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Orthorhombic Electron-Spin-Resonance Spectra of Yb^{3+} Ions in CaF_2

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Four orthorhombic electron-spin-resonance spectra have been observed from CaF_2 doped with small amounts of Yb_2O_3. In each case the z axis of the g tensor lies along the [110] direction, while the x and y axes lie in the (110) plane and are tilted at an angle δ to the $[\bar{1}10]$ and [001] axes, respectively. The g factors of the two strongest spectra are: Spectrum R_1: $g_x=6.99\pm0.01$, $g_y=1.355\pm0.002$, $g_z=1.094\pm0.002$, $\delta=3.2°\pm0.2°$. Spectrum R_2: $g_x=7.24\pm0.01$, $g_y=0.992\pm0.002$, $g_z=0.957\pm0.002$, $\delta=26.3°\pm0.2°$. The values of δ for the two weaker spectra are 8.8° and 0°. These observations cast doubt on the pair model previously proposed to explain the orthorhombic spectra observed in γ-irradiated Tm_2O_3:CaF_2. Possible alternative models are discussed.

1. INTRODUCTION

In a recent paper[1] we described an electron-spin-resonance (ESR) spectrum having orthorhombic symmetry which occurred in γ-irradiated crystals of CaF_2 grown from a melt containing Tm_2O_3. We suggested that during the growth process pairs of Tm^{3+} ions enter the lattice and occupy adjacent substitutional Ca^{2+} sites, charge neutrality being maintained by the presence of two O^{2-} ions on the common F^- sites. Irradiation with γ rays then converts a small fraction of the impurity ions to the divalent state, producing Tm^{2+}-Tm^{3+} pairs which give rise to the observed spectrum. If this interpretation of the thulium spectrum is correct, it would appear likely that pairs of other rare-earth ions could also be produced by doping CaF_2 with their sesquioxides. In particular, the Yb^{3+} ion, which is isoelectronic with the Tm^{2+} ion, might be expected to exhibit a similar spectrum without the necessity for γ irradiation; one then might also expect to find evidence of a magnetic interaction between the adjacent Yb^{3+} ions which would further strengthen the case for the pair model.

Previous ESR studies of Yb^{3+} ions in CaF_2, using samples doped in the form of YbF_3, have revealed ions situated in purely cubic sites,[2] and ions having tetragonal[3] and trigonal[4] symmetries. In crystals of CaF_2 doped with Yb_2O_3 we have observed four different spectra with orthorhombic symmetry, together with the two previously reported trigonal spectra, but no trace of lines arising from cubic or tetragonal sites. This paper gives details of the new orthorhombic spectra.

2. APPARATUS AND CRYSTALS

The experiments described below were performed at 1.5 and at 16°K; no significant difference was found between the spectra at these two temperatures and so most of the observations were made at 1.5°K. The X-band (9000 Mc/sec) spectrometer described in our previous paper[1] was used with the exception that the magnetic field in the present experiments was produced by a much larger electromagnet having 8-in.-diam pole pieces with a separation of 2.5 in., which enabled fields up to 12 kG to be attained. The crystals were oriented by using the {111} cleavage planes and a precision Teflon wedge; final adjustments were then made by tilting the Dewar assembly so that the appropriate rhombic lines became degenerate, which provided a very sensitive method of checking the alignment.

The crystals were grown by the Czochralski method[5] from vitreous carbon crucibles in an atmosphere of 99.998% pure argon. Ytterbium was either added to the melt as YbF_3 or as Yb_2O_3 at concentrations of 0.05 at. % and 0.2 at. %. The fluoride-doped crystals showed only the previously reported cubic and axial spectra, but no trace of rhombic spectra. As grown the crystals were colorless but showed absorptions in the 9000- to 10 400-Å region arising from transitions between the $^4F_{7/2}$ and $^4F_{5/2}$ levels of Yb^{3+} ions. Strong absorption bands were also found in the ultraviolet between 2000 and 4000 Å which have been attributed by Kaplyanskii and Feofilov[6] to Yb^{2+} ions. Unfortunately the relative concentrations of these two types of ion cannot be deduced from these measurements since the appropriate oscillator strengths are not known.

