

is difficult. The part of the beaker down which the film flows is so designed that the superfluid velocity is only a fifth of the critical velocity at the point where the film enters the bulk liquid of the second-sound cavity. It is unlikely, therefore, that much vorticity is generated in a region other than that of the limiting perimeter, i.e., the top of the beaker. The initial rise of the value $\alpha'(t)$ represents the complex process of the generation and decay of vortices in the film itself together with the gradual increase and decay of vortices reaching the bulk He II in the second-sound cavity. When z is reduced to zero, $\alpha'(t)$ drops almost exponentially to some lower value with a relaxation time of about 20 sec. This must represent the time for the decay of a given amount of vorticity in the cavity.

We hope in future experiments to investigate in greater detail the growth and decay of vortices in the film by altering such parameters as the film length and the smoothness of the substrate. We would also like to look more carefully at the ap-

parently widely different amount of vorticity generated in runs on different days with a given value of z .

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ANTIRESONANCE PHENOMENA IN THE ABSORPTION SPECTRA OF RARE-EARTH IONS IN X-IRRADIATED CaF_2

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Some absorption lines of rare-earth ions in calcium fluoride were found to be considerably affected by irradiation with x rays. These narrow lines, which appeared superimposed on a broad background of color-center absorption, were in some cases over 100 times stronger after irradiation and had strongly asymmetric line shapes, often resulting in an antiresonance dip. It is proposed that these effects are caused by interaction of the rare-earth ion and a neighboring color center.

It is well known that asymmetric lines can occur in absorption spectra as the result of interference between coupled states. For instance, when the absorption into a discrete state is superimposed upon a much broader background of absorption into other states with which the discrete state interacts, then the absorption spectrum may show an asymmetric peak or a dip (net decrease of absorption) which has been called an antiresonance. Several examples of this phenomenon have been found in both gaseous and solid systems. In solid-state optics such effects were first reported from systems in which exciton or excitonlike peaks are superimposed on background absorption due to either indirect exciton-phonon transitions or to the continuum of band-to-band transitions in certain insulators.^{1,2} More recent-

ly Pysh, Rice, and Jortner³ have observed sharp asymmetric lines in the absorption spectra of organic molecules introduced as impurities into rare-gas solids. In the case the effect results from interference between the excited state of the molecule and the continuum energy band of the host crystal.

The purpose of the present paper is to report the observation of a similar effect in the absorption spectra of crystals of calcium fluoride containing certain rare-earth ions after the crystals had been irradiated by x rays. The rare earths were incorporated as their oxides, yielding crystals which tended to color deeply when subjected to ionizing radiations.⁴ The asymmetric absorption lines in question, which coincided with the positions of normally very weak absorption lines

of the rare-earth ion, appeared superimposed upon a background of color-center absorption, and they grew in strength as the color-center bands grew. Such lines were observed from crystals doped with dysprosium and with praeosdymium, but not with other rare-earth ions. It is, however, conceivable that a more detailed search might well show additional smaller effects with some of the other rare-earth ions, and in particular, the spectral regions outside 350 to 750 nm remain to be investigated.

The actual shape of the lines depended to some extent on the way the crystals were grown⁵ and on the impurity concentration; in some cases there was a mild asymmetry and in others an almost complete antiresonance. A typical spectrum of the dysprosium-doped material, taken with a Perkin-Elmer Model No. 137 spectrophotometer, modified for work at low temperatures, is shown in Fig. 1. Two lines with dispersionlike profiles are seen in the region of 450 nm. On the same scale the weak dysprosium absorption lines of the unirradiated crystal in this region are virtually invisible. However, the spectrum obtained with a path length of 30 nm through an unirradiated piece of this material (see the inset in Fig. 1) shows that there are in fact dysprosium lines at these positions. The difference in strength of the 452-nm line after irradiation is about 330 times. The amplitude of the dispersionlike profiles decreased by a factor of 10 as the sample was warmed to room temperature. The praeosdymium lines which undergo a similar transfor-

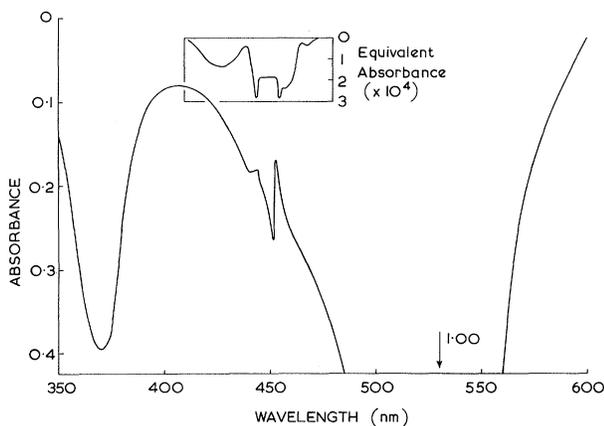


FIG. 1. Absorption spectrum at 105°K of a 2-mm-thick sample of CaF_2 containing 0.05 at.% dysprosium (with 0.01 at.% yttrium) after irradiation for about 3 min with x rays from a gold target with a 30-kV, 30-mA beam. Inset: spectrum of an unirradiated sample taken with a 30-mm path but normalized to a 2-mm path.

