

Anomalies in the vacuum uv absorption spectrum of Yb^{3+} in CaF_2

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The vacuum uv absorption spectrum of Yb^{3+} in CaF_2 shows marked differences from the consistent pattern of the other rare-earth ions. The differences suggest that the interaction between the ion and the crystal is unusually weak, possibly due to a contraction in the mean-square radius of the excited $5d$ electronic wave function.

INTRODUCTION

In a sequence of previous papers,¹⁻⁴ we have studied the vacuum uv absorption spectra of a number of triply ionized rare-earth ions introduced as a small impurity into a CaF_2 host crystal. The absorption is due to electronic transitions of the type $4f^n \rightarrow 4f^{n-1}5d$, together with associated phonon side bands. Although the spectra differ in detail, the general features are very similar for all the rare-earth ions from Ce^{3+} to Tm^{3+} . The purpose of this Comment is to report on some marked changes from the usual pattern in the spectrum of the last rare-earth ion, Yb^{3+} , and to offer a possible explanation.

EXPERIMENTAL

The crystals used in the present investigation were obtained from Optovac Inc. The impurity was added to the melt in the trifluoride form (YbF_3). Care was taken to ensure that the crystals were oxygen free. Under such circumstances, one expects the triply ionized rare-earth sites to be charge compensated by an F^- ion located in the neighboring otherwise empty cube (C_{4v} point symmetry). Some centers with nonlocal charge compensation (O_h point symmetry) are also possible.

The experimental setup for the absorption measurements was the same as described previously.^{3,4} The light sources in the present work were homemade rf-excited noble-gas lamps. Emission from intentionally introduced impurities provided an accurate wavelength calibration. The optical resolution in the present measurements was better than 0.4 Å.

RESULTS AND DISCUSSION

The absorption spectra due to Yb^{3+} are shown in Fig. 1 at two different concentrations. Curves (a) and (b) are for an impurity concentration of 0.05 at. % and curve (c) for a concentration of 0.005 at. %. While curve (a) was taken at room

temperature, curves (b) and (c) were recorded at liquid-helium temperature (4.2 °K). For comparison, we show in Fig. 2 a similar set of curves for Tm^{3+} which is typical of the other rare-earth ions in CaF_2 . (Note the change in wavelength scale.)

The qualitative features of the spectra in Figs. 1 and 2 differ in two important ways: (i) the zero-phonon lines in Fig. 1 are closely grouped together with little evidence of phonon structure, while in Fig. 2 the zero-phonon lines are widely separated with well-developed phonon side bands; (ii) at room temperature, the zero-phonon lines are still visible in Fig. 1, while they are totally washed out in Fig. 2.

The usual explanation for the spectra typified by Fig. 2 is that the wave function for the $5d$ electron in the excited $4f^{n-1}5d$ configuration has a large amplitude outside the $5p^6$ closed shell. The $5p^6$ closed shell normally screens the inner $4f^n$ electrons in the ground state, allowing it to interact only weakly with the host crystal. For this reason, $4f^n - 4f^n$ type transitions remain well defined, even at room temperature. On the other hand, the $5d$ electron in the excited state is largely unscreened. This accounts for the strong crystal-field splitting of the excited state evident in Fig. 2 ($\sim 6000 \text{ cm}^{-1}$), the well-developed phonon structure, and the smearing-out of structure at higher temperatures.

The different nature of the Yb^{3+} spectrum in Fig. 1 suggests that the interaction between the $5d$ electron and the crystal is unusually weak. It may be that a contraction occurs in the $5d$ wave function relative to the other rare-earth ions so that it lies largely within the screening influence of the $5p^6$ shell. Whether the effect is present in the free ion, or is a result of crystal-field interactions must await detailed calculations.

Our interpretation of the peaks between 1360 and 1440 Å in Fig. 1 as a closely spaced group of crystal-field-split electronic transitions is supported by a more detailed study of the spectrum. The lowest excited state of the Yb^{3+} free