3. THE SPIN HAMILTONIAN

The ground state of the Yb^{3+} ion is $^4F_{7/2}$ and in a field of cubic symmetry the Γ_7 level of the $J=\frac{7}{2}$ manifold lies lowest in energy. Transitions between the components of this doublet give rise to the observed spectrum which behaves like a simple spin $S=\frac{1}{2}$ and can thus be described by the spin Hamiltonian,

$$\mathcal{H}=\beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+\mathbf{I}\cdot\mathbf{A}\cdot\mathbf{S}, \qquad (1)$$

where the g tensor has components g_x, g_y, and g_z which reflect the deformation of the basic cubic symmetry of

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[1] P. A. Forrester and S. D. McLaughlan, Phys. Rev. 138, 1682 (1965).

[2] W. Hayes and J. W. Twidell, J. Chem. Phys. 35, 1521 (1961).

[3] U. Ranon, Phys. Letters 9, 17 (1964).

[4] W. Low and U. Ranon, in *Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), p. 167.

[5] Some of the crystals used were grown by Green of these laboratories, others were obtained from Barr and Stroud, Ltd.

[6] A. A. Kaplyanskii and P. P. Feofilov, Opt. i Spektroskopiya 13, 235 (1962) [English transl.: Soviet Phys.—Opt. Spectry. 13, 129 (1962)].

Table I. Direction-cosine matrices relating the x, y, and z axes of the g tensor to the a, b, and c cubic axes.

(a)	(b)	(c)	(d)
$\begin{bmatrix} -\cos\delta/\sqrt{2} & \cos\delta/\sqrt{2} & \sin\delta \\ \sin\delta/\sqrt{2} & -\sin\delta/\sqrt{2} & \cos\delta \\ 1/\sqrt{2} & 1/\sqrt{2} & 0 \end{bmatrix}$	$\begin{bmatrix} -\cos\delta/\sqrt{2} & \cos\delta/\sqrt{2} & -\sin\delta \\ -\sin\delta/\sqrt{2} & \sin\delta/\sqrt{2} & \cos\delta \\ 1/\sqrt{2} & 1/\sqrt{2} & 0 \end{bmatrix}$	$\begin{bmatrix} -\cos\delta/\sqrt{2} & -\cos\delta/\sqrt{2} & \sin\delta \\ \sin\delta/\sqrt{2} & \sin\delta/\sqrt{2} & \cos\delta \\ -1/\sqrt{2} & 1/\sqrt{2} & 0 \end{bmatrix}$	$\begin{bmatrix} -\cos\delta/\sqrt{2} & -\cos\delta/\sqrt{2} & -\sin\delta \\ -\sin\delta/\sqrt{2} & -\sin\delta/\sqrt{2} & \cos\delta \\ -1/\sqrt{2} & 1/\sqrt{2} & 0 \end{bmatrix}$

the lattice. Ytterbium has five isotopes with abundances in excess of 10%. The isotopes Yb^{171} and Yb^{173} have nuclear spins $I=\frac{1}{2}$ and $I=\frac{5}{2}$ and abundances of 14% and 17%, respectively; these isotopes exhibit hyperfine structure which appears as satellites about the position of the main line which arises from the other isotopes with $I=0$. Because of the complexity of the spectrum and because our main interest has been in the symmetry of the surroundings of the ions we have not determined the A parameters of Eq. (1) for the various spectra, but have limited our measurements to the central $I=0$ lines. These may be described by the equation

$$h\nu = g\beta H\,,$$

where

$$g=[(g_xh_x)^2+(g_yh_y)^2+(g_zh_z)^2]^{1/2} \tag{2}$$

and h_x, h_y, and h_z are the direction cosines of the applied field H with respect to the axes of the g tensor.

