perature values of μ_h for the seven crystals lie in a range between 10 and 18 cm^2 v^{-1} sec^{-1} with a mean value of about 15 cm^2 v^{-1} sec^{-1}. The good linearity of the calculated curves supports the validity of the assumptions made in deriving Eq. (1).

The temperature dependence of μ_h has been investigated between 500°K and 77°K for five of the specimens. The agreement between different curves is very satisfactory. The interesting feature of the results is a mobility maximum at about 210°K after which all $\log\mu_h$ vs $1/T$ curves decrease linearly towards the lower temperatures with an activation energy of 0.019 ± 0.002 ev. It may be possible that this energy is associated with transitions of free holes between the upper two valence bands of CdS. Such an interpretation appears to be supported by recent work on the band structure of CdS,[7] in which the dichroism of absorption edge is explained in terms of transitions from the upper two valence bands to the conduction bands. From the optical data it is concluded that the energy separation between these bands is 0.02 ev at room temperature and 0.016 ev at 4.3°K, which agrees with the above activation energy, measured between 200°K and 77°K.

Further work on the possible interpretation of these results in terms of the valence band structure is in progress.

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FREE CHARGE CARRIER EFFECTS IN CADMIUM FLUORIDE

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We have found optical absorption and conductivity due to free electrons in single crystals of CdF_2 doped with several trivalent rare earth ions. CdF_2 has a band gap of[1] 6 ev and the fluorite structure. This is the first observation of a large concentration of conduction electrons in an ionic crystal with such a large band gap.

It was shown by the determination of the crystal field splitting of the low-lying Eu^{+3} levels as obtained from an analysis of the fluorescence spectrum of CdF_2:Eu that, for concentrations of Eu in the range 10^{-3} to 10^{-5} mole fraction, charge compensation is ordinarily achieved by means of interstitial fluoride ions.[2] Earlier measurements of the x-ray lattice constant and density of CdF_2:Ce^{+3} yielded the same conclusion at larger impurity concentrations.[3] A similar conclusion holds for CaF_2 doped with trivalent ions.[4,5] We have now found that charge compensation can also proceed by means of electrons in the conduction band or in shallow (0.06 ev deep) traps.

When CdF_2:Sm^{+3} crystals of about 0.1 cm^3 are heated in a saturated cadmium metal vapor at 500°C, for times as little as 15 minutes, the originally colorless crystals become colored blue uniformly and transmission measurements from 0.4 μ to 6.0 μ show a continuously rising absorption. In crystals containing 10^{-3} Sm the absorption coefficient varied as $\lambda^{3.5}$, and crystals containing 10^{-4} Sm yielded a $\lambda^{3.0}$ dependence.

The resistivities of these crystals, as obtained by a four-point probe method, were about 1 ohm cm. Both thermoelectric power and Hall measurements indicated *n*-type conductivity with a room-temperature mobility of 7 to 10 cm^2/volt sec and carrier concentrations from 5×10^{17} to 10^{18}/cm^3.

We propose that heating in Cd vapor results in the diffusion of the interstitial F^- ions to the surface and the diffusion of electrons in from the surface, CdF_2 being then formed at the surface. In CdF_2:Sm^{+3},Na^{+1}, in which the substitutional Na^{+1} ion compensates the charge of the Sm^{+3} ion, no coloration was observed nor could pure CdF_2

crystals be colored. The blue color could be bleached by heating the crystals in a vacuum at 300°C with the concurrent deposition of a Cd mirror on the cooler glass walls. Changes observed in the Sm^{+3} fluorescence after coloration are consistent with the idea that the local symmetry about the rare earth ion is changed due to the absence of the nearby interstitial fluoride ion in the colored crystal.

In addition to Sm-doped CdF_2, free-carrier absorption has also been observed in material doped with Tb and Dy. With CdF_2:Eu^{+3} the electrons are trapped in the $4f$ Eu states, giving rise to a Eu^{+2} absorption band in the near ultraviolet. Although free-carrier absorption has been observed in several other binary compounds (e.g., in[6] ZnO and[7] CdS), CdF_2 is the first material with a 6-ev band gap to show these effects.

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SUPERCONDUCTIVE TUNNELING*

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Experiments[1-3] involving the tunneling of electrons between superconducting films covered by a thin (~20 Å) oxide layer and either normal or superconducting metals have shown that the tunneling current between, e.g., normal and superconducting metals is directly proportional to $\rho_S(E)$, the superconducting density of states as predicted by the BCS theory,[4]

$$\rho_s(E)=\rho_n(E)\times[E/(E^2-\Delta^2)^{1/2}], \quad |E|>\Delta$$

$$=0, \qquad |E|<\Delta. \tag{1}$$

Several attempts have been made to explain this result. Bardeen[5] has obtained the formula for the tunneling rate from state a to state b,

$$R_{ab}=(2\pi/\hbar)|T_{ab}|^2\rho(E_b)f_a(1-f_b). \tag{2}$$

Here f_a and f_b are the occupation numbers of states a and b, respectively. Bardeen has used the Gor'kov[6,7] formalism to argue that the matrix element T_{ab}, which usually contains energy-dependent coherence factors, should be constant. In order to obtain this result, assumptions must be made about the number of particles in a quasiparticle state.[8]

Other treatments[9] have used the two-fluid model[10] in analogy with semiconductors. Harrison[11] has emphasized the fundamental problem of the two-fluid picture, i.e., according to the WKB treatment of quasi-particle tunneling,

$$|T_{ab}|^2\sim V_aV_b|I_{ab}|^2, \tag{3}$$

where I_{ab} is the exponential tunneling integral and V_a and V_b the velocity of the quasi-particle in the states a and b. Because $V_b\sim[\rho(E_b)]^{-1}$, the single-particle $\rho(E_b)$ cancels from (2), leaving the transition rate independent of $\rho(E_b)=\rho_S(E)$.

Here we present a Hamiltonian treatment of the tunneling process from normal metal to superconductor:

$$H=H_n+H_s+H_T, \tag{4}$$

where H_n and H_S are the exact Hamiltonians for the normal metal and the superconductor. The coupling term H_T transfers electrons from the normal metal to the superconductor and vice versa.

We choose representations such that

$$H_n=\sum_{k\sigma}\epsilon_k a_{k\sigma}^{\dagger}a_{k\sigma}, \tag{5}$$