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[2]An additional term ϵeFx, ϵ being a local dielectric constant, has been dropped from the Hamiltonian since it has very little effect for fields less than 10^7 V/cm. Hed and Freud [A. Z. Hed and P. J. Freud, J. Non-Crystalline Solids 2, 484 (1970)] suggest that this term can result in switching to normal conduction at high fields because it replaces A with $A_{eff} = A - \epsilon eF$, and a large value of F will then decrease A_{eff} until the criteria for formation of a polaron band are no longer satisfied. Note that ϵ should be close to unity, since the field in a spherical cavity is never more than 50% greater than that in the surrounding dielectric. Hed and Freud take ϵ between 10 and 100, and therefore get large changes at fields of 10^5–10^6 V/cm. Further, these authors failed to note that negative values of F would increase A, so no breakdown occurs in the back direction. Symmetry under field reversal is expected in most materials (including theirs, which were cubic) and can be restored by supposing that A changes sign from site to site. One then finds that A_{eff} is given by

$$A_{eff}^2 = \tfrac{1}{2}(A - \epsilon eF)^2 + \tfrac{1}{2}(-A - \epsilon eF)^2 = A^2 + \epsilon^2 e^2 F^2;$$

i.e., an applied field can generally be expected to augment A and therefore increase the stability of a polaron band.

[3]Lebwohl and Tsu [P. A. Lebwohl and R. Tsu, J. Appl. Phys. 141, 2664 (1970)] have recently used the Boltzmann transport equation to calculate the current density due to carriers with degenerate statistics in a "miniband" arising from a one-dimensional superlattice. They find that the current is inversely proportional to the field at large fields, as is found above in the negative resistance region when L is large. Their current maximum is sharper than mine and occurs at a field that is about 50% greater for a given bandwidth. Both calculations deserve criticism; mine principally because the correlation between scatterings has been included in a quite arbitrary manner; theirs because local momentum eigenfunctions and a relaxation time are not appropriate to the problem of a narrow band in a large electric field. Lebwohl and Tsu's method is, however, likely to be the more accurate of the two, though not readily applied when the discrete nature of electron sites must be allowed for.

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Mobilities of Electrons and Holes in CaF_2

J. Dresner and P. M. Heyman
RCA Laboratories, Princeton, New Jersey 08540
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The Hall mobility of electrons and holes in CaF_2 (0.005% Tb) was measured under illumination by near-uv radiation (3100–4000 Å) in the temperature range 25–200 °C. At 334 °K $= \frac{1}{2}\theta_{LO}$, the maximum measured mobilities were 236 and 100 $cm^2V^{-1}sec^{-1}$, respectively, for electrons and holes. These magnitudes are consistent with those predicted by wide-band optical-phonon theories (large polaron). Upper limits of $m^* \leq 0.12m$ and $m^* \leq 0.21m$ were estimated respectively for the electron and hole band masses. Because of two-carrier effects, it was not possible to determine whether the charge transfer during the photochromic process occurs via the conduction or valence bands.

INTRODUCTION

This paper reports the first Hall-mobility measurements for electrons and holes in CaF_2. The samples were doped with 0.005 mole% Tb (and additively colored) to provide some photoconductivity in the region 3100–4000 Å, where a weak absorption band is created.[1]

Some of the properties of CaF_2 relevant to this work are listed: optical band gap[2]-10 eV; dielectric constants at[3] 300 °K—static $\epsilon_0 = 6.63$, optical $\epsilon_\infty = 2.04$; energy of LO phonons[3]—463 $cm^{-1} = 668$ °K $= \theta_{LO}$.

These measurements were motivated by two problems.

(a) Unlike the weakly doped samples measured in this work, CaF_2 containing higher concentrations of rare earths (e.g., 0.1% Tb, La, Ce, and Gd), which has been colored either by ionizing radiation or by chemical reduction exhibits photochromism when irradiated by light in the range 3100–4000 Å (hereafter referred to as switching light). Evidence obtained from optical and electron-paramagnetic-resonance (EPR) data[4,5] shows that the broad absorption band at $\lambda_{max} \approx 4000$ Å originates in a complex center consisting of a RE^{+2} and a nearest-neighbor F center. Upon application of switching light, the complex center loses an electron while a RE (rare earth) located in a state of cubic symmetry, which is trivalent in the stable state, becomes divalent. There is circumstantial evidence[1,4,5] that the charge transfer is effected by electrons through the conduction band. However the alternate process through hole motion cannot be ruled out.[1] The two processes should be distinguishable by the Hall effect.

