PHYSICAL REVIEW VOLUME 155, NUMBER 2 10 MARCH 1967

Correlation of Electron Paramagnetic Resonance and Optical-Absorption Spectra of $CaF_2:Yb^{3+}$

J. KIRTON AND S. D. MCLAUGHLAN
Royal Radar Establishment, Malvern, Worcestershire, England

(Received 26 September 1966)

An account is given of a combined optical and paramagnetic resonance investigation of trivalent ytterbium ions in ten different sites in calcium fluoride. Correlation between site geometry and optical absorption has been obtained for six of these by examining crystals prepared by different methods. A single optical-absorption line was observed for all but one of these sites, so that it was impossible to deduce the magnitudes of the Stark splittings. However, there is some evidence to indicate that they are large (of the order of hundreds of cm^{-1}), rather than small, as suggested by Low. A new rhombic paramagnetic resonance is also reported and is thought to arise from pairs of Na^+ and Yb^{3+} ions on adjacent Ca^{2+} sites.

1. INTRODUCTION

CALCIUM fluoride consists of a simple cubic lattice of fluorine ions in which every other body center position is occupied by a divalent calcium ion. When trivalent rare-earth ions are introduced into the lattice they occupy Ca^{2+} sites, the valence mismatch being compensated in a variety of ways. When the charge compensation is remote from the rare-earth ion the O_h cubic symmetry of the crystalline field is preserved, but if it is sufficiently close, the symmetry of the electric field can be reduced from cubic to tetragonal, trigonal,[1] or even rhombic.[2] Each type of site produces a characteristic optical-absorption spectrum. A number of investigations [3,4] have been made into the optical-absorption spectrum of Yb^{3+} ions, reputed to be on cubic sites, but the results are conflicting because in the samples examined Yb^{3+} ions were present on more than one type of site. In this paper we describe the classification of the optical-absorption spectra observed from differently prepared samples into one or more lines, arising from each of six different site geometries, whose presence was determined by electron paramagnetic resonance (EPR) measurements on the same samples. It will be shown how the previous investigators were misled regarding the magnitude of the cubic field splitting of Yb^{3+} in CaF_2.

2. APPARATUS

The EPR equipment used to determine site geometries in the crystals was similar to that described previously.[5] Most measurements were made at 1.4°K with the magnetic field rotated in the (110) plane. Orientation of the crystal into this plane was achieved using the {111} cleavage planes of CaF_2 and a 35.3° Teflon wedge in the cavity. Any residual misorientation was removed by tilting the cryostat assembly.

In the optical investigation the samples were normally examined in absorption using a tungsten or tungsten-iodine source and a single-beam Jarrell Ash 3.4-m spectrometer operating in first order. An RCA C70102B cooled photomultiplier was used for detection and the signals, after passing through a dc amplifier, were recorded on a strip chart. Except where better resolution was required, the spectral slit width was kept at 0.5 cm^{-1}. Wavelengths, reproducible to within 0.2 Å, were obtained from recordings marked every 10 Å and calibrated by means of standard spectral lamps. Initial difficulty with atmospheric absorption in the 0.9–1.0-μ region was overcome by passing dried air through the spectrometer rather than by using a double-beam technique. In all the fluorescence experiments, excitation was achieved by means of a high-pressure mercury lamp fitted with a quartz envelope.

The samples were cooled by mounting them on the cold finger of a liquid-helium Dewar whose temperature was monitored by a calibrated carbon resistor. With the Dewar filled with liquid helium and the tungsten source illuminating the sample, the cold-finger temperature was about 35°K. However, since calcium fluoride has a low thermal conductivity it is difficult to get a meaningful estimate of sample temperature in a Dewar of this type, and this may explain slight discrepancies between published wavelengths and our own values for lines which we consider to be the same.

Optical linewidths were measured as a function of temperature between 35 and 290°K as the Dewar warmed up. Measurements were also made with the sample immersed in liquid nitrogen. During fluorescence experiments we were unable to obtain any estimate of the sample temperature, but it is likely to be significantly higher than in the absorption measurements because of the considerable heating by the mercury-arc source.