4. THE ANGULAR VARIATION OF THE SPECTRA

The angular variation of the spectra is best described in terms of a set of direction-cosine matrices. Let us take the edges of the unit cube as our reference axes, and let a, b, and c be unit vectors lying along these axes. If x, y, and z are unit vectors lying along the principal axes of the g tensor, the two sets of axes can be related by a matrix equation of the form

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} ax & bx & cx \\ ay & by & cy \\ az & bz & cz \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix} = [A] \begin{bmatrix} a \\ b \\ c \end{bmatrix}, \tag{3}$$

where the element ij of the matrix A is the cosine of the angle between the i and j axes. If the direction cosines of the external magnetic field H with respect to the axes a, b, and c are h_a, h_b, and h_c, respectively, the direction cosines of H with the axes x, y, and z are related by the equation

$$\begin{bmatrix} h_x \\ h_y \\ h_z \end{bmatrix} = [A] \begin{bmatrix} h_a \\ h_b \\ h_c \end{bmatrix}. \tag{4}$$

The effective g value for any orientation of the external field can then be calculated using Eq. (2).

For the orthorhombic spectra, the axes x, y, and z are defined as follows. The z axis lies along the [110] axis, and the x and y axes lie in the (110) plane and are displaced by an angle δ from the $[\bar{1}10]$ and [001] axes, respectively. Since there are twelve ways of permuting the axes to form a right-handed system, there are twelve different matrices, each corresponding to a physically distinguishable orientation of the charge compensation axes, which for an arbitrary direction of H, produce twelve different ESR lines.

Four of the twelve matrices, expressed in terms of the tilt angle δ, are given in Table I. The remaining eight matrices can be obtained by two cyclic permutations of the a, b, and c axies. Matrix (a) corresponds to the situation where the z axis bisects the a and b directions, and the y axis is tilted by $+\delta$ from the c axis, while matrix (b) corresponds to a tilt of $-\delta$ from the c axis. For matrices (c) and (d), the z axis bisects the $-a$ and $+b$ directions, (c) corresponding to a tilt of $+\delta$ from the c axis, and (d) to a tilt of $-\delta$.

Table II. Measured parameters of Yb^{3+} ions in CaF_2 in various rhombic fields.

Spectrum	g_x	g_y	g_z	δ (degrees)
R_1	6.99±0.01	1.355±0.002	1.094±0.002	3.2±0.2
R_2	7.24±0.01	0.992±0.002	0.957±0.002	26.3±0.2
R_3	unable to measure	1.241±0.002	1.096±0.002	8.8±0.5
R_4	6.45±0.02	2.175±0.002	1.667±0.002	0

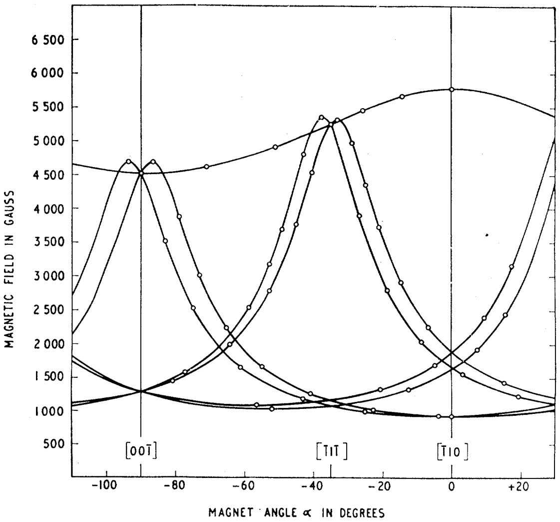

Fig. 1. The angular variation of the resonance field for spectrum R_1 of ytterbium ions in CaF_2 when H is rotated in the (110) plane. Data were taken at 8888 Mc/sec.

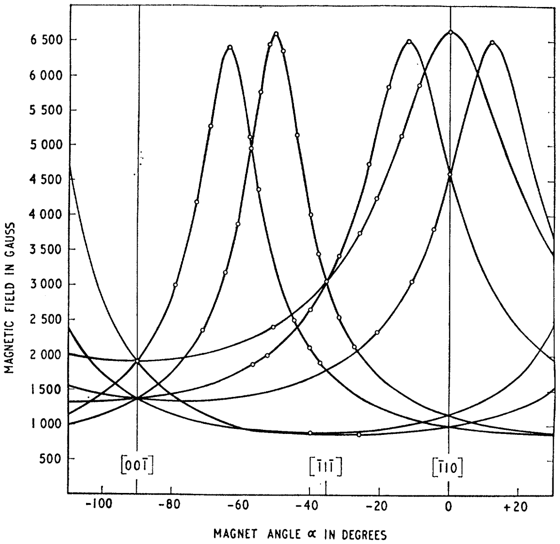

FIG. 2. The angular variation of the resonance field for spectrum R_2 of ytterbium ions in CaF_2 when H is rotated in the (110) plane. Data were taken at 8888 Mc/sec.