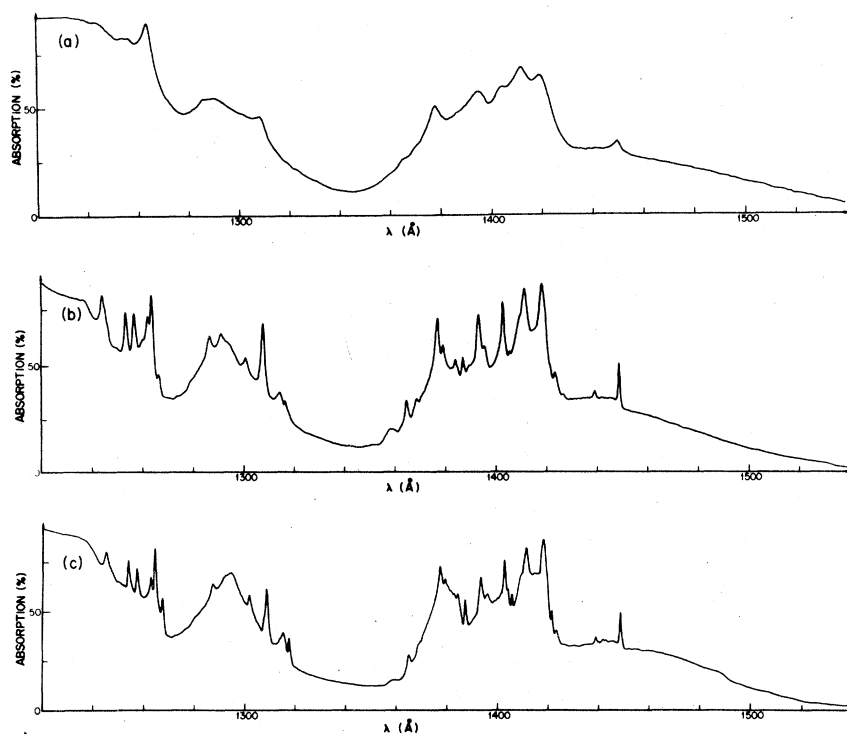


FIG. 1. Absorption spectra of $\text{CaF}_2:\text{Yb}^{3+}$ in the 1220–1540-Å region, for two crystals: (a) impurity concentration of 0.05-at.-% sample of 0.32-mm thickness; (b) same as (a); (c) impurity concentration of 0.005-at.-% sample of 1.6-mm thickness. Curve (a) taken at room temperature, curves (b) and (c) at 4.2°K.

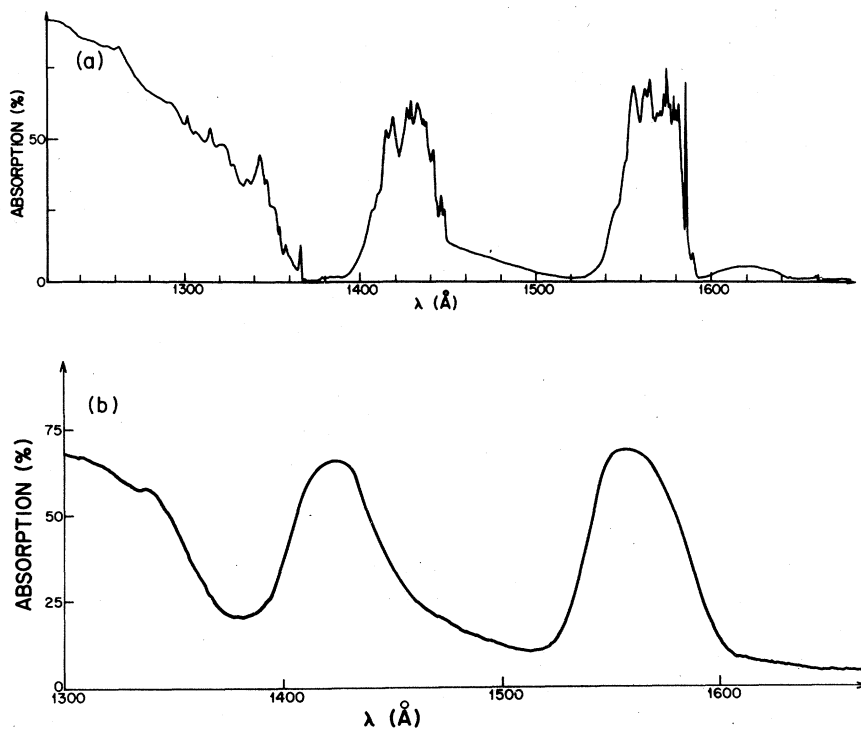


FIG. 2. Absorption spectra of $\text{CaF}_2:\text{Tm}^{3+}$ in the 1220–1680-Å region for two crystals with impurity concentration of 0.05 at.-%. (a) sample of 0.35-mm thickness; measurement at 4.2°K. (b) sample of 0.47-mm thickness; measurement at room temperature.

ion reported by Brewer⁵ is the $4f^{12} 5d 4H_{9/2}$ at $88\,195\text{ cm}^{-1}$. The expected number of levels for a $J = \frac{9}{2}$ state at a crystal site with C_{4v} symmetry is 5.⁶ It is therefore gratifying to find five main peaks in the above wavelength interval. The measured crystal field splittings for the $4f^{12} 5d 4H_{9/2}$ term listed in Table I are about a factor of 10 smaller than the corresponding $4f^{n-1} 5d$ term splittings for the other rare-earth ions, and a factor of 5 larger than the typical splittings in the $4f^n$ configuration.⁸ The $5d$ electron therefore appears to be unusually well screened in Yb^{3+} compared with the other rare-earth ions, but the screening is not as complete as for the $4f$ shell. The other structure below 1320 \AA probably corresponds to a number of other electronic states of the free ion beginning at $94\,636\text{ cm}^{-1}$ as reported by Bryant.⁷ The measurements cannot be extended to shorter wavelengths because the CaF_2 host crystal becomes opaque.

In summary, our data suggest that the interaction between the CaF_2 crystal and the $5d$ electron of excited Yb^{3+} is much weaker than in the other rare-earth ions. The weaker interaction may be evidence for a contraction in the mean square radius of the $5d$ wave function.

TABLE I. Tetragonal (C_{4v}) crystal-field-split levels of the ($4H_{9/2}$) $4f^{12} 5d$ term in Yb^{3+} .

λ (\AA)	Energy (cm^{-1})	$\Delta\nu$
1418.2	70 512	
1411.5	70 847	335
1402.8	71 286	439
1393.3	71 772	486
1377.2	72 611	839

Note added in proof. Relativistic Hartree-Fock calculations have now been done by us for the Yb^{3+} free ion in the $4f^{12} 5d$ configuration. The results do not show any evidence of contraction of the $5d$ orbital relative to the other rare earth ions in the corresponding $4f^{n-1} 5d$ configurations. If the suggested contraction is real, it could still be the result of configuration mixings induced by the crystal field.

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