3. CRYSTAL PREPARATION

The crystals were grown by the Czochralski and by the Stockbarger processes with the concentration of ytterbium in the melt ranging from 0.05 to 0.2 at.%. The dopants were either in oxide or fluoride form, and

---

[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] W. Low, J. Chem. Phys. **37**, 30 (1962).
[4] Z. J. Kiss, Phys. Rev. **127**, 718 (1962).
[5] P. A. Forrester and S. D. McLaughlan, Phys. Rev. **138**, 1682 (1965).

TABLE I. Summary of ytterbium-doped calcium-fluoride samples.

Type	Source	Method of preparation	Dope
a	Barr and Stroud Ltd.	Pulled at 1½ in./h from graphite crucible in argon atmosphere	YbF_3
b	Barr and Stroud Ltd.	Pulled at 1½ in./h from graphite crucible in argon atmosphere	Yb_2O_3
c	Barr and Stroud Ltd.	Pulled at 1½ in./h from graphite crucible in argon atmosphere	YbF_3+NaF
d	Royal Military College of Science	Pulled at 2½ in./h from molybdenum crucible in helium atmosphere	Yb_2O_3
e	Type-b crystal heated at 950°C in hydrogen atmosphere for 25 h		

in some cases NaF was added. Some crystals were subsequently heated in hydrogen at 900°C in a way similar to that used by Hall and Schumacher.[6] By examining the EPR and optical-absorption spectra of about thirty samples, we were able to obtain many cross checks on the assignment of the optical lines. A list of the various types of crystals is given in Table I.

4. EPR OF CaF_2:Yb^{3+}

Ytterbium-doped CaF_2 has been the subject of a number of paramagnetic-resonance investigations and a great variety of sites have been observed. The data on the ten most common sites are summarized in Table II. All of these EPR spectra have been previously reported apart from R_5, which was observed for the first time in the course of this investigation. This rhombic spectrum is most intense in the crystals doped with NaF, and its intensity increases with the ratio of Na:Yb. The axes of the g tensor are aligned along the [110], [$\bar{1}$10], and [001] directions, a result which can be produced by a distortion along a $\langle 110\rangle$ direction. The most likely model for this center is a Yb^{3+}-Na^+ pair occupying adjacent Ca^{2+} sites. A more detailed discussion of this center is given in Sec. 7C. The charge compensation mechanisms for the other sites will not be discussed here, as these have been considered fully in the original publications.

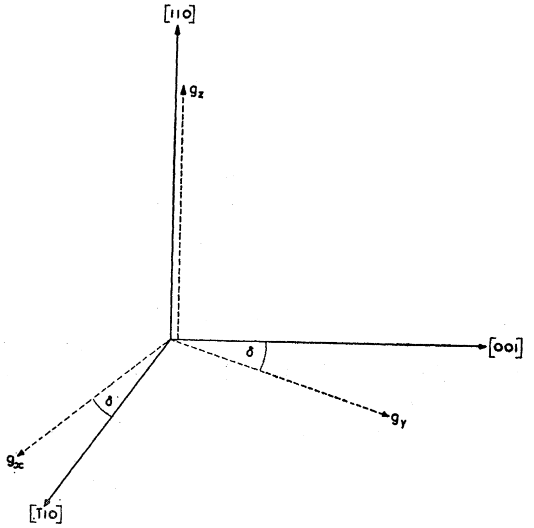

FIG. 1. The relation between the crystal axes and the coordinate axes used in Table II.

5. OPTICAL SPECTRA OF CaF_2:Yb

The absorption and luminescence properties of Yb^{2+} and Yb^{3+} ions in CaF_2 have been investigated by Kaplyanskii and Feofilov.[7] Yb^{2+} has a full $4f$ shell, and its optical-absorption spectrum is characterized by two very broad bands in the ultraviolet at 3500 and 2500 Å, corresponding to the $4f$-$5d$ transitions. The optical spectrum of Yb^{3+} ions, on the other hand, shows not only a broad absorption band at 2550 Å but also some very sharp lines around 9700 Å corresponding to $4f$-$4f$ transitions.