(b) It is likely that in an ionic crystal such as CaF_2, the electron-lattice interaction should be

strong enough to view charge transport in terms of polaron theories. The electron-phonon coupling is characterized by the Frohlich coupling constant

$$\alpha = (m^* e/2\hbar^3\omega_{LO})^{1/2}(\epsilon_\infty^{-1} - \epsilon_0^{-1}) ,$$

where m^* is the "bare" band mass. For CaF_2, $\alpha = 5.23\ (m^*/m)^{1/2}$, where m is the free-electron mass. In the intermediate-coupling regime, $1 < \alpha < 10$, polaron effects should be in evidence. In the range of temperatures $T \geq \frac{1}{2}\theta_{LO}$, to which our measurements are restricted, one should expect an exponential dependence of mobility with T. Reviews of the relevant theories may be found in Refs. 6 and 7. To date, there exist no measurements of m^* for CaF_2; for electrons a value of the polaron mass $m_p = 0.6m = m^*\ (1 - \frac{1}{6}\alpha)^{-1}$ has been calculated by Bennett.[8]

Sample Preparation and Experimental Methods

The three wafers measured were cut normal to the [100] axis of a CaF_2 boule grown by the gradient-freeze technique. In addition to the 0.005 mole% Tb, the amounts of other impurities measured in ppm were Si < 0.1, Y < 0.6, Ba 1–10, Cu 1–10, Al 1–10, Fe 1–10, Mg 10–100, Sr 30–300. The wafers, approximately 1 mm thick, were then colored by heating in an evacuated container under a Ca vapor pressure of 10^{-2} Torr at 600 °C for 1 h. Subsequent polishing removed approximately 0.25 mm from each face.

The dc Hall measurements were made using the apparatus and cross-shaped electrode geometry described previously.[9] Because of the low conductivity under illumination [$\sigma \approx 10^{-12}(\Omega\ \mathrm{cm})^{-1}$] near room temperature, the interelectrode spacing was reduced to 0.5 mm. Since the optical density of the samples for switching light is only 0.5, carrier production occurs throughout the sample volume, and the two-dimensional expression for the mobility μ derived in Ref. 9 must be corrected. The correction factor was obtained by measuring samples of CdS, n-type Si, and p-type Si of known mobility having the desired geometry. The expression for the mobility is then given by

$$\mu = \frac{V_{Hall}10^8}{V_x BG}\ \mathrm{cm^2V^{-1}sec^{-1}} ,$$

where V_x is the voltage between the current electrodes and the geometrical factor $G = 0.32$ rather than the value 0.56 calculated for the two-dimensional case. An implicit assumption of the method is that the voltage drop at the current electrodes is a negligible fraction of V_x. For Ag electrodes, this condition appears to be fulfilled, under illumination, above 50 °C, since no polarization effects were observed. At lower temperatures, electrode polarization may lower the measured value of μ. These electrode effects were minimized by reversing the current direction for consecutive measurements. From measurements on other materials, it has been established that values of μ obtained by the cross geometry are from 10 to 20% lower than those given by the standard Hall bar geometry in the absence of electrode effects. All measurements were made in a dry He or N_2 ambient.

EXPERIMENTAL RESULTS

Figures 1(a) and 1(b) show the measurements of σ and μ, under dark (σ_d, μ_d) and illuminated (σ_l, μ_l) conditions, for freshly prepared samples, i.e., samples kept in darkness at room temperature and not exposed to switching light until measured. For samples 1 and 2, the initial μ_l was p type. This was an unstable state, which changed to n type under illumination and heating. Both samples remained p type for about 30 min, sufficient to make several measurements at constant temperature. In sample 1, the points of Fig. 1(b) joined by the dashed line were taken on consecutive days. For sample 2, the values of μ were measured during one continuous slow heating cycle. The arrows indicate the sequence of measurements during the original heating cycle. The initial p-type mobility could not be reproduced after cooling following the heating cycle. Sample 3 did not exhibit this original p-type mobility. Samples 1, 2, and 3 showed values of n-type μ_l of approximately 40–70 $\mathrm{cm^2V^{-1}sec^{-1}}$ in the range 25–50 °C, in the steady state. These values were not significantly changed by annealing sample 1 for 4.5 h at 140 °C and sample 2 for 1 h at 200 °C in N_2.