We have analyzed in detail four different orthorhombic spectra, each being characterized by a different tilt angle δ. The tilt angles and the corresponding g values are given in Table II. We have studied the angular variation of these spectra when the external field H was rotated in the two principal planes, (100) and (110).

With H lying in the (110) plane, and making an angle α with the $[\bar{1}10]$ axis, the direction cosines h_a, h_b, and h_c are, respectively, $-2^{-1/2}\cos\alpha$, $2^{-1/2}\cos\alpha$, and $\sin\alpha$. Because of spatial degeneracies, there are only seven sets of lines, five being doubly degenerate and two being singly degenerate. The angular variation of the two strongest sets of lines with $\delta=3.2°$ and $\delta=26.3°$ is shown in Figs. 1 and 2, respectively. The solid lines are theoretical curves using the parameters of Table II in the relations described above, and the small circles are experimental points, which are seen to be in excellent agreement. The spectrum simplifies considerably when H lies along directions of high symmetry; equations for the line positions when H is directed along the three principal directions are given in Table III. The spectrum is simplest with H directed along a $\langle 001\rangle$ axis, and consists then of only two lines, one line being fourfold degenerate and the other being eightfold degenerate. As H is rotated to lie along a $\langle 111\rangle$ direction, the lines regroup to form one sixfold degenerate line and two triply degenerate lines, and with H along a $\langle 110\rangle$ direction there are two doubly degenerate lines and two triply degenerate lines.

With H lying in the (100) plane, and making an angle α with the [011] axis, the direction cosines h_a, h_b, and h_c are 0, $\cos(\alpha+45)$, and $\cos(\alpha-45)$, respectively. The angular variations of the two strong spectra in this plane are shown in Figs. 3 and 4.

TABLE III. Equations for the effective g values with H directed along the three principal axes.

H oriented along	Effective g values	Degeneracy
$\langle 001\rangle$	$g=[g_x^2\sin^2\delta+g_y^2\cos^2\delta]^{1/2}$	4
	$g=[\frac{1}{2}g_x^2\cos^2\delta+\frac{1}{2}g_y^2\sin^2\delta+\frac{1}{2}g_z^2]^{1/2}$	8
	$g=[\frac{1}{3}g_x^2\sin^2\delta+\frac{1}{3}g_y^2\cos^2\delta+\frac{2}{3}g_z^2]^{1/2}$	6
$\langle 111\rangle$	$g=[g_x^2\sin^2(\delta+\phi)+g_y^2\cos^2(\delta+\phi)]^{1/2}$	3
	$g=[g_x^2\sin^2(\delta-\phi)+g_y^2\cos^2(\delta-\phi)]^{1/2}$	3
	$g=[\frac{3}{4}g_x^2\cos^2(\delta-\phi)+\frac{3}{4}g_y^2\sin^2(\delta-\phi)+\frac{1}{4}g_z^2]^{1/2}$	4
	$g=[\frac{3}{4}g_x^2\cos^2(\delta+\phi)+\frac{3}{4}g_y^2\sin^2(\delta+\phi)+\frac{1}{4}g_z^2]^{1/2}$	4
$\langle 110\rangle$	$g=g_z$	2
	$g=[g_x^2\cos^2\delta+g_y^2\sin^2\delta]^{1/2}$,	2
	where $\phi=\tan^{-1}2^{1/2}$	

The agreement between theory and experiment for these two spectra is good as demonstrated by Figs. 1–4; plots of g^2 against $\cos^2\alpha$ are straight lines to within the experimental error, indicating that these spectra are adequately described by the simple spin Hamiltonian of Eq. (1). However, spectrum R_3 shows a slight departure from this simple behavior. A plot of the variation of g^2 in the (110) plane against $\cos^2\alpha$ for the line described by matrix (c) of Table I with $\delta=8.8°$ shows a small departure from a straight line (the corresponding line for spectrum R_1 is the uppermost curve of Fig. 1 which moves from $g_{110}=g_z$ to $g_{001}=[g_x^2\sin^2\delta+g_y^2\cos^2\delta]^{1/2}$); the deviation is most pronounced along the $[1\bar{1}1]$ direction where the value of $\Delta g/g_{111}$ is 0.5%. Measurements on the two weaker spectra (R_3 and R_4) in the low-field region are made extremely difficult by overlap with much more intense lines from the other spectra, and the values for g_x were obtained by extrapolation