The $4f^{13}$ configuration of the free Yb^{3+} ion gives rise to one term ^2F which is split by spin-orbit coupling into a ground-state level $^2F_{7/2}$ and an upper level $^2F_{5/2}$ lying 10 000 cm^{-1} above (see Fig. 2). In a crystalline electric field having cubic symmetry, the $^2F_{7/2}$ ground-state manifold breaks up into Γ_6, Γ_7 doublets and a Γ_8 quartet, the Γ_7 doublet being lowest in energy. The $^2F_{5/2}$ manifold splits into a Γ_8 quartet above a Γ_7 doublet. In crystalline fields having tetragonal or lower symmetry the Γ_8 quartets are further split so that the ground manifold consists of four doublets and the $^2F_{5/2}$ of three doublets. The transitions indicated in Fig. 2 are allowed in unpolarized light irrespective of whether they are electric or magnetic dipole in character.

6. CORRELATION OF OPTICAL ABSORPTION AND EPR OF CaF_2:Yb^{3+}

Correlations were made on the basis of the simultaneous presence or absence of lines in the optical and EPR absorption spectra observed from differently prepared samples. Further support for our assignments was obtained from the good correspondence between the intensities of such correlated optical and EPR absorptions over a range of site concentrations. However, we have assumed that no optical transition has an oscillator strength which differs by more than one order of magnitude from any other, apart from the magnetic-dipole transitions arising from ions on cubic sites.

---

[6] J. L. Hall and R. J. Schumacher, Phys. Rev. **127**, 1892 (1962).

[7] A. A. Kaplyanskii and P. P. Feofilov, Opt. i Specktroskopiya **13**, 235 (1962) [English transl.: Opt. Spectry. (USSR) **13**, 129 (1962)]; P. P. Feofilov, Izv. Akad. Nauk SSSR, Ser. Fiz. **26**, 435 (1962).

TABLE II. Summary of paramagnetic resonance results on Yb^{3+} in CaF$_2$.

Site	g values			g tensor axes	Reference
Cubic (C)	3.443±0.002				(a)
	$g_{\parallel}$	$g_{\perp}$			This paper See also
Tetragonal (Tet)	2.412±0.003	3.802±0.005		[001]	(b)
Trigonal (T_1)	1.323±0.001	4.389±0.004		[111]	(c)
Trigonal (T_2)	1.421±0.001	4.389±0.004		[111]	(c)
Trigonal (T_{3H})	1.516±0.002	4.147±0.005		[111]	(d)
Trigonal (T_{3D})	1.512±0.002	4.147±0.005		[111]	(d)
	g_x	g_y	g_z	δ (degrees) (see Fig. 1)	
Rhombic (R_1)	6.99 ±0.01	1.355±0.002	1.094±0.002	3.2±0.2	(e)
Rhombic (R_2)	7.24 ±0.01	0.992±0.002	0.957±0.002	26.3±0.2	(e)
Rhombic (R_3)	Unable to measure	1.241±0.002	1.096±0.002	8.8±0.5	(e)
Rhombic (R_4)	6.45 ±0.02	2.175±0.002	1.667±0.002	0	(e)
Rhombic (R_5)	3.926±0.005	3.289±0.005	3.102±0.005	0	This paper

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

[b] Our measurements agree with those of U. Ranon and A. Yaniv (see Ref. c) who reported a tetragonal spectrum having $g_{\parallel}=2.420\pm0.004$, $g_{\perp}=3.802\pm0.003$. Weber and Bierig (Ref. 1) have also observed a tetragonal spectrum but in this case the g values were $g_{\parallel}=2.423\pm0.001$ and $g_{\perp}=3.878\pm0.001$.

[c] U. Ranon and A. Yaniv, Phys. Letters **9**, 17 (1964). Dr. Ranon has informed us that there is a misprint in this paper. For spectrum T_2, $g_{\parallel}$ should be 1.421 and not 1.341 as stated.

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

[e] Reference 2.

When a particular site was present in sufficiently high concentration, a number of smaller satellite lines were observed around the principal absorption line. For example, those associated with the main T_2 absorption line are indicated in Fig. 3. No related paramagnetic resonance spectra could be found, and their intensities did not depend systematically on that of the principal absorption line. Wittke *et al.*[8] observed similar effects in the spectrum of uranium-doped CaF$_2$ and attributed them to the formation of clusters of uranium ions. A similar explanation seems likely for the lines which we have observed, and they will not be given further consideration.

