supplied the single-crystal V_3Si, to Professor C. G. Shull and H. J. Levinstein for helpful discussions, and to L. D. Fullerton for experimental assistance.

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*On temporary leave from Institute for the Study of Metals, The University of Chicago, Chicago, Illinois.

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OSCILLATORY PHOTOCONDUCTIVITY OF CdS

Y. S. Park and D. W. Langer
Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio

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Periodic oscillations of the photoconductivity in the impurity region have been observed previously for Ge,[1] InSb,[2] and in the intrinsic region for InSb[3,4] and GaSb.[4] Similar observations made at 4°K on selected CdS single crystals will be discussed here.

The photoconductivity near the absorption edge as a function of the exciting wavelength usually differs somewhat from crystal to crystal, even when grown as platelets and not intentionally doped. Many crystals exhibit photoconductivity peaks at energies corresponding to the positions of the free excitons.[5,6] Some crystals show, in addition to this, an oscillatory photoconductivity spectrum toward higher energies as shown in Fig. 1. Figure 1(a) is recorded with the *E* vector of the crystal perpendicular to the *c* axis and Fig. 1(b) for light polarized parallel to the *c* axis. The period between the minima is 0.036 ± 0.001 eV. There are two series of the minima indicated by long arrows and short arrows. The *A* series of minima, indicated by long arrows, is spaced successively by 0.036 eV from the *A* ($n = 1$) exciton peak ($\Gamma_5 = 4854$ Å), and the *B* series, originating from *B* ($n = 1$) exciton peak (4826 Å) by exactly the same spacing, is indicated by short arrows. The position of the *B* minima is less conspicuous because of the composite nature of the two series; however, their positions become more clear when the composite spectral response curves are decomposed as shown by the dashed curve.

No corresponding oscillatory structure is known to exist in the optical absorption or reflection spectra of CdS. These measurements, however, have not been made as accurately as those reported by Phillips[7] for Si.

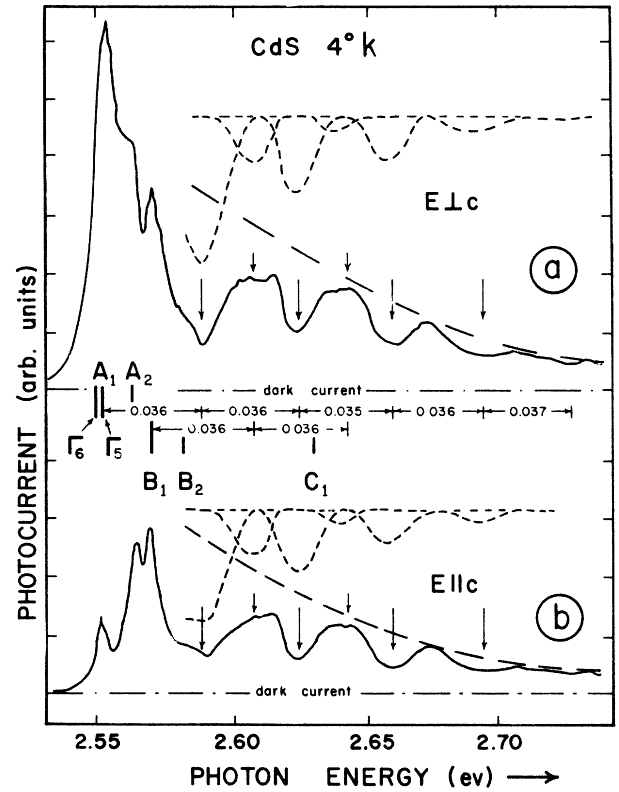
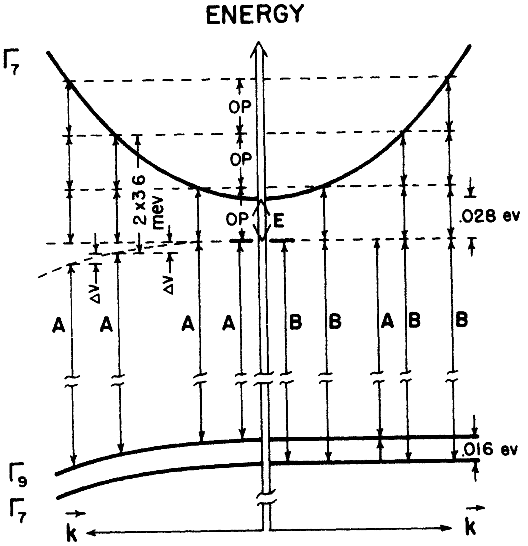


FIG. 1. Photoconductivity vs energy of exciting photons with (a) *E* vector perpendicular to the *c* axis and (b) *E* vector parallel to the *c* axis of a CdS platelet at 4.2°K. Indicated by bars are the positions of excitons *A*, *B*, and *C*. Long arrows indicate *A* minima, short arrows *B* minima, and the dashed curves show the separated contributions of the processes causing *A* and *B* minima.

