bmatrix} +0.0695 & & \\ & +0.0695 & \\ & & -0.1390 \end{bmatrix} = \begin{bmatrix} +0.0320 & & \\ & -0.0160 & \\ & & -0.0160 \end{bmatrix}. \tag{15}$$

The difference between the experimental $\overleftrightarrow{\mathcal{J}}$ tensor and the magnetic dipole-dipole interaction then appears to be an *axial* tensor, with principal axis along $P \parallel z \parallel [001]$.

An axially symmetric coupling along the z axis is not unexpected for anisotropic exchange since the two Cr ions and the two oxygens through which the superexchange interactions take place lie in the

xy plane. A similar situation has been reported by Benê[27] for Cr-Cr pairs in BiI_3, where the anisotropy is several orders stronger than the magnetic dipole-dipole interaction ($J = 14\ cm^{-1}$, $\mathcal{J}_{an} = 3\ cm^{-1}$, $A_{dd} = 0.01\ cm^{-1}$) and the difficulty of separating these effects is absent. Here the exchange anisotropy is also found to be axial along the z axis

The magnitude of the effect may be compared with Moriya's estimate[28]

$$|\mathcal{J}_{an}| \simeq (\Delta g/g)^2 J \simeq 3\times 10^{-3}\ cm^{-1}\ , \qquad (16)$$

where J is the ground-state exchange parameter. This is a factor 5 smaller than the "experimental" value deduced in Eq. (15). The discrepancy should not be taken too seriously, since Eq. (16) is a very rough approximation. A major problem in applying Eq. (16) is: What value of J should be inserted? For 90° Cr-Cr interactions it has been shown[3] that the ground-state J value is built up from four distinct "elementary" contributions,

$$J = \tfrac{1}{9}(2J_c + 4J_c' + J_d + 2J_\pi)\ , \qquad (17)$$

which tend to cancel each other. The orbital-dependent exchange parameters J_c, J_c', J_d, and J_π give the strength of the coupling between electrons in the separate t_{2g} orbitals (see Ref. 3). From the analysis given by Benê[27] it is seen that anisotropic exchange contains a large number of contributions. The simple correspondence suggested by Eq. (16) only applies to the case of one predominant exchange mechanism. The complexity of the problem and the absence of experimental information about exchange interactions in optically excited states of Cr-Cr pairs in $MgAl_2O_4$ seriously hampers any meaningful discussion for the time being.

C. Local Lattice Distortions

From the angular dependence of the $\Sigma = 3$ line positions it follows that the zero-field splitting $\Delta_p = [D_p^2 + 3E_p^2]^{1/2}$ of the nn chromium pair is about 14% larger than that of the single Cr ions. Moreover, the symmetry is lowered from axial to orthorhombic. A comparison with the analogous system $ZnGa_2O_4:Cr^{3+}$, where $D_p = D$ and $E_p = 0$, shows that this change in Δ cannot be attributed to the mere presence of a Cr^{3+} in the first Al^{3+}-shell. It is therefore due to a local distortion.

A qualitative consideration,[29] in which only first (O^{2-}) and second neighbors (Al^{3+}) are included, shows that an increase of Δ may be explained if we allow the oxygens to move away from the chromium sites, thus creating more room for the rather voluminous Cr^{3+} ions. In the model used in Ref. 29 this means a formal reduction of the local u parameter.

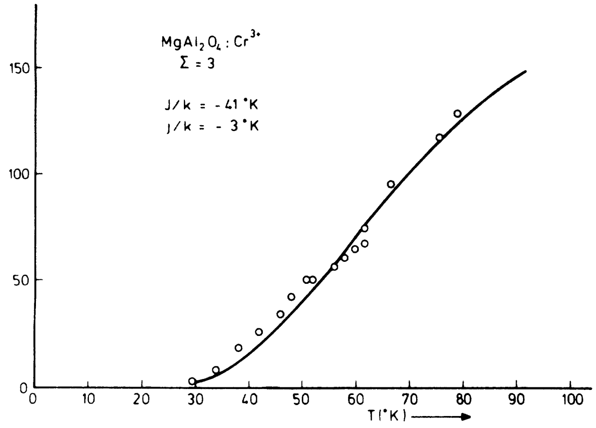

FIG. 6. Intensity vs temperature for a $\Sigma = 3$ transition. The solid line is the theoretical curve Eq. (9) with $J/k = -41\ °K$, $j/k = -3\ °K$.

In summing up the arguments obtained in Secs. IV A, IV B, and IV C we arrive at the following qualitative picture of the local lattice distortion around a Cr-Cr pair:

(i) The value of J and the postulate that $\overleftrightarrow{\mathcal{J}}_{an}$ should be axial along the z axis leads to a Cr-Cr separation 1–2% greater than the Al-Al separation. The most plausible directions, along which the Cr ions move, are $[\bar{1}\bar{1}\bar{1}]$ and $[11\bar{1}]$, respectively.

(ii) The fact that $D_p > D$ and $E_p \neq 0$ cannot be explained by this shift of the chromium ions, but must be due to a shift of the oxygens away from the chromiums.

The model is rather speculative and needs a further verification. One way to check it would be to observe the influence of an electric field on the pair lines. A first-order Stark effect[13] is expected since odd crystal-field components will be present as a consequence of the above-mentioned distortion.

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