leave an uncertainty in the sign of J. In addition, there is the possibility that J could change sign as R decreases further, in line with the prediction of BP, although our calculations do not indicate this behavior.

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ENERGY TRANSFER FROM COPPER AND SILVER TO RARE EARTHS IN II-VI COMPOUNDS

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We have found that rare-earth fluorescence can be excited by energy transfer from copper and silver in ZnS, CdS, and ZnSe. No report of a similar sensitization has been made by previous investigators of the fluorescence of rare-earth-doped ZnS.[1-4] A specific example of this system is ZnS:Cu, Er, whose strongest group of lines near 18 100 cm^{-1} corresponds to the transition $^4S_{3/2} \rightarrow {}^4I_{15/2}$ of the free Er ion. The excitation spectra of these lines, for samples of widely varying Cu content, are shown in Fig. 1. The enhancement produced by the addition of copper is clearly significant, and even the high-purity fluorescent-grade ZnS used in these experiments apparently contains enough Cu (about 0.3 ppm) to make its presence obvious.

Line emission has been observed in ZnS:Cu, Ln for Ln = Pr, Nd, Tb, Dy, Ho, Er, and Tm. Fluorescence generally occurs from several levels for each ion, but except for Tm the strongest emission occurs from levels between 18 000 and 21 000 cm^{-1} above the ground state. No line emission has been similarly excited when Ln = Sm, Eu, and Yb. The excitation and emission spectra indicate that these three ions are reduced to the divalent state in our samples.

The tendency for all of the lanthanides in ZnS:Cu, Ln to emit from levels near 20 000 cm^{-1} indicates that the sensitization may involve a resonance transfer from an energy level of a Cu defect at or slightly above 20 000 cm^{-1}. To determine if such a level is present we have studied the spectra of ZnS:Cu, Gd. No energy transfer can occur to Gd since its lowest excited states lie above 32 000 cm^{-1} (4.0 eV), which is greater than the band gap of ZnS. The emission of ZnS:Cu, Gd is thus likely to be characteristic of the Cu sensitizing defect. This emission is a broad band which maximizes at 23 000 cm^{-1} (2.86 eV) and decreases to 10% intensity at 20 800 and 24 900 cm^{-1}. The excitation spectrum of this band is identical to that of the line emission of ZnS:

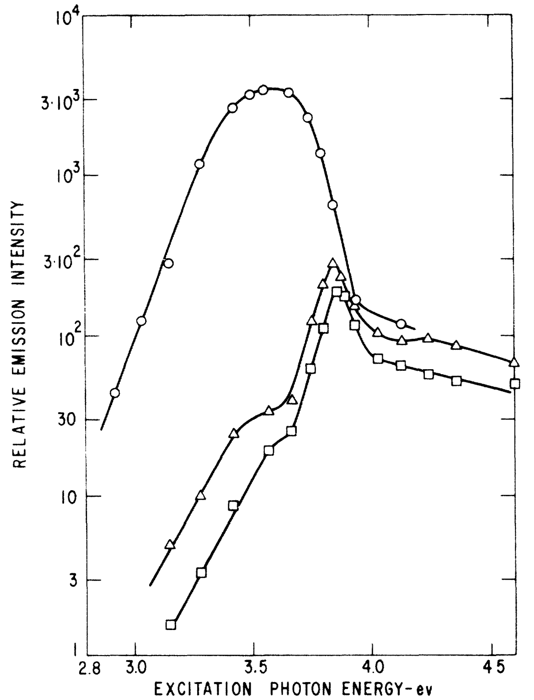

FIG. 1. Intensity of the $^4S_{3/2}\rightarrow{}^4I_{15/2}$ emission from ZnS:Cu, Er for different excitation photon energies. Circles: 10^{-4} Cu, 10^{-4} Er; triangles: 10^{-6} Cu, 10^{-4} Er; squares: 10^{-4} Er, no intentionally added Cu.

Cu, Er, indicating that the same Cu defect is present in both samples as would be expected from the close chemical similarity of the rare earths. Those rare earths which show line emission all have energy levels lying within the emission band of ZnS:Cu, Gd.

By substituting Ag for Cu as the sensitizing impurity, we can further demonstrate that the energy transfer is a resonant one. It is known that all of the group-I*b* dopants introduce analogous defects in II-VI compounds.[5] For example, ZnS:Cu, Al has an emission band at 2.82 eV (22 800 cm^{-1}), and ZnS:Ag, Al has a band at 3.20 eV (25 800 cm^{-1}) due to a similar defect. There is thus reason to believe that energy transfer should occur to higher lying states in ZnS:Ag, Ln than in ZnS:Cu, Ln, and this has proved to be the case. ZnS:Ag, Er emits most strongly from the transition $^2K_{15/2}\rightarrow{}^4I_{15/2}$ at 25 050 cm^{-1} when excited in a broad band maximizing at 3.66 eV (29 500 cm^{-1}).

The hypothesis of a resonant transfer has also been tested by varying the energy available from the Cu sensitizer. This has been done with the mixed compounds $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{S}$:Cu, Er.[5] As x decreases, the band gap and position of emission bands decrease, and progressively lower Er^{+3} energy levels are excited. The highest level excited in CdS:Cu, Er is the $^4I_{9/2}$ at 12 300 cm^{-1}.