The oscillatory behavior of the photoconductivity is due to an oscillatory value of the electron lifetime in the conduction band as function of its energy. The lifetime of the conduction electron at certain energy values is smaller than at adjacent energy values whenever that energy coincides with the sum of the energies of a shallow impurity[3] (or bandgap[4]) plus an integral multiple of a principal optical-phonon energy. The explanation of our data requires the ground states of excitons to play the role of the "shallow impurity." Figure 2 shows a simplified model of the band structure of CdS at the center of the Brillouin zone. Figure 2(a) shows the idealized case where transitions occur only from and to the top (Γ_9) valence band. The minimum of the conduction band is actually not exactly at $k = 0$ and its slope at $k = 0$ is less than 5×10^{-10} eV cm. The curvature of the valence bands is at least three times smaller than the curvature of the conduction band.[8] With downward-sloped valence bands one would expect the observed energy difference between adjacent photoconductivity minima to exceed the energy of the phonon involved by ΔV, which is the energy difference of the valence band for a Δk corresponding to an energy difference of the conduction band equivalent to the phonon energy. The phonon involved may be the longitudinal optical phonon at the zone boundary, which has an energy of 0.0366 eV at 300°K.[9] The observed energy difference between minima agrees within the experimental accuracy with this value. The magnitude of ΔV, therefore, cannot be determined and has to be smaller than our limit of error.



$\vec{E} \perp c : \Gamma_7 \leftrightarrow \Gamma_9, \Gamma_7 \leftrightarrow \Gamma_7$ (a)

$\vec{E} \parallel c : \Gamma_7 \leftrightarrow \Gamma_7$ (b)

FIG. 2. Band model showing upper valence bands and conduction band in CdS. OP stands for the energy of an optical phonon and A and B for the energies of excitons A and B, respectively. The binding energy of both excitons is identical (0.028 eV). Allowed transitions are $\Gamma_9 \leftrightarrow \Gamma_7$ for the E vector perpendicular to the crystal c axis and $\Gamma_7 \leftrightarrow \Gamma_7$ for the E vector parallel or perpendicular. (a) Illustrates the proposed origin of A minima. ΔV reflects the curvature of the valence band. (b) Here the curvature of the valence band is neglected for simplicity. The origins of A and B minima corresponding to the case realized in Fig. 1(b) are indicated. The case shown in Fig. 1(a) corresponds to the sum of the mechanisms illustrated in Figs. 2(a) and 2(b).

Similar to the suggestion by Stocker et al.[3] for InSb, we think that in CdS the higher excited conduction electrons lose their energy by dropping or cascading down to the exciton levels. An indication for this assumption appears from a closer look at Fig. 1. In Fig. 1(b), according to selection rules, the excited electrons originate predominantly in the Γ_7 valence band as is also apparent by the nearly vanishing A-exciton peak. In Fig. 1(a), using light polarized perpendicularly to the c axis, electron transitions originate as well from the Γ_9 as from the Γ_7 valence band. In both cases we see, in addition to the A series of minima, lesser minima (indicated by short arrows) again approximately 0.036 eV apart and 0.036 eV displaced from the peak corresponding to the B ($n = 1$) exciton ground state. This shows the reduced lifetime of conduction electrons with energy values $B + \mathrm{OP}$ and $B + 2\mathrm{OP}$. Startling at first glance is that even in Fig. 1(b) the A minima are still the predominant ones. With predominant $\Gamma_7 \rightarrow \Gamma_7$ excitation, a cascading from the position of the A minima by emission of phonons cannot lead the electron to the exciton level. However, the appearance of A-minima series is probably due to transition of the photoexcited holes from Γ_7 valence band to Γ_9 valence bands, thereby forming A excitons and combinations of A excitons with multiple phonons.

The initial absorption of light at the exciton energy leads to the formation of direct excitons followed by their dissociation into current carriers, thus appearing as photoconductivity maxima in the spectral response curves of photoconductivity. The dissociation might occur either by interaction with an impurity center or by absorption or emission of phonons. The energies which can be divided into an exciton plus multiple phonons give another mode of decay causing a minimum to appear in the photocurrent.