All our samples showed strong ultraviolet absorption bands due to $4f$-$5d$ transitions of Yb^{3+} and Yb^{2+}. The remaining absorption was concentrated in the 0.9–1.0-μ region and consisted of very sharp lines arising from $4f$-$4f$ transitions of Yb^{3+} (see Fig. 3). Figure 3(a) is an example of the optical spectrum consistently observed from type-a samples (YbF$_3$ doped) at 35°K. The principal lines in the spectrum were α, γ, δ, ϵ, and η, and their wavelengths are listed in Table III. EPR examination of these crystals revealed Yb^{3+} ions in cubic, tetragonal, trigonal (T_2), and rhombic (R_5) sites. Type-b samples (doped with Yb$_2$O$_3$) gave quite different spectra and from the optical spectrum shown in Fig. 3(b) it can be seen that lines γ, δ, and ϵ were absent, α and η were still present, and the new lines β, ζ, θ, and λ appeared. The EPR spectrum revealed Yb^{3+} ions on sites T_1, T_2 and R_1 to R_4. Since the only EPR spectrum common to both crystals was T_2, we can immediately identify optical-absorption lines α and η with these trigonal sites. Apart from α and η, type-c samples doped with 0.05 at.% YbF$_3$ and 1.0 at.% NaF showed optical-absorption lines γ and δ but not ϵ, while EPR revealed Yb^{3+} ions on cubic, T_2, and R_5 sites. Comparison of the optical spectra of a- and c-type crystals shows that line ϵ arises from ions having tetragonal symmetry. Increasing the Na:Yb ratio from 1:1 to 20:1 in type-c samples caused δ to grow relative to γ, while the EPR spectrum revealed that R_5 had grown in intensity relative to the cubic spectrum. Thus the optical line γ arises from Yb^{3+} ions on cubic sites, while the line δ comes from those on rhombic sites, corresponding to the EPR resonance R_5.

Type-d samples were notable in that the optical-absorption line λ dominated the other lines in the spectrum (α, ζ, η, and θ). EPR studies of these crystals revealed that most of the Yb^{3+} ions were on T_1 sites and very few on T_2 and R_1 to R_4 sites. Hence it is possible to relate optical line λ to Yb^{3+} ions on T_1 sites. Confirmation of this assignment was later obtained by heating type-b crystals to 900°C in a hydrogen-gas

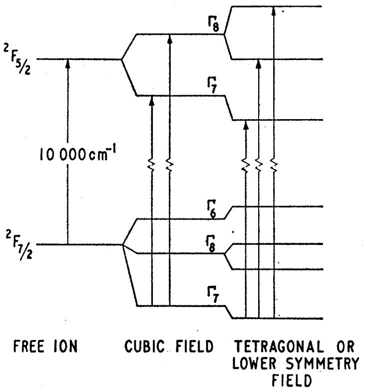

FIG. 2. The energy levels of trivalent ytterbium in crystalline fields having cubic and lower symmetries.

---

[8] J. P. Wittke, Z. J. Kiss, R. C. Duncan, and J. J. McCormick, Proc. IEEE **51**, 56 (1963).

TABLE III. Observed optical-absorption and EPR spectra for different types of crystal.

Sample type \ Optical line Å / cm⁻¹	α 9095.2 10 995	β 9101.7 10 987	γ 9629.8 10 384	δ 9636.8 10 377	ε 9685.2 10 325	ζ 9736.6 10 271	η 9749.1 10 257	θ 9764.7 10 241	λ 9815.0 10 188	μ 9824.4 10 179	Observed EPR spectra C	Tet	T_1	T_2	T_3	R_1	R_2	R_3	R_4	R_5
a	√	...	√	√	√	...	√	...	...	...	√	√	...	√	...	...	...	...	...	√
b	√	√	...	...	...	√	√	√	√	...	...	...	√	√	...	√	√	√	√	...
c	√	...	√	√[a]	...	...	√	...	...	...	√	...	...	√	...	...	...	...	...	√[c]
d	√	...	...	...	...	√	√	√	√[b]	...	...	...	√[b]	√	...	√	√	√	√	...
e	...	...	...	...	...	...	...	...	√	√	...	...	√	...	√	...	...	...	...	...
Assignment	T_2	R_1 or R_2	C	R_5	Tet	R_1 or R_2	T_2	R_1 or R_2	T_1	T_3										

