

Orthorhombic Electron Spin Resonance Spectrum of U^{3+} in CaF_2 †

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An orthorhombic spectrum of U^{3+} in CaF_2 was measured. The orthorhombic X , Y axes are found to lie in the (110) plane and the Z axis perpendicular to these axes. The X axes are at $\pm(19\pm 1)^\circ$ with the $[1\bar{1}0]$ direction. There are, in general, twelve inequivalent magnetic sites. The g factors corresponding to one set of axes are $g_x=1.38\pm 0.01$, $g_y=2.85\pm 0.02$, and $g_z=2.94\pm 0.01$. Various models explaining this spectrum are discussed. The most likely model is that of an interstitial F^- in the second-nearest neighbor position.

I. INTRODUCTION

THE crystal structure of CaF_2 is cubic. The Ca^{2+} ion is situated in the center of alternate cubes surrounded by eight fluorine ions. The substitution of a trivalent ion such as U^{3+} for Ca^{2+} causes a charge unbalance. Different charge compensations corresponding to different point symmetries have been reported. Bleaney *et al.*¹ have measured a spectrum corresponding to a tetragonal symmetry which is explained to arise from an interstitial fluorine ion in the nearest cube. Title² has measured electron spin resonance (ESR) spectrum of U^{3+} in a cubic symmetry. Porto and Yariv^{3,4} and Title² have reported a U^{4+} spectrum with trigonal symmetry, where the charge compensation is caused by O^{2-} ions replacing the F^- ion at one of the eight corners of the cube. A spectrum of U^{3+} with trigonal symmetry has not been reported so far although such spectra are found in rare earth ions.^{5,6} In this paper we describe the ESR spectrum of a new charge compensation site, one of orthorhombic symmetry, which was previously reported by Yariv.³

II. EXPERIMENTAL RESULTS

We report here in detail a spectrum of orthorhombic symmetry of U^{3+} in CaF_2 . One of the crystals was grown by Solid-State Materials Corporation. The starting doping material was $NaUF_4$. This compound was expected to dissociate into UF_3 and NaF at sufficiently high temperatures, resulting in a possible charge compensation through Na^+ which is expected to replace

Ca^{2+} . Other crystals were grown at Optovac, Inc. without Na^{1+} charge compensation.

The spectrum was measured with a conventional ESR spectrometers. The measurements were made at 1.2-cm and at 3-cm wavelength and at liquid-hydrogen temperatures. We could not observe any spectrum at liquid-nitrogen temperatures presumably because of short relaxation times.

Two stronger spectra were observed. The strongest lines, about ten times more intense than the other lines, could be assigned to the tetragonal spectrum. The measured g factors agree within the experimental errors with those reported by Bleaney *et al.*¹ The other stronger lines were assigned to a spectrum of orthorhombic symmetry. Some of the crystals in which the orthorhombic spectrum was found also contained U^{4+} ions. Additional anisotropic weak lines were observed which we have not investigated in detail. One of these crystals showed an isotropic spectrum which could be assigned to Er^{3+} in a cubic field.

The direction of the three orthorhombic axes X , Y , Z , and the g factors along these axes were found as follows. The X axis was defined as the direction of the magnetic field in which the g value would have the smallest value (i.e., the direction of the magnetic field in which the magnetic resonance field, H , would be a maximum, when the microwave frequency is held constant). This direction was found to be in the (110) plane, and to make an angle of $(19\pm 1)^\circ$ with the $[1\bar{1}0]$ direction (i.e., an angle of $90\pm 19^\circ$ with respect to the cubic axes). The angular variation of this line in this plane is shown in Fig. 1.

The second site with an X axis in the (110) plane has a spectrum which is obtained by reflection about the $[1\bar{1}0]$ axis and is indicated only by its maximum at $\theta=109^\circ$. The Y axis was found to be in the (110) plane, and in the direction at which the ESR of this particular line could be observed. To make sure that this axis lies indeed in the (110) plane, the following experiment was performed. The (110) plane was slightly tilted. If the angular variation of the line was followed from g_x towards g_y , one would expect two lines to appear because of the two unequal projections of the g factors of

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¹ B. Bleaney, P. W. Llewellyn, and D. A. Jones, *Proc. Phys. Soc. (London)* **B69**, 858 (1956).

² R. S. Title, in *Proceedings of the First International Conference on Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), p. 178.

³ A. Yariv, in *Proceedings of the First International Conference on Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), p. 189.

⁴ S. P. S. Porto and A. Yariv, *J. Appl. Phys.* **33**, 1620 (1962).

⁵ J. Sierro, *J. Chem. Phys.* **34**, 2183 (1961).