The decrease in the n-type μ_l with increasing temperature was found to be reproducible; the region of strongest decrease coincides with the rapid rise in σ_l above 50 °C. For sample 1, μ_l becomes p type when i_d becomes an appreciable fraction of i_l. For sample 2, the p-type regime could not be reached, our apparatus being limited to $T < 250$ °C. In the higher-temperature region, i_d was sufficiently large to permit measurements of μ_d. These were performed on sample 3, yielding p-type mobilities ranging from 4 to 8 $\mathrm{cm^2V^{-1}sec^{-1}}$ at $T = 204$–212 °C. The values of μ_l at low temperature for this sample are close to those for samples 1 and 2 as shown in Fig. 1(b).

The effect of x-ray irradiation (10^6 rad, $h\nu_{max}$ = MeV) was studied on samples 1 and 2. The samples were maintained at 15 °C during the irradiations, which increased the optical absorption in the switching band ($\lambda < 4000$ Å) by about 10%.

On both samples, the major effect of the irradiation was to make the sample n type, regardless of its previous state, as described below, and to always increase the value of μ_n at a given temperature, by a factor as great as 4. Since the x rays

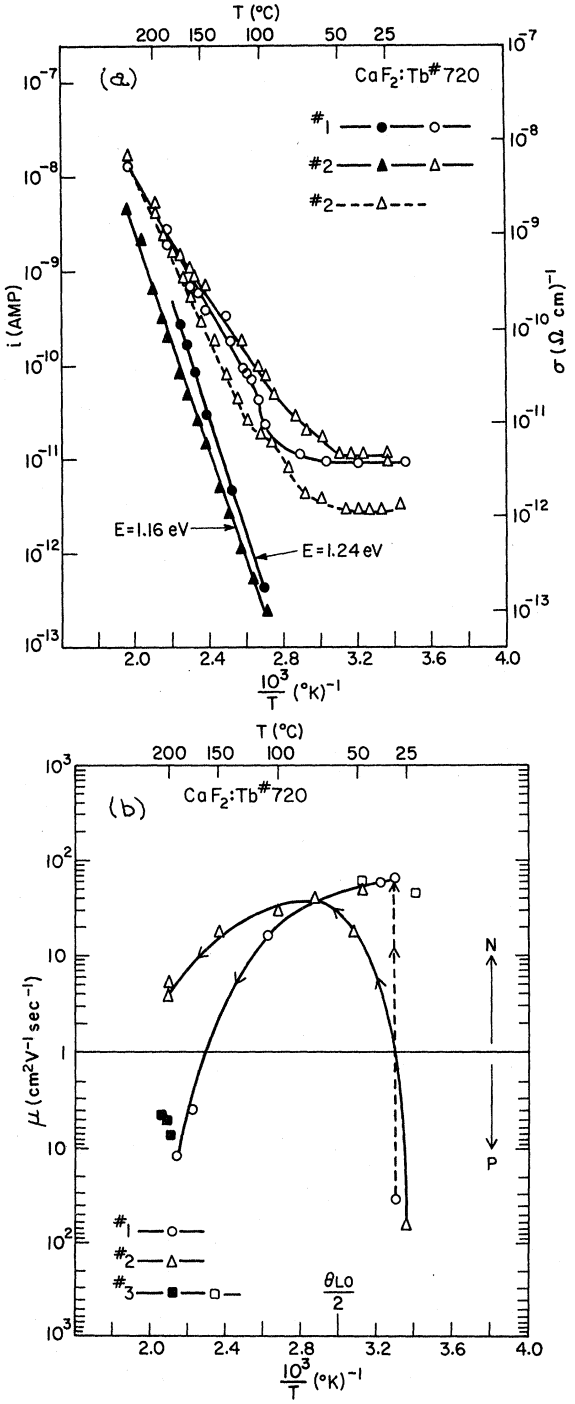

FIG. 1. (a) Conductivity vs temperature for samples 1 and 2. The open points represent photocurrents and the filled points represent dark currents. The dashed curve for sample 2 was taken after approximately 1 h at 200 °C and slow cooling to 22 °C. (b) Mobility vs temperature for samples 1, 2, and 3. Open points under illumination; filled points in darkness. The arrows indicate the sequence of measurements on freshly prepared samples (see text). The higher mobility point at 50 °C for sample 2 is that obtained after completion of the heating cycle and annealing. The value of $\frac{1}{2}\theta_{LO} = 334$ °K.

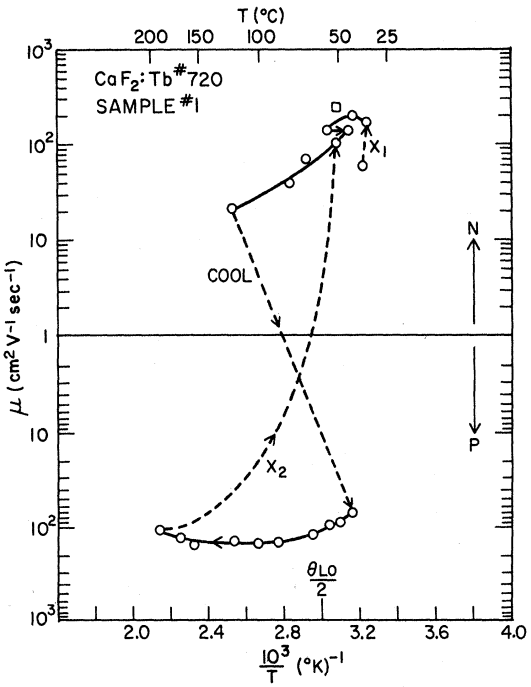