[a] Much greater intensity relative to γ than in type-a crystals.
[b] Much more intense than other lines.
[c] Much greater intensity relative to C than in type-a crystals.

atmosphere in a similar manner to that described by Hall and Schumacher. These crystals showed only λ and μ optical-absorption lines and resonances T_1 and T_3, T_3 being a new center not present in untreated material. This confirms the assignment of optical line λ to the T_1 center and relates the line μ to the new trigonal center T_3. By a process of elimination, the remaining optical lines (β, ζ, and θ) in type-b crystals must be related to one or more of the four rhombic spectra R_1 to R_4. These strong lines are most likely to be associated with R_1 and R_2 sites, the EPR intensities of which were at least an order of magnitude stronger than those of R_3 and R_4. Attempts to alter the relative intensities of R_1 and R_2 have not met with much success, and further progress would seem to depend on their selective production. The width of the absorption line ε varied as $\exp(-E/kT)$ where $E=130$ cm^{-1}, but the widths of the other absorption lines appeared to have complex exponential

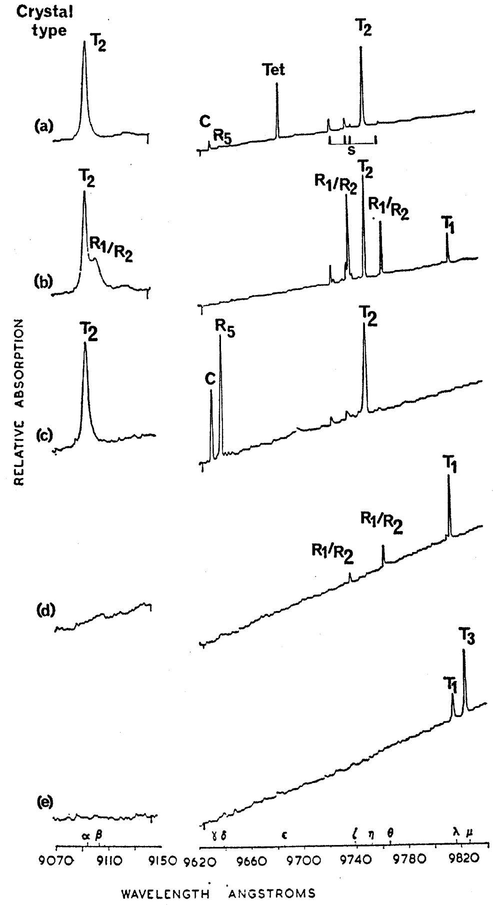

FIG. 3. The near-infrared absorption spectra of trivalent ytterbium in differently prepared calcium-fluoride crystals at about 35°K. Crystal types are described in Table I. Greek letters have been used as labels for the absorption lines and latin letters refer to the EPR centers with which they have been correlated. The satellite lines associated with the sharp T_2 line (η) are indicated by S in spectrum (a).

dependences which were not analyzed. At room temperature the widths of lines η, ζ, and θ were ~ 5 cm^{-1}, while α was very broad (~ 40 cm^{-1}) and could only be seen when site T_2 was present in large concentrations. The remaining lines (γ, δ, ϵ, β, λ, and μ) had linewidths of the order of 1 cm^{-1} at 77°K but were too broad to be seen at room temperature.

No new optical lines were seen in fluorescence, those observed being in resonance with the absorption lines η, γ, δ, ϵ, ζ, and θ. The absence of some of the lines previously observed in the absorption spectrum cannot be taken as indicating that they are due to transitions between the upper levels of the excited manifold and the ground state, as it is possible that severe line broadening was caused by an increase in the sample temperature during ultraviolet excitation.