⁶ W. Low, in *Proceedings of the International Conference on Magnetism and Crystallography 1961* (The Physical Society of Japan, Bunkyo-Ku-Tokyo, 1962), Vol. I, p. 440.

the two possible Y axes on this new plane. No such doubling was found and, therefore, the Y axis is contained in the (110) plane. The Z axis being perpendicular to both the X and Y axes is in the $[1\bar{1}0]$ direction.

A partial plot of the spectrum of a site whose Z axis is in the $[1\bar{1}0]$ direction and from which g_z was measured is shown in Fig. 1. The remaining two maxima at 4320 G are due to two sites whose X axes are in the (101) and $(\bar{1}10)$ planes. These two sites become equivalent when the magnetic field is in the (110) plane. The small departures from perfect orientation present in the experiment spoiled the perfect equivalence of these two sites and caused the appearance of a closely spaced doublet which served as a confirmation for the site

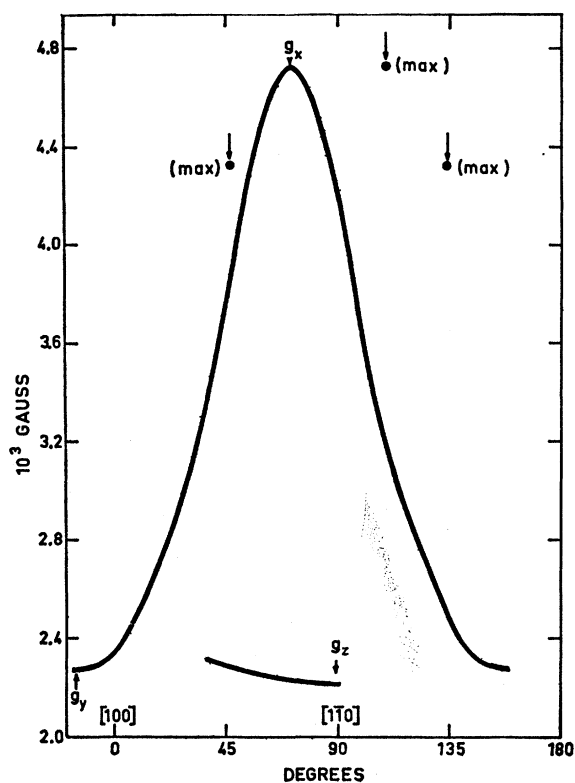


FIG. 1. The angular variation of spectrum in the (110) plane. The arrows indicate the extreme magnetic fields at which the spectrum was observed in this plane.

assignment. Figure 2 illustrates these three axes as related to the cubic axes. Clearly, each (110) plane contains two ions belonging to two different sites. In general, there are six different (110) planes; therefore, twelve lines corresponding to twelve different sites can be observed.

The g values along the three X, Y, Z directions were determined as follows. The crystal was mounted in the (110) plane and the g_x and g_y value measured at the maximum and minimum magnetic fields of one line related to one of the two possible sites in this plane (as seen in Fig. 1). The g_z value was measured on a line

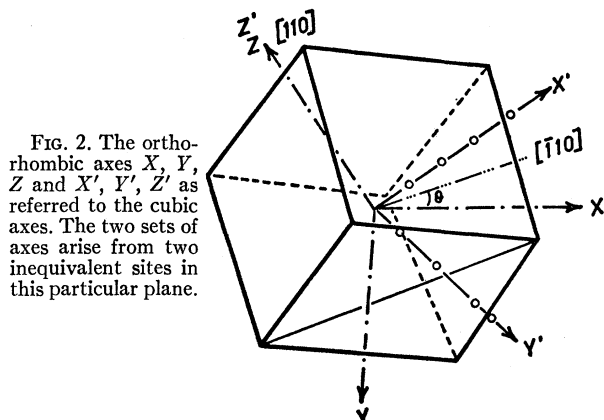


FIG. 2. The orthorhombic axes X, Y, Z and X', Y', Z' as referred to the cubic axes. The two sets of axes arise from two inequivalent sites in this particular plane.

belonging to a different site whose z axis is in the same plane. This is also indicated in Fig. 1. These g factors were confirmed by plotting the angular variation of the spectrum in the two planes, in the (110) plane and in a plane which is obtained by rotating the (110) plane by 20° around the $[110]$ axis and g_x, g_y , and g_z calculated from these data. The magnetic field directions with respect to the cubic axes were determined as follows. The g factors of the three lines of tetragonal symmetry depend on the cosine of the angles which the tetragonal axes make with the magnetic field. Hence, by measuring carefully the g factors of these three lines the cosine of

