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Paramagnetic Resonance of Pr^{3+} and U^{4+} Ions in CaF_2

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Paramagnetic resonance has been observed from Pr^{3+} and U^{4+} ions in CaF_2, in sites having trigonal symmetry. These spectra have been fitted to a spin Hamiltonian:

$$H=\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+\Delta_xS_x+\Delta_yS_y+AS_zI_z.$$

Two trigonal spectra have been observed for Pr^{3+}:

$$(1)\quad g_\parallel=5.65\pm0.01,\quad g_\perp\leq0.1,\quad A^{141}=(2675\pm7)\times10^{-4}\text{ cm}^{-1}\quad \Delta=0.05\pm0.01\text{ cm}^{-1},$$

$$(2)\quad g_\parallel=5.83\pm0.01,\quad g_\perp\leq0.1,\quad A^{141}=(2667\pm7)\times10^{-4}\text{ cm}^{-1}\quad \Delta=0.05\pm0.01\text{ cm}^{-1}.$$

The new trigonal spectra observed for U^{4+} are:

$$(1)\quad g_\parallel=4.02\pm0.01,\quad g_\perp\leq0.1,\quad \Delta=0.03\pm0.01\text{ cm}^{-1},$$
$$(2)\quad g_\parallel=5.66\pm0.02,\quad g_\perp\leq0.1,\quad \Delta=0.03\pm0.01\text{ cm}^{-1}.$$

Two overlapping, almost isotropic resonances having $g\sim2$ are also observed from uranium oxide–doped crystals, and these are thought to arise from U^{4+} in sites having cubic symmetry.

INTRODUCTION

Calcium fluoride consists of a cubic lattice of fluorine ions in which every other body-center position is occupied by a divalent calcium ion. Rare-earth ions enter the lattice substitutionally at Ca^{2+} sites, normally in the trivalent state, the extra positive charge being compensated by an extra negative charge. This negative charge generally sits near the trivalent rare-earth ion and locally distorts the cubic symmetry of the crystal field. A wide variety of distortions can be produced in CaF_2 depending on the method, conditions of growth, and starting materials. If crystals are pulled from a melt containing CaF_2 and a small amount of rare-earth fluoride, then one generally observes the rare-earth ions in sites having cubic, tetragonal, or trigonal symmetry.[1] If, however, the crystals are pulled at a rapid rate from a melt of CaF_2 and 0.05% rare-earth oxide, then one usually observes resonances from sites having rhombic symmetry[2–5] and also in a few cases,[2–4] from axial sites normally present in crystals doped with rare-earth fluorides. The results obtained for Pr^{3+} and its related ion in the actinide group, U^{4+}, are described in this paper.

CRYSTAL PREPARATION AND EXPERIMENTAL PROCEDURE

The crystals were grown by the Czochralski method by G. W. Green of these laboratories and by Barr and Stroud Ltd. They were pulled from the melt at a rate of 1–4 in./h from a vitreous carbon crucible in an atmosphere of 99.998% pure argon. The praesodymium was either introduced into the melt in the oxide form or as a fluoride while the uranium was in oxide, fluoride, or metal form. In all cases the level of doping was 0.05 at %.

The measurements were taken at 1.4°K using 9 and 35 Gc/sec superheterodyne spectrometers which have been described in a previous paper.[5] Most observations were made with the crystals in the (110) plane and orientation into this plane was achieved by using {111} cleavage planes and a 35.3° Teflon wedge in the cavity. Any residual misorientation was then removed by tilting the cryostat assembly.

SPIN HAMILTONIAN

Having integral J quantum numbers, Pr^{3+} and U^{4+} are non-Kramers ions and their spectra can be interpreted in terms of the spin Hamiltonian[6]

$$\mathcal{H}=\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+\Delta_xS_x+\Delta_yS_y+AS_zI_z+B(S_xI_x+S_yI_y),$$

where $\Delta^2=\Delta_x^2+\Delta_y^2$; the first term is the Zeeman energy of an effective spin $S=\frac{1}{2}$ in a dc magnetic field H, the second and third terms describe the zero-field splitting, and the remaining terms represent the hyperfine interaction. For praesodymium, the nuclear spin $I=\frac{5}{2}$ arises from the 100% abundant Pr^{141} isotope. Natural uranium, on the other hand, is composed of almost 99% U^{238}, which has zero nuclear spin, so that only the first three terms of the Hamiltonian are required in this case.