7. DISCUSSION

The number of absorption lines observed was considerably less than that expected from group theory which predicts the occurrence of two absorption transitions for ions on cubic sites and three for those having lower symmetries. Only in the case of the ions on T_2 sites have we been able to positively identify more than one line as being associated with a particular type of center. The most likely explanation of this is that the other transitions do occur but are so strongly broadened by phonon relaxation processes that they were not detected. Generally in absorption the long-wavelength transition, i.e., that to the lowest level of the excited multiplet, is observed to be the sharpest, while transitions to the higher levels become progressively broader. A good example of this effect can be found in the spectrum of Pr^{3+} in LaF_3.[9] The absorption lines missing from our spectra could possibly be detected using a more sensitive and less refined spectrometer than the one used in this investigation. While the optical-absorption lines arising from Yb^{3+} ions on T_1 and T_3 sites have not been reported, most of those associated with the cubic, T_2 and rhombic sites have previously been observed but incorrectly assigned. We will now show how the correct assignment leads to an invalidation of the estimates which other authors have made of the crystal-field splittings of Yb^{3+} in CaF_2.

A. The Cubic Spectrum

Only one of the absorption lines (γ at 10 384 cm^{-1}) has been correlated with Yb^{3+} ions on cubic sites; also the width of this line was not a simple exponential function of temperature so that we have been unable to make any estimate of the cubic field splittings of the $^2F_{5/2}$ and $^2F_{7/2}$ manifolds. However, it is most unlikely for the crystal field potential to be dominated by the sixth-order terms in which case the splittings of the two manifolds should be of comparable magnitude. If they were small (~ 10 cm^{-1}), the second cubic absorption line would not be expected to be so severely phonon-broadened as to be unobservable. It is more likely that the splittings are not very different from the 410-cm^{-1} splitting measured by Kiss[4] for the isoelectronic ion Tm^{2+}.

Optical spectra from Yb^{3+} ions which were presumed to be on cubic sites in CaF_2 have been previously studied by Low.[3] He observed two strong, sharp absorption lines at 10 385 and 10 377 cm^{-1} and attributed these to the transitions from the ground state to the two components of the $^2F_{5/2}$ manifold. These lines are, however, near enough the measured values of lines γ and δ (10 384 and 10 377 cm^{-1}) for us to be certain that they are identical, the discrepancies between measurements probably resulting from differences in temperatures at which the experiments were conducted. Hence we conclude that Low not only had cubic sites in his crystal but also sites corresponding to the EPR spectrum R_5. Thus despite the care taken to suppress noncubic sites, the strength of the electric-dipole transitions from the 5–10% of Yb^{3+} ions on R_5 sites was comparable with that of the weaker magnetic-dipole transitions arising from the 90–95% of Yb^{3+} ions on cubic sites.

Kiss[4] has also investigated the optical spectrum of Yb^{3+} in CaF_2, and here again some confusion has arisen because of the simultaneous presence of Yb^{3+} ions in sites with different symmetries. He reported that the absorption lines were grouped about two lines, one at 10 240 cm^{-1} and the other at 10 870 cm^{-1}, and suggested that these might correspond to the absorption lines from ions on cubic sites. While we have frequently observed a line at 10 241 cm^{-1} which we associate with a rhombic site, we have never observed an absorption line at 10 870 cm^{-1}. Hence we conclude that the two lines observed by Kiss do not correspond to the same site. In a figure in the same paper the strongest lines at 4.2°K appear at approximately 10 256 and 11 000 cm^{-1}, which correspond well with our lines α and η, so that it would appear that a number of ions in his crystals were on T_2 sites.

B. Trigonal Spectrum T_2

The absorption lines η and α (10 257 and 10 995 cm^{-1}) arise from Yb^{3+} ions on T_2-type trigonal sites. Line η, which remains sharp (~ 4 cm^{-1}) at room temperature is probably the transition between the lowest levels of the $^2F_{7/2}$ and the $^2F_{5/2}$ Stark multiplets. Line α, on the other hand, broadens considerably as the temperature is raised above 77°K until at 300°K its linewidth is ~ 40 cm^{-1}. A possible interpretation is that α is a transition from the lowest level of $^2F_{7/2}$ to one of the two excited levels of the $^2F_{5/2}$ manifold, indicating that the over-all splitting of the $^2F_{5/2}$ manifold is ≥ 738 cm^{-1} for Yb^{3+} ions in this particular site. Another possible explanation is that line α is a vibrational satellite of line η, involving an improbable three-phonon process ($k\theta_D/hc$

---

[9] W. M. Yen, W. C. Scott, and A. L. Schawlow, Phys. Rev. **136**, A271 (1964).