We would like to thank Mr. Don Naas of this laboratory for the growth of the crystals.

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MAGNETICALLY INDUCED LINE ABSORPTION IN $CaF_2(Sm^{2+})$ AND $SrF_2(Sm^{2+})$

M. H. Crozier
National Magnet Laboratory,* Massachusetts Institute of Technology, Cambridge, Massachusetts

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By the use of high magnetic fields, up to 110 kilogauss, we have been able to observe directly at 4.2°K the symmetry-forbidden absorption from the $^7F_0(A_{1g})$ ground state to the A_{1u} excited state, the lowest state of u parity, for Sm^{2+} in CaF_2 and in SrF_2. This is the first time high magnetic fields have been used to break down selection rules and make possible direct observation of levels which are important for the interpretation of fluorescence spectra, and the results serve to establish more clearly the relation between the $4f^6$ and $4f^5 5d$ configurations in the cubic crystal fields of these materials.

The relevant energy levels of the Sm^{2+} ion are shown in Fig. 1. The lower levels belong to the ^7F multiplet of $4f^6$, with $^7F_0(A_{1g})$ lowest and $^7F_1(T_{1g})$ next. In CaF_2 the upper levels from which line spectra are seen belong to $4f^5 5d$, with a state of A_{1u} symmetry lowest and one of T_{1g} symmetry next.[1,2] The magnetic field term $\beta\vec{B}\cdot(\vec{L}+2\vec{S})$ in the Hamiltonian of the Sm^{2+} ion causes mixing of A_{1g} and T_{1g} states, and of A_{1u} and T_{1u} states, so that the $A_{1g}\rightarrow A_{1u}$ transition can occur through the nonvanishing electric dipole matrix elements connecting A_{1g} to T_{1u} and A_{1u} to T_{1g}. Between $^7F_0(A_{1g})$ and $^7F_1(T_{1g})$, perturbation theory gives a mixing coefficient of $0.0076(\beta B)$, where (βB) is measured in cm^{-1}, and a similar magnitude may be expected between the A_{1u} and T_{1u} states, so that the intensity conferred is very small at low fields but increases quadratically to become significant at high fields.

In a highly doped (dark green) sample of $CaF_2(Sm^{2+})$, 0.74 cm thick, we observed an induced absorption line at 6957.4 Å with an absorption coefficient of $0.030(\beta B)^2$. Accompanying this effect there should be a small quadratic shift in the position of the line, but within the limits set by the linewidth (~1 cm^{-1}) no effect was observed. This is reasonable since the shift would be the difference in the depression of the A_{1u} and A_{1g} levels, and one may calculate that at 110 kilogauss the depression of A_{1g} is only 0.1 cm^{-1}.

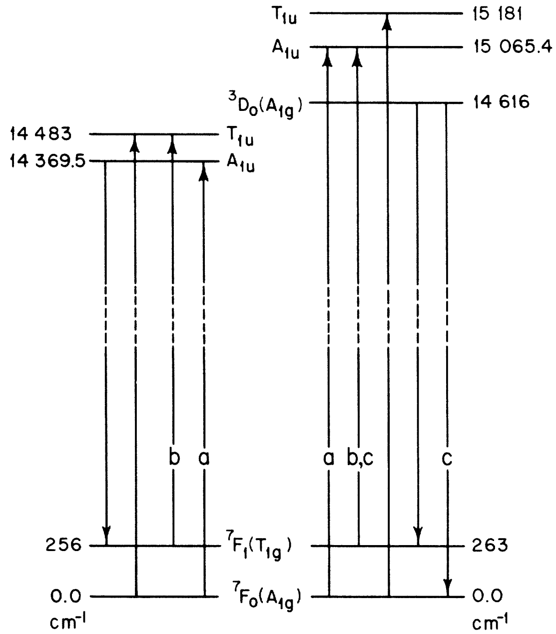

FIG. 1. Relevant energy levels of $CaF_2(Sm^{2+})$ and $SrF_2(Sm^{2+})$. (a) Observed only in high magnetic fields; (b) observed only at 77°K; (c) weak fluorescence reported in reference 2.

It is important to note that the line is completely polarized parallel to the applied magnetic field. That this must be so may readily be seen by observing that as a consequence of the O_h symmetry the effect must be isotropic, so that it is sufficient to consider the field applied along a