The ground state of a non-Kramers ion has a degeneracy which can be removed in two ways. Either the crystal field produces a static splitting and leaves singlet states lowest, or it leaves a time-reversed doublet lowest, which is then split by a dynamic Jahn-Teller distortion. If transitions are observed between singlet

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[1] M. J. Weber and R. W. Bierig, Phys. Rev. **134**, 1492 (1964).

[2] S. D. McLaughlan, P. A. Forrester, and A. F. Fray, Phys. Rev. **146**, 344 (1966).

[3] S. D. McLaughlan, Phys. Letters **20**, 486 (1966).

[4] S. D. McLaughlan and P. A. Forrester, Phys. Rev. (to be published).

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

[6] J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) **A245**, 156 (1958).

states then it can easily be shown[7] that a symmetrical resonance line results, while if a time reversed doublet is lowest, then one observes an asymmetric resonance line. In both the Pr^{3+} and the U^{4+} spectra, asymmetrically shaped lines were observed, thus showing that the resonances were from transitions between the components of a time reversed doublet. From the asymmetry of the resonance lines a value of Δ can be obtained[6] in the following way. If H is the magnetic field at the peak of the resonance line and H_0 the magnetic field corresponding to the high-field cutoff point then,

$$\Delta^2 = 2h\nu g_{\parallel}\beta(H_0 - H),$$

where $g_{\parallel}$ is the true g value measured at H_0. This estimate of Δ can also be verified by measuring the field at which the peak of the resonance line occurs at two widely different frequencies. In the cases of Pr^{3+} and U^{4+} where $g_{\perp}$ and B are zero to within experimental error, this field is given by

$$H = \{[(h\nu)^2 - \Delta^2] - Am/g\beta\}.$$

Both methods were used in these experiments and gave results which were in good agreement.

$\mathbf{Pr^{3+}}$ $\mathbf{4f^2\ {}^5H_4}$ $\mathbf{\Delta = \frac{4}{5}}$

Previously paramagnetic resonance has been observed from Pr^{3+} in lanthanum magnesium nitrate.[8] This consisted of six well-resolved hfs lines due to the nuclear spin of the only stable isotope Pr^{141} ($I = \frac{5}{2}$), the spectrum having $g_{\parallel} = 1.55$ and $g_{\perp} \sim 0$. Resonance has also been seen from Pr^{3+} in yttrium ethyl sulfate[6] having $g_{\parallel} = 1.525 \pm 0.02$ $A = (755 \pm 20) \times 10^{-4}$ cm^{-1} and a distortion parameter $\Delta = 0.11 \pm 0.04$ cm^{-1}.

In the present work no paramagnetic resonance attributable to Pr^{3+} was detected when CaF_2 was doped with 0.05 at.% PrF_3. Doping with praesodymium oxide produced no rhombic resonances as have been observed from crystals doped with other rare-earth oxides. However two sets of resonances arising from two types of sites having trigonal symmetry were observed. The strongest, spectrum 1, was about twice as intense as spectrum 2, both spectra having very similar g and A values (see Table I). The distortion parameter was estimated from measurements made at 9 and 35 Gc/sec and also from the asymmetry of the absorption lines at 9 Gc/sec. These measurements were in reasonable agreement and gave $\Delta = 0.05 \pm 0.01$ cm^{-1} for both spectra. $A/\beta g_{\parallel}$ is 1014 and 980 G for trigonal spectra 1 and 2, respectively, and should be compared with 1050 G measured for Pr^{3+} in yttrium ethyl sulphate and 1060 G in lanthanum magnesium nitrate.

TABLE I. Summary of paramagnetic-resonance data for Pr^{3+} and U^{4+} in CaF_2.

Ion	Crystal-field symmetry	$g_{\parallel}$	$g_{\perp}$	Δ (cm^{-1})	A (10^{-4} cm^{-1})
Pr^{3+}	trigonal 1	5.65 ± 0.01	≤ 0.1	0.05 ± 0.01	$A^{141} = 2675 \pm 7$
Pr^{3+}	trigonal 2	5.83 ± 0.01	≤ 0.1	0.05 ± 0.01	$A^{141} = 2667 \pm 7$
U^{4+}	trigonal 1	4.02 ± 0.01	≤ 0.1	0.03 ± 0.01	...
U^{4+}	trigonal 2	5.66 ± 0.02	≤ 0.1	0.03 ± 0.01	...
U^{4+}	trigonal 3[a]	3.238 ± 0.005	≤ 0.1	0.1	...
U^{4+}	cubic	2.00[b]	...	...	...