We thus are able to vary the energy levels of the sensitizer while the levels of the rare-earth activator remain fixed, a situation unique in sensitized fluorescence systems. In this way the effect of the resonance between the sensitizer and activator on the efficiency of the transfer can be studied. Our preliminary investigations of the system $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{S}$:Cu, Tb show that when the rare-earth ion has no energy levels in resonance with the sensitizer, band emission is seen, while if the transitions of the sensitizer and activator overlap, the band emission is strongly suppressed. If the energy transfer occurred through emission from the Cu defect and reabsorption by the rare-earth ion, the band emission would be suppressed only at the positions of the rare-earth absorption lines. However, the rare earth does not "eat holes" in the band emission, but suppresses it uniformly, indicating that the energy transfer is not radiative. For $x \geq 0.7$, line emission from the $^5D_4$ level at 20 400 cm^{-1} (2.53 eV) predominates. For $x \leq 0.6$, band emission predominates. For $x = 0.6$, this band occurs at 2.28 eV, and its intensity at 2.53 eV (the Tb^{+3} excitation energy) is roughly 1% of the maximum.

All of our samples also emit well-known lower energy bands,[5] which have excitation spectra distinct from those previously discussed. This emission band is at 2.46 eV in ZnS:Cu, Ln, and in ZnS:Ag, Ln it is at 2.87 eV. We have not yet found definite evidence that excitation of the centers responsible for these emission bands results in the transfer of any energy to the rare-earth ions, regardless of the relative positions of the rare-earth energy levels and the lower energy emission bands.

Although firm conclusions cannot be drawn regarding the microscopic nature of the sensitizer and activator centers of this system until analyses of the optical or paramagnetic resonance spectra have been made, there is some evidence that the copper or silver ions and rare-earth ions are close enough to mutually alter their optical spectra. ZnS:Er, ZnS:Cu, Er, and ZnS:Ag, Er each has a distinct emission spectrum. For example, the transition $^4S_{3/2}\rightarrow{}^4I_{15/2}$ lies about 300 cm^{-1} lower in energy for ZnS:Ag, Er than for ZnS:Cu, Er. This sensitivity of the rare-earth spectrum to the specific group-I*b* element used implies that the two ions are closely associated.

The previous discussion pertains only to ZnS and CdS. We have also found that the addition of Cu to ZnSe strongly enhances the intensity of rare-earth fluorescence. ZnSe:Cu, Er, for example, emits most strongly from the transition $^4S_{3/2} \to {}^4I_{15/2}$ at 18 100 cm^{-1}. As in the case of ZnS and CdS, preparative conditions favoring the high-energy Cu band at 2.36 eV over the low-energy Cu band at 1.95 eV produce samples with the strongest rare-earth emission. Our preliminary data indicate, however, that the rare-earth excitation spectra of ZnSe are qualitatively different from Fig. 1, which may imply a somewhat different mechanism of transfer. On the other hand, all of the II-VI compounds show analogous emission bands due to group-I*b* dopants,[5] so we expect that the system described here can be extended to include all II-VI compounds and I*b* dopants.

The experiments discussed here have all been done on powder samples to simplify the control of the dopants. They were prepared from high-purity ZnS, CdS, and ZnSe, and fired in an atmosphere of purified H_2S or H_2 + Se at temperatures from 950 to 1150°C. We are now in the process of extending these studies using single crystals.

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FRANZ-KELDYSH EFFECT ABOVE THE FUNDAMENTAL EDGE IN GERMANIUM

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This Letter reports on the effect of an electric field on interband transitions well above the fundamental absorption edge. The effect is observed as a field-induced change in the reflectivity which peaks at approximately the photon energy of the particular transition. This pronounced structure of peaks should be profitable in the analysis of the band structure of semiconductors.

Although the Franz-Keldysh effect was observed in transmission at the fundamental absorption edge of several semiconductors, difficulties are encountered in extending this transmission measurement into the regions of strong absorption above this edge. It could not be determined, therefore, whether an electric field affects the transitions at higher photon energies in a similar manner.

We reported previously that the electric field in the potential barrier at the surface of germanium is strong enough to cause a Franz-Keldysh effect which is observed in reflection rather than in transmission.[1-3] The study could now be extended beyond the fundamental edge into the region of strong absorption.

The experiment employs the familiar field-effect configuration, with a transparent field electrode in close proximity to the electropolished germanium surface[4] at which the reflection of monochromatic light takes place at near normal incidence. The surface potential at the interface is modulated at 250 cps by an electric field of approximately 10^5 V/cm peak amplitude. Modulation impressed on the reflected beam is detected by either a photomultiplier or a PbS cell, followed by a narrow-band phase-sensitive amplifier. Applying this ac method, changes $\Delta R/R$ of the relative reflected intensity of as small as 5×10^{-6} can be measured.

As previously described for the fundamental edge,[1-3] the electric field affects the absorption mechanism such that for an increase in the height of the potential barrier in either direction the reflectivity decreases. Since the 30-Ω-cm n- and p-type germanium samples were treated to give n-type surfaces, most of the peaks in Fig. 1 go negative, indicating a decrease in reflectivity for the positive half-wave of the modulating field and vice versa for the negative. Depending upon the particular surface condition, this center peak is sometimes accompanied by one or two positive satel-