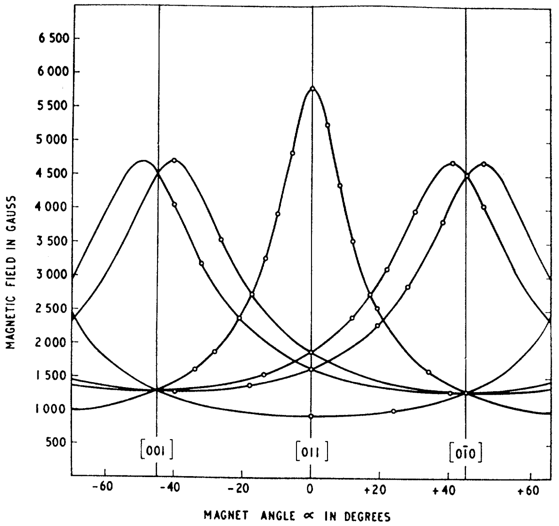

FIG. 3. The angular variation of the resonance field for spectrum R_1 of ytterbium ions in CaF_2 when H is rotated in the (100) plane. Data were taken at 8836 Mc/sec.

from the high-field region and consequently only approximate values can be given. We have therefore not been able to fit spectrum R_3 to a more exact Hamiltonian. The departure from the simple Hamiltonian presumably reflects either the presence of an additional interaction which may be due to the presence of a magnetic neighbor or an admixture with a near-lying excited level. Some evidence for the existence of such an excited level was found by the observation at 16°K of a weak rhombic spectrum which is absent at 1.5°K; in the (110) plane a line moving from $g_z=0.675$ with H lying along the [110] axis to $g=[g_x^2\sin^2\delta+g_y^2\cos^2\delta]^{1/2}=1.381$ with H lying along the [001] axis was observed; g^2 for this line also was not a simple linear plot against $\cos^2\alpha$. However, the remaining lines of the spectrum were weak and it has not so far been possible to determine the other g values or the angle δ and further work will be required.

The appearance of the ESR absorption spectra at 1.5°K with H directed along the [111] axis is shown in Fig. 5. The spectrum is complicated by hyperfine lines from the Yb^{171} and Yb^{173} isotopes which make identification of the weaker lines of the $I=0$ ytterbium spectra extremely difficult in the low-field region.

5. DISCUSSION

The interpretation of the rhombic spectra in terms of impurity ions situated in sites with different types of charge compensation is, unfortunately, not straightforward. In contrast to the thulium case, there is no doubt as to the valence state of the ytterbium ion; we can be sure from the g values of the ESR spectra that the ions giving rise to the rhombic spectra are in the trivalent state. The presence of Yb^{3+} ions situated in sites with various types of charge compensation can also be inferred from the infrared absorption spectrum; the results of this work will be reported in detail in a separate paper.[7] This result thus supports our earlier conclusion that the spectrum I of the Tm_2O_3:CaF_2 system arises from divalent rather than from tetravalent thulium ions since the mean of the trace of the g tensors of the orthorhombic spectra from Yb^{3+} and Tm^{2+} ions are very close (3.14 for spectrum R_1 of Yb^{3+} and 2.86 for Tm^{2+}, respectively).