[a] A. Yariv (Ref. 9).
[b] See text.

These new trigonal spectra are much more anisotropic than those previously reported for the other lattices. Under the influence of the C_{3v} crystal field the nine-fold degeneracy of the ${}^3H_4$ ground state is split into three doublets and three singlets and the observed resonances arise from the lowest doublet. Assuming no admixture from the ${}^3H_5$ level, the wave functions of this doublet are made up of linear combinations of the $J = 4$ manifold wave functions, and are of the form

$$|\alpha\rangle = a|4\rangle + b|1\rangle + c|-2\rangle,$$
$$|\beta\rangle = a|-4\rangle - b|-1\rangle + c|2\rangle.$$

Since we have only one nonzero g value and the normalization condition, the wave function of the ground state cannot be determined without optical-absorption data. If however this linear combination is dominated by one particular J_z component, then $g_{\parallel} \sim 2\Lambda|J_z\rangle$. Assuming $J_z = 4$, then $g_{\parallel} \sim 6.4$, which is not too far removed from $g_{\parallel} = 5.65$ and 5.83 observed for spectra 1 and 2, respectively. Hence we can conclude that the wave function is largely composed of the $J_z = 4$ element since this is the only component that can generate the observed large g values.

$\mathbf{U^{4+}}$ $\mathbf{5f^2\ {}^3H_4}$, $\mathbf{\Delta = \frac{4}{5}}$

U^{4+} is the ion in the actinide group which has the same number of unpaired electrons as Pr^{3+} and hence is also a non-Kramers ion. Previous investigations into this ion in CaF_2 by Yariv[9] and by Title *et al.*[10] revealed a trigonal resonance with $g_{\parallel} = 3.238 \pm 0.005$, $g_{\perp} \sim 0$ and $\Delta = 0.1$ cm^{-1}. Yariv attributed this resonance to U^{4+} ions which were compensated by two O^{2-} ions replacing two F^- ions along any of the $\langle 111 \rangle$ directions.

In our crystals, those doped with UF_4 appeared either dark red in color showing the previously reported U^{3+} resonances,[11] or dark brown showing a new U^{4+} trigonal resonance (type 1), presumably depending on the amount of oxygen contamination during growth. This new resonance has a $g_{\parallel} = 4.02 \pm 0.01$ and $g_{\perp} \leq 0.1$ and the line split into at least five irregularly spaced components as H was rotated away from the parallel position. Crystals doped with uranium metal appeared either light green or dark brown in color and showed

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[7] J. Kirton, Phys. Rev. **139**, 1930 (1965).

[8] A. H. Cooke and H. J. Duffus, Proc. Roy. Soc. (London) **A229**, 407 (1955).

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

[10] R. S. Title, P. P. Sorokin, M. J. Stevenson, G. D. Pettit, J. E. Scardefield, and J. R. Lankard, Phys. Rev. **128**, 62 (1962).

[11] B. Bleaney, P. M. Llewellyn, and D. A. Jones, Proc. Phys. Soc. (London) **A69**, 858 (1956).

either the type-1 U^{4+} trigonal resonance as observed in fluoride-doped crystals, or yet another new U^{4+} resonance (type 2) with g values very similar to the new spectra observed for Pr^{3+} i.e.

$$g_{\parallel}=5.66\pm0.02, \quad g_{\perp}\leq0.1\,.$$

This spectrum showed superhyperfine structure on the asymmetric line up to 45° from the $\langle 111\rangle$ compensation axis. Both these new U^{4+} resonances had distortion parameters $\Delta=0.03\pm0.01$ cm^{-1}. Crystals doped with uranium oxide also appeared dark brown in color and showed a very weak type-2 spectrum as observed in the crystals doped with uranium metal. As in the case of Pr^{3+} no rhombic resonances were observed from any of the crystals, no matter how they were doped, nor was there any trace of the trigonal resonance observed by Yariv. The wave functions for the U^{4+} trigonal spectra are similar to those for Pr^{3+} but again as in the case of Pr^{3+} there is insufficient information to determine these exactly.