$\sim$300 cm^{-1} in CaF$_2$) or the excitation of some high-energy local mode.

Feofilov[10] has also examined the optical spectrum of Yb^{3+} ions in what he called type-1 crystals. At room temperature he observed lines corresponding to our α, γ, ζ, and η, and also lines at 10 152 and 9652 cm^{-1}, both in fluorescence and absorption. The spectrum was assumed to originate from Yb^{3+} ions on one type of site, and two strong lines at 10 270 and 10 261 cm^{-1} (corresponding to our ζ and η) were interpreted as transitions from the ground state to two of the components of the $^2F_{5/2}$ manifold, suggesting that the Stark splitting is small. However, we have shown that these lines arise from Yb^{3+} ions on different sites and thus Feofilov's interpretation is incorrect.

C. Rhombic Spectra

Sites R_1 and R_4 were always present in similar proportions in type-b crystals. Changes in relative intensities produced by heat treatment in hydrogen caused substantial conversion of Yb^{3+} to Yb^{2+}, and the rhombic EPR spectra which remained were too weak for a proper analysis of relative amplitudes to be carried out. Consequently, we have been unable to do more than show that the lines β, ζ, and θ arise from R_1 and R_2 sites. The position regarding R_5 is much better since the intensities of the optical-absorption line δ and the EPR spectrum increase with the sodium/ytterbium doping ratio, thus showing that they are related. Bleaney[11] has suggested that a possible charge compensation for a trivalent rare-earth ion could be a monovalent ion like sodium in a nearest-neighbor calcium site. Such a model would explain the rhombic symmetry and the disposition of the axes of the g tensor observed in the EPR experiments. A small number of R_5 sites are observed in crystals not deliberately doped with sodium. These could arise from the accidental presence of the latter, but the possibility of a Yb^{3+}-Ca^{2+} vacancy pair being responsible for the R_5 sites cannot be ruled out on the present evidence. The Yb^{3+}-Na^{+} pair model suggested here for R_5 could be established by growing ytterbium-doped crystals compensated with lithium or cesium and examining the crystals by EPR for rhombic resonances similar to R_5. Increasing the Na:Yb ratio in type-c crystals leads to a reduction in the number of tetragonal sites, suggesting that the presence of sodium leads to the suppression of interstitial fluorine ions.

8. CONCLUSIONS

We have correlated the optical and paramagnetic resonance spectra arising from Yb^{3+} ions in six different sites in CaF$_2$. It has been shown how previous assignments of the optical-absorption lines have been incorrect, principally because of the presence of Yb^{3+} ions on more than one site in the crystals examined. In particular, we have traced the reasons for the disagreement about the magnitude of the cubic crystal-field splittings. The absence of many of the expected optical-absorption lines, probably due to phonon broadening, has prevented us from constructing energy-level schemes for the various sites observed. However, there are indications that the Stark splittings are large rather than small. It may be possible to detect the missing lines using a spectrometer with lower resolution but greater sensitivity than the one used in this investigation. A new rhombic site for the Yb^{3+} ion has been observed, and it is thought that this arises from a Yb^{3+}-Na^{+} pair located on adjacent calcium sites. Most of all, we have illustrated the importance of carrying out an EPR investigation on the same samples used in optical studies in cases where many site geometries are possible and known to exist.

ACKNOWLEDGMENTS

We are grateful to M. O'Brien for obtaining the optical spectra, to A. F. Fray for assistance with the EPR experiments, and to Dr. R. C. Newman for providing some of the treated crystals. We also wish to thank Barr and Stroud Ltd. and the Royal Military College of Science for supplying the calcium fluoride crystals.

---

[10] P. P. Feofilov, Opt. i Spektroskopiya 4, 216 (1958).

[11] B. Bleaney, J. Appl. Phys. Suppl. 33, 358 (1962).