gy 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 $^4S_{3/2} \rightarrow {}^4I_{15/2}$ 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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(Received 30 December 1964)

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 halfwave 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-

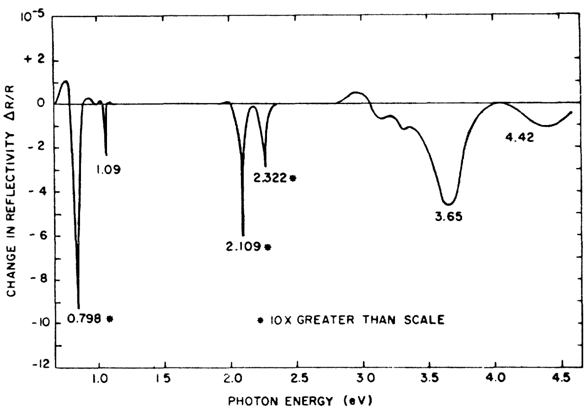

FIG. 1. Relative change of the reflectivity, $\Delta R/R$, as a function of photon energy. The recorder trace going negative indicates a decrease of the reflectivity caused by the positive half-wave of the modulating ac field. For three peaks marked *, multiply the scale by 10.

lite peaks. The overall magnitude of the peak structure in Fig. 1 is determined by the surface condition and can vary by as much as an order of magnitude, depending upon the surface treatment. The height of the peaks with respect to each other varies much less and their position is constant within 0.005 eV.

The trace in Fig. 1 marks clearly all the transitions in the band structure of germanium between 0.7 and 4.5 eV, as previously determined from the analysis of absorption and reflection measurements. A peak group centered at 0.798 eV precedes slightly the fundamental edge, followed by a much smaller peak at 1.09 eV. This represents the transition from the split-off valence band at $k = 0$,[5] which was not observed in reflection before.

The following region, particularly between 1.8 and 2.0 eV, was carefully searched for indications of the $L_{3'}-L_1$ transition, which is observed in some II-VI[6] and III-V[7] compounds, but can apparently not be resolved in germanium. Two strong peaks follow, split by 0.21 eV, the first one being about twice the height of the second one. Again they precede slightly their correlated absorption peaks,[8] which are assigned to transitions at the Λ point of the [111] direction,[9] starting from a valence band which is spin-orbit split by about 0.2 eV. The structure between 2.8 and 4.0 eV, resolved by this technique for the first time, suggests a quadruplet, with the first three components rising above the noise level, however, by only a factor of 2 to 3. No explanation can be given for the inverted phase relation between reflectivity and modulating field around 3.0 eV. Brust, Phillips, and Bassani's pseudopotential calculations place the transition $\Gamma_{25'}-\Gamma_{15}$ at 3.6 eV, with either end spin-orbit split, so that a quadruplet could result. Notice that the strongest peak appears at 3.65 eV, although absorption and reflection measurements show structure at 3.2 eV only.[10-12] The X and Σ transitions, which produce the strong reflectivity peak at 4.5 eV, respond rather weakly to the electric field at 4.42 eV. Our equipment cuts off at 4.6 eV, preventing us from looking for a possible splitting of this peak.

We conclude, from the presence of peaks at photon energies at which current analysis of the band structure places transitions between the bands, that the edges of these higher bands are affected by an electric field in a manner similar to the Franz-Keldysh effect of the fundamental edge. The size of the peak, however, does not represent so much the strength of the correlated transition as its sensitivity to a disturbance by an electric field. This should introduce a new parameter into the present analysis. It seems plausible, for instance, that an M_0 transition, which operates across a relative minimum of the gap (E_c-E_v), is affected stronger than an M_1 or M_2 transition at saddle points of E_c-E_v. Speaking qualitatively, the electric field stretches the band edge into energy regions formerly inaccessible to the electrons for the M_0 transition, while levels are produced for the M_1 or M_2 transition which were already available without electric fields at slightly different k values.

Evidence of this can be seen in the approximate 2:1 ratio of the response in the 2.2-eV doublet: In the 2.11-eV transition, both initial and final band edges are adjacent to the forbidden gap, extending into it under the influence of an electric field from either end. In the 2.32-eV transition, starting from the split-off band, only one edge stretches out into the forbidden gap. Notice further that the superposition of strong M_1 and M_2 transitions at 4.5 eV produces only the rather weak response at 4.42 eV. If this argument stands up against calculations of the field-induced change in the joint-density-of-states function[13] for the different types of transitions, one might even reconsider the present assignment of the strongly responding 2.11-eV and 2.32-eV doublet to an M_1 transition. The failure to observe any response in the 1.8- to 2.0-eV region is of significance in this respect. Aside from these theoretical aspects, the new technique marking the transitions as pronounced peaks will almost certainly complement the present methods from an experimental viewpoint, especially for materials which cannot be prepared by the sophisticated techniques applicable in the case of germanium.

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EFFECTIVE PAIR HAMILTONIANS AND GIANT EXCHANGE-ENHANCED *g* SHIFTS AND MOMENTS IN $CoCl_2$

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(Received 4 January 1964)

In a recent work, Hutchings and Wolf[1] observed small g shifts in some garnets and interpreted these shifts as induced by exchange through an admixture of the excited states of different magnetic ions. Unfortunately, the smallness of the observed shifts, ~1%, coupled with a lack of knowledge of the rare-earth single-ion wave functions and energies, precluded any conclusive interpretation of these results.

In the process of constructing a general spin-Hamiltonian formalism for pairs which uses the same mechanism to account for the admixture of excited states, we have found that specific application of theory to $CoCl_2$ predicts results in agreement with the very large experimentally observed exchange enhancement of the g factors and moments[2,3] for $CoCl_2$ relative to the single-ion paramagnetic-resonance values.[4] The example of $CoCl_2$ conclusively verifies the mixing mechanism and, moreover, establishes it as an invaluable tool for the independent measurement of the isotropic exchange parameters in appropriate magnetic systems.

The effective pair Hamiltonian formulation provides a fully dynamic Hamiltonian which is appropriate both to the dilute systems of identical or nonidentical pairs, and also to the pure magnetic system upon taking the sum over all effective pair interactions. In the derivation, we assume that the crystal-field problem with the inclusion of spin-orbit coupling has been solved for the single ion in the absence of magnetic fields. The single-ion wave functions are represented by $|\Phi_i^{\alpha}n\rangle$, with associated eigenvalues E_{in}. Here the indices correspond to the α state of the nth degenerate manifold of the ith ion. If the separation between the ground-state manifold and the next highest is $\gg kT$, and the interactions are small compared to the splitting, we need only consider matrix elements within the actual ground-state manifold. In direct analogy to the conventional spin-Hamiltonian methods, we desire to find an effective Hamiltonian which has the same matrix elements with unperturbed states, through second order in the mixing in of excited states, as the Hamiltonian has with the actual states, $|\psi_{i0}^{\alpha}\rangle$. We have

$$\langle \psi_{i0}^{\alpha}\psi_{j0}^{\beta}|\mathcal{H}_i+\mathcal{H}_j+V_{ij}|\psi_{i0}^{\alpha'}\psi_{j0}^{\beta'}\rangle = \langle \Phi_{i0}^{\alpha}\Phi_{j0}^{\beta}|\mathcal{H}_i^{\mathrm{eff}}+\mathcal{H}_j^{\mathrm{eff}}+V_{ij}^{\mathrm{eff}}|\Phi_{i0}^{\alpha'}\Phi_{j0}^{\beta'}\rangle, \qquad (1)$$