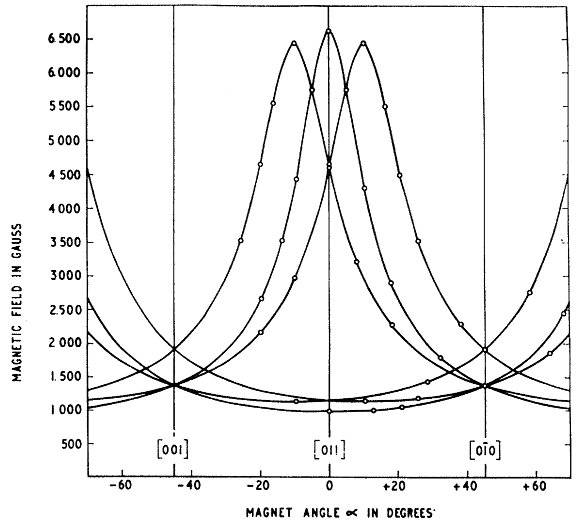

FIG. 4. The angular variation of the resonance field for spectrum R_2 of ytterbium ions in CaF_2 when H is rotated in the (100) plane. Data were taken at 8836 Mc/sec.

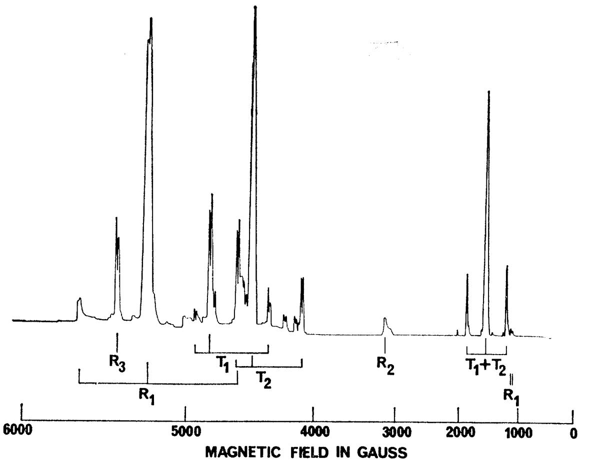

FIG. 5. The absorption spectrum of ytterbium ions in CaF_2 at 8888 Mc/sec when H is directed along the [111] axis. T denotes lines arising from centers having trigonal symmetry and R from those having rhombic symmetry. Spectrum R_4 is too weak to be observed in this recording, and can only be seen at higher gains.

The fact that one component of the g tensor in each case lies along a ⟨110⟩ axis indicates that all four spectra probably arise from variants of the same basic charge-compensation mechanism. If the basic distortion lies along a ⟨110⟩ axis, this most likely involves a modification of a neighboring Ca site; this could occur by the complete removal of the Ca ion to form a vacancy, or by a modification of its valence state, or by its replacement with another impurity ion. Alternatively, such a distortion could be produced by a symmetrical modification of two of the adjacent fluorine sites; this would most likely be by replacement with O^{2-} ions. However, we feel that this mechanism is less probable than a modification of the calcium site since two O^{2-} ions would be most likely to occupy sites at opposite corners of the F^- cube as was suggested by Yariv[8] in the case of U^{4+} ions in CaF_2.

Both classes of distortion would, however, only produce an orthorhombic spectrum where the x and y components of the g tensor lie along the [110] and [001] crystal axes. In order to produce a finite tilt angle δ the point symmetry about the Yb^{3+} ion must be further reduced; this indicates the presence of an extra charge which causes the x and y axes to be rotated in

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[7] J. Kirton and S. D. McLaughlan (to be published).

[8] A. Yariv, Phys. Rev. 128, 1588 (1962).

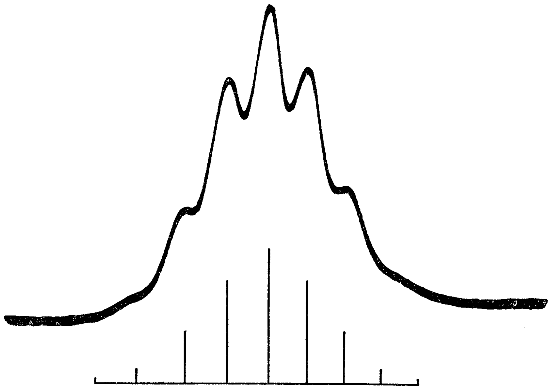

FIG. 6. The superhyperfine structure on spectrum R_3 when H is directed along the [001] axis. The components are separated by about 8 G.