Crystals doped with uranium oxide not only showed the weak type-2 trigonal resonance but also a much stronger, sharp, almost isotropic resonance, having $g=2$ which on closer examination could be resolved into two lines in some directions. The greatest splitting was observed when H was along the [110] direction, and was of the order of 10 G. These resonances may arise from U^{4+} in cubic sites. The cubic field ground state of U^{4+} should be either a Γ_1 or Γ_5 depending on the ratio of fourth- to sixth-order crystal-field parameters.[12] Weber and Bierig[1] estimate that in the case of Pr^{3+} the Γ_5 is lowest. The cubic-field wave functions describing the Γ_5 state for $J=4$ are

$$\Psi_1=(\tfrac{7}{8})^{1/2}|\pm3\rangle-(\tfrac{1}{8})^{1/2}|\mp1\rangle$$

and

$$\Psi_2=1/\sqrt{2}\{|2\rangle-|-2\rangle\}\,.$$

In a magnetic field this state will behave like a spin-1 triplet yielding an isotropic resonance having $g=2$. It is therefore possible that the two resonances observed are from this triplet, the degeneracy being lifted slightly by an admixture from the $^3H_5$ level.

CHARGE-COMPENSATION MECHANISMS

A crystal field having trigonal symmetry can be produced by the replacement of one of the eight nearest-neighbor F^- ions by an O^{2-} ion, a mechanism discussed by Feofilov.[13] Most trigonal resonances in CaF_2 are ascribed as being due to this mode of compensation. In some cases where two trigonal spectra have been seen e.g. Gd^{3+},[14] Yb^{3+},[15] the second spectrum has been attributed to OH^- compensation on the basis of hydrolysis experiments performed by Sierro.[14] In the case of Yb^{3+} however this assignment is very much in doubt.[16] Another interesting possibility has been suggested by Ranon,[17] in which compensation is achieved by an F^- ion in the next-nearest interstitial site. This is not thought to be a likely mechanism for the trigonal sites described here since one would only expect this to occur in crystals having an excess of F^- ions, and hence one should also observe the usual tetragonal sites due to nearest-neighbor interstitial F^- compensation. A similar objection can be raised against Yariv's second model for charge compensation for U^{4+}. He suggests that O^{2-} in the next-nearest interstitial site may be responsible for the distortion of the crystal field along the [111] axis. If this were so then again there seems no good reason why there should not be a tetragonal spectrum present as well, due to O^{2-} ions in the nearest interstitial sites to the U^{4+} ions.

In the case of U^{4+} the total charge compensation need not be local as demonstrated by the apparent appearance of U^{4+} on cubic sites. Charge compensation for the U^{4+} ions can also be partly local, producing the observed trigonal distortion, for example, by replacing a nearest neighbor F^- ion by an O^{2-} ion, the full charge compensation being achieved by another O^{2-} ion on a remote F^- site. It may be that charge compensation is produced by other ions in the material, such as sulphur or chlorine, which have been observed in large quantities in some CaF_2 crystals.[18]

CONCLUSIONS

The observation of these new spectra shows that charge compensation mechanisms in CaF_2 are still not fully understood. There appear to be at least two new methods of compensation for U^{4+}, the nature of which has not been established though various possibilities have been outlined. These then make Yariv's assignment less certain since any one of the observed spectra could be due to this form of compensation.

The reason why these ions form new axial spectra rather than rhombic spectra when the crystals are doped with the oxide is not known. It may lie in the fact that the previous rare earth ions investigated i.e. Ce^{3+}, Nd^{3+}, Yb^{3+} and Tm^{2+} were all Kramers ions whereas Pr^{3+} and U^{4+} are both non-Kramers ions. We hope to examine Tb^{3+} and Ho^{3+} to determine the behaviour of other non-Kramers ions.

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[12] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

[13] P. P. Feofilov, Dokl. Akad. Nauk SSSR **99**, 731 (1954).

[14] J. Sierro, J. Chem. Phys. **34**, 2183 (1961).

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

[16] S. D. McLaughlan and R. C. Newman, Phys. Letters **19**, 552 (1965).

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

[18] B. Bardsley and G. W. Green, Brit. Appl. Phys. **16**, 911 (1965).