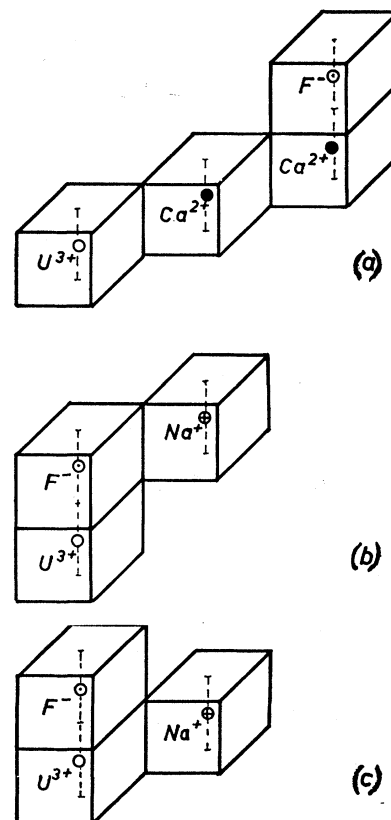


FIG. 3. Possible models to explain the charge compensation which leads to the anisotropy of the g factor. Figure 3(a) shows an interstitial F^- ion in the second-nearest neighbor position. Figure 3(b) and 3(c) assume a combination of a substitutional Na^+ and interstitial F^- ion to explain the orthorhombic axes.

these angles is determined and, therefore, the direction of the magnetic field. The tetragonal lines serve, in a sense, as an internal goniometer. The agreement between these various methods of determining the g factors was good.

The spin Hamiltonian with which the spectrum can be described is given by

$$H = \beta [g_x H_x S_x + g_y H_y S_y + g_z H_z S_z], \quad S = \frac{1}{2}$$

$$g_x = 1.38 \pm 0.01, \quad g_y = 2.85 \pm 0.02, \quad g_z = 2.94 \pm 0.01.$$

It is to be noted that $(g_x + g_y + g_z)/3 = 2.39$ and in the case of the tetragonal symmetry $(g_{11} + 2g_{12})/3 = 2.41$. This close agreement gives strong confirmation that the spectrum observed is indeed caused by the $U^{3+}(f^3)$ ion. Additional confirmation is obtained from the optical spectrum which showed new lines in the regions where the spectrum of U^{3+} —tetragonal symmetry is found.

DISCUSSION

A number of models can explain the observed spectrum. The X axis is pointing to the center of second-nearest neighbor cube. The charge compensation must, hence, be either an F^- ion or a combination of monovalent ion such as Na^+ and F^- ions compensating for

the excess charge of two U^{3+} ions. The possibility of charge compensation by O^{2-} is dismissed, since the orthorhombic spectrum has been seen in crystals in which no evidence of trigonal U^{3+} or U^{4+} has been found.

The most likely possibility is to assume an F^- ion in the second-nearest interstitial position as shown in Fig. 3(a). The anisotropy in the observed spectrum is a little smaller than that of the tetragonal spectrum. The crystal field is smaller and this gives rise to a smaller anisotropy than in the case where the F^- ion is at a tetragonal site, although a still smaller anisotropy would have been expected because of the large U^{3+} — F^- separation in this model. Other possibilities are shown in Figs. 3(b) and 3(a). In this case the combination of a substitutional Na^+ ion in a corner cube, or in an edge cube and an interstitial F^- ion in the adjacent cube can give rise to the distortions observed. These two models can be dismissed since the orthorhombic spectrum is also observed in crystals which have not been co-doped with Na^+ .

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Neutron Diffraction Investigation of the Magnetic Properties of Compounds of Rare-Earth Metals with Group V Anions

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The magnetic properties of heavy rare-earth compounds with the NaCl-type structure have been investigated at temperatures between 295 and 1.3°K by neutron diffraction experiments on powdered specimens. All of the nitrides except TmN have a net ferromagnetism at low temperatures, but the diffraction patterns indicate a complicated type of magnetic order. HoP also has an unusual magnetic structure at low temperatures and this structure is presumably stabilized by dipole forces. The other phosphides, antimonides, and arsenides were found to have magnetic ordering transitions to the Mn-O type of antiferromagnetic structure. Low values of the atomic moments and large magnetic anisotropies in the ordered magnetic structures indicate the effects of crystal field interactions at low temperatures.

INTRODUCTION

ALTHOUGH a large amount of research has been performed in recent years on various types of rare-earth compounds, the magnetic properties of these systems are not well understood. In most of these compounds, interpretation of the experimental results has been seriously complicated by crystal distortions or by the presence of other magnetic ions. Consequently, an investigation of the magnetic properties of compounds formed by rare-earth ions and Group V anions was of considerable interest, because these compounds

crystallize in the simple NaCl-type structure and should be more amenable to theoretical analyses.

Only a few experiments of any type have been performed on these compounds, so that there is very little information which is helpful in the understanding of their magnetic properties. The interpretation of the magnetic ordering that exists at low temperatures is based entirely on the neutron diffraction results and on the theoretical calculations by Trammell.^{1,2}

¹ G. T. Trammell, *J. Appl. Phys.* **31**, 362S (1960).

² G. T. Trammell, following paper, *Phys. Rev.* **131**, 932 (1963).