the (110) plane. Obviously this charge must then occupy different lattice positions to produce the different types of spectra. Unfortunately one can not use the experimentally observed values of δ to deduce the position of this charge since its position and the minor axes of the g tensor are not necessarily related in a simple manner. Thus without additional evidence the exact nature of the charge compensation can only be somewhat speculative. Further evidence might be obtained, for example, from electron-nuclear-double-resonance studies, which should be able to determine whether the neighboring F^- shells are complete. In one case (spectrum R_3 with $\delta=8.8°$) the superhyperfine structure is well resolved when H is directed along the [001] direction (see Fig. 6). The weighting of the components, which are separated by about 8 G, agrees to within the experimental error with that expected from equal interaction with eight similar ions with nuclear spin $I=\frac{1}{2}$ (1:8:28:56:70:56:28:8:1), but this could well be fortuitous. Spectra R_1 and R_3 also exhibit a splitting of the resonance lines into doublets with a separation of ~10 G when the external field H is directed along a $\langle 111\rangle$ direction. This effect was previously reported by Low and Ranon[4] for spectra with trigonal symmetry. This splitting is caused by a preferential interaction with the nuclear spin of one of the nearest-neighbor F^- ions.[9]

Mahlab *et al.*[10] have reported a spectrum from U^{3+} ions in CaF_2 having the same symmetry as those which we describe here. In their case δ was 19±1°. They proposed that this spectrum arose from a U^{3+} ion with an F^- ion occupying one of the nearby interstitial sites; more precisely, if the U^{3+} ion was situated at the position (0,0,0), they proposed that the F^- ion occupied sites of the type $(1,1,\frac{1}{2})$. The two ions lie in the (110) plane and the line joining them is tilted by an angle of 19.5° from the $[\bar{1}10]$ axis. The fact that the x axis of their spectrum passed through the center of an interstitial site may have been coincidental, but if their model is correct it is surprising that a spectrum corresponding to the nearer $(1,0,\frac{1}{2})$ type of interstitial sites was not observed as well. It seems unlikely to us that a model based on a distribution of interstitial F^- ions could explain our spectra since the simplest of this type of compensation, leading to a spectrum with tetragonal symmetry, is not observed at all in our crystals.

In our earlier paper we suggested that when CaF_2 is doped with a rare-earth sesquioxide the rare-earth ions enter the lattice as trivalent ion pairs. In the thulium case the interaction between the magnetic Tm^{2+} ion and the nonmagnetic Tm^{3+} ion would be solely through the Coulomb force, but for two Yb^{3+} ions situated on adjacent sites one would expect to find evidence of a magnetic coupling as well. For example, Baker[11] has observed a dipolar coupling between neighboring Nd^{3+} ions in lanthanum ethyl sulphate. However, the two strongest ytterbium spectra show no evidence of such an interaction. Spectrum R_3 does show a slight departure from the simple spin Hamiltonian but this spectrum accounts for only a small proportion of the total number of Yb^{3+} ions. Considerable doubt is thus cast upon the pair model. It is possible that the neighboring ion could be a nonmagnetic Yb^{2+} ion, since the presence of Yb^{2+} ions in the "as grown" crystals is evident from the strong uv absorption band. The Yb^{2+} ion would be expected to be particularly stable since it has a complete $4f$ shell; this idea is supported by the observation that the total concentration of Yb^{3+} ions present in an "as grown" crystal grown from a melt containing 0.05 at. % can be reduced by a factor of 10 by heating in a hydrogen atmosphere at 1000°C for 20 h. However, there would appear to be no good reason why large numbers of Yb^{3+}-Yb^{2+} pairs should be formed in the crystal at concentrations as low as 0.05 at. % without the simultaneous production of Yb^{3+}-Yb^{3+} pairs as well.

6. CONCLUSIONS

It is apparent from the results presented above, from our earlier measurements on thulium, and from initial work on cerium, terbium and dysprosium, that CaF_2 doped with rare-earth sesquioxides exhibits ESR spectra with lower symmetries than are normally found in crystals doped with the corresponding fluorides. These spectra reflect a charge compensation mechanism which is rather more complex than the various types involving a single ion which are usually found in CaF_2. The presence of oxygen during growth appears to be crucial to the formation of these centers and is probably directly involved in the charge compensation itself. In our earlier paper on thulium we suggested that Tm^{3+} ions entered the lattice in pairs on adjacent calcium sites and were bonded together by two substitutional

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[11] J. M. Baker, Phys. Rev. **136**, 1341 (1964).