mation by irradiation lie at 607 and 629 nm. The strength of the corresponding absorption lines in the unirradiated material varied directly in both cases with the concentration of the dopant and there were no other impurities to which they could be attributed, although there was an appreciable concentration of yttrium in most crystals. Voron'ko, Osiko, Udovenchik, and Fursikov, have also observed the lines shown by the inset in Fig. 1 in their dysprosium-doped, oxygen-contaminated CaF_2 crystals. Other authors have shown^{7,8} that those rare-earth impurities that normally take up the trivalent state in fluoride-doped CaF_2 do so also in the oxide-doped material. Differences in the structure of the optical spectra are caused by crystal-field effects associated with the presence of oxygen in the lattice. It is therefore reasonable to attribute the lines that we have observed to Dy^{3+} and Pr^{3+} ions, and comparison with the spectra of the free ions⁹ suggests that the transitions involved are ${}^6H_{15/2} - {}^4I_{15/2}$ and ${}^3H_4 - {}^1D_2$, respectively.

The possibility that the asymmetry is caused by a fluorescence peak having a slightly shifted wavelength is ruled out by the fact that no difference in the effect could be found when using different spectrometers which had the wavelength selection either before or after the light had passed through the sample, or when the solid angle of the optical system was varied.

A plausible explanation of this phenomenon involves the interaction of the rare-earth ion with a color center produced by the x rays. There is indirect evidence for this interaction from the effect of the rare-earth ion on the color-center bands themselves. Essentially the same color center is formed no matter which of the rare-earths is included, the spectrum having two main absorption bands in the visible region, as shown in Fig. 1. However, varying the rare-earth impurity does cause a strong shift in the bands that varies uniformly as one progresses through the rare-earth series, as shown in Fig. 2. The peak wavelengths and widths of the bands depend slightly on the doping level and history of the crystal but the general trend of Fig. 2 is always maintained. We earlier found that the color centers in the cerium-doped material have the properties of M centers aligned along the cube axes.¹⁰

Shibatani and Toyazawa¹¹ have recently extended original calculations by Fano¹² and find that for an ionic system one of the most likely situations that can lead to antiresonance phenomena is

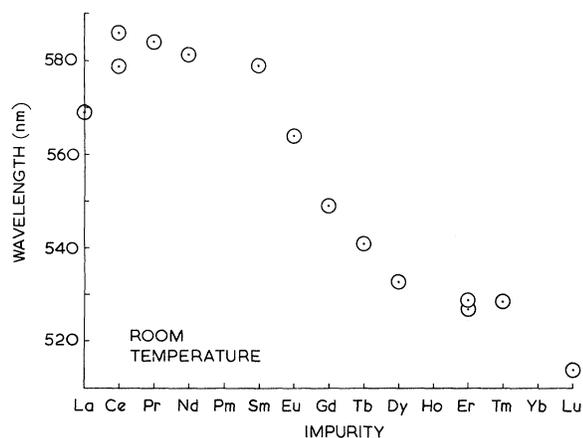


FIG. 2. Peak wavelength of the main color-center absorption band in CaF_2 as a function of the rare-earth impurity, from crystals doped with about 0.05 at.% of the rare-earth impurity.

that in which a transition of the free ion is forbidden but then becomes weakly allowed when the ion is incorporated into a solid material due to the perturbing effect of its surroundings. This situation is well known to exist for electric dipole transitions of rare-earth ions between states which have a $4f$ electron configuration; these transitions are parity forbidden but they become weakly allowed in most solids due to a mixture of small amounts of opposite-parity orbital (e.g., $5d$) by odd terms in the crystalline potential. It is conceivable then that the perturbing effect of a neighboring color center will further modify and even increase the transition probability of electric dipole transitions, and that this is the interaction mechanism which gives rise to the observed effects. It is difficult at this stage to deduce selection rules for the process because of a lack of detailed knowledge about the symmetry of the interaction Hamiltonian. Some progress towards understanding rare-earth-oxide-doped CaF_2 has been made in the ESR studies of Forrester et al.⁷ and Kask, Kornienko, and Rybaltov-

skii.⁸ Both groups find rare-earth ions having symmetries that are not found in fluoride-doped material. Kask, Kornienko, and Rybaltovskii record a rhombic spectrum from Dy^{3+} that changes to trigonal after γ irradiation. However, there is as yet no general agreement on a model to explain these observations.

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