O^{2-} ions, the Tm^{2+}-Tm^{3+} pairs then being formed by γ irradiation. This model provided the required distortion along the $\langle 110\rangle$ axes and accounted for the need for oxygen during the growth process. However, the absence of spectra corresponding to Yb^{3+}-Yb^{3+} pairs seems to argue against this model. It is still possible that the spectra could arise from Yb^{3+}-Yb^{2+} pairs, and that the rotation of the x and y axes in the (110) plane could be produced by a migration of one of the O^{2-} ions to a more remote F^- site, but this seems to us to be rather unlikely. The construction of a detailed model for the compensation must therefore await further experiments.

ACKNOWLEDGMENTS

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Spherical Model with Long-Range Ferromagnetic Interactions*

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The behavior of the spherical model of a ferromagnet with an interaction energy between the magnetic spins which varies with distance as $1/r^{d+\sigma}$ (where d is the dimensionality of the lattice and $\sigma>0$) is analyzed. It is shown that the model exhibits a ferromagnetic transition in one and two dimensions, providing $0<\sigma<d$. (The usual spherical model with nearest-neighbor interactions does not have a transition in one and two dimensions.) The critical-point behavior is investigated. It is found that the singularities in the specific heat and susceptibility are dependent on σ and d, but the behavior of the magnetization is independent of σ and d. In three dimensions the susceptibility diverges as $(T-T_c)^{-\gamma}$, where $\gamma=1$ for $0<\sigma<\frac{3}{2}$, $\gamma=\sigma/(3-\sigma)$ for $\frac{3}{2}<\sigma<2$ and $\gamma=2$ for $\sigma>2$. The asymptotic form of the spin-spin correlation function $\Gamma(\mathbf{r})$ is studied in the neighborhood of the critical temperature T_c. At $T=T_c$, $\Gamma(\mathbf{r})$ decays for large r as $1/r^{d-\sigma}$. Several two-dimensional models with long-range interactions falling off as $1/r^2$ in certain directions only are also investigated.

1. INTRODUCTION

In this paper, the properties of the spherical model with long-range ferromagnetic interactions between the spins, varying as $1/r^{d+\sigma}$, are determined. The spherical model may be considered as an approximate representation of the "more realistic" Ising model. Although considerable success has been achieved in the understanding of systems with certain types of long-range interactions, little detailed information is available concerning the behavior of systems with interaction potentials decaying as $1/r^{d+\sigma}$. Some of the main results so far obtained are now briefly reviewed, in order to see what light they throw on the properties of $1/r^{d+\sigma}$ interactions.

Exact results have been obtained by Kac, Uhlenbeck, and Hemmer[1–4] for a one-dimensional model of hard rods with exponential attractive interactions, and by Baker,[5,6] and Kac and Helfand[7] for the Ising model in one and two dimensions with exponential interactions in certain directions. In the limit that the exponential interaction becomes infinitely long-range, the one-dimensional gas has a phase transition, which is described exactly by the van der Waals equation (with the Maxwell equal-area rule), while the Ising models show a Bragg-Williams-type transition in this limit.[7a] Whether the properties of these systems (especially the critical properties) are characteristic of systems with more realistic interactions of the form $1/r^{d+\sigma}$ is not at present known. There is, however, as we shall see, some evidence to suggest that this is not so.

Using diagrammatic methods, Brout[8] has developed an expansion of the thermodynamic functions of the Ising model, as a power series in the reciprocal range of the interaction. It is found that the expansion reduces to the Weiss-Bragg-Williams result in the limit of infinite-range interactions. However, for finite-range interactions, the expansion breaks down in the critical region. Brout[8] and, later, Horwitz and Callen[9] have partially overcome these difficulties by obtaining self-

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[7a] *Note added in proof.* It has been shown rigorously by J. L. Lebowitz and O. Penrose [J. Math. Phys. **7**, 98 (1966)] that, for a general class of interaction potentials which have a range parameter $1/\gamma$, the van der Waals–Maxwell result is obtained in the limit $\gamma\rightarrow 0$, in any dimension.

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