FIG. 2. One sequence of μ vs T measurements upon x-ray irradiation in sample 1. See text for measurement sequence. The square point is the highest value of electron mobility measured, 236 $cm^2V^{-1}sec^{-1}$ at 51 °C $= 0.49\theta_{LO}$.

produce free electrons and holes, all available types of states in the forbidden gap may be filled. One sequence of measurements is shown in Fig. 2. Upon the first x-ray irradiation X_1, μ_i increased by a factor of 3. Upon heating, μ reaches a maximum, then decreases. Allowing the sample to cool slightly after reaching 60 °C shows that μ_i has decreased by the action of switching light and heating. Polarization effects were found to be negligible. After reaching 120 °C, the sample was cooled and kept in the apparatus, in darkness at room temperature for 22 days (2×10^6 sec). A new heating curve showed a p-type state with $\mu_i > 100$ cm^2V^{-1} sec. Upon cooling and a second x-ray irradiation X_2, the sample reverted to n type. The highest value of electron mobility obtained in any of these experiments was 236 $cm^2V^{-1}sec^{-1}$ at 51 °C $= 0.49\theta_{LO}$. The highest hole mobility was 156 $cm^2V^{-1}sec^{-1}$ at 157 °C.

DISCUSSION

In CaF_2, unlike the alkali halides where holes do not appear to contribute appreciably to the conductivity, two-carrier effects are ubiquitous. Since the bandgap is 10 eV and the illumination has $h\nu \lesssim 4$ eV, transitions are induced in two separate sets of levels, respectively near the conduction and valence bands.

TABLE I. Measured and calculated mobilities at $T=\frac{1}{2}\theta_{LO}$.

		m^*/m	m_p/m	α	θ_{LO}(°K)	$\mu(\frac{1}{2}\theta_{LO})$ ($cm^2V^{-1}sec^{-1}$) measured	$\mu(\frac{1}{2}\theta_{LO})$ ($cm^2V^{-1}sec^{-1}$) calculated[a]
Electrons	KBr	0.428[b]	0.93[b]	3.52	238	70[c,d]	90
	KCl	0.496[b]	1.25[b]	3.97	296	100[c]	55
	RbCl	0.515[b]	1.38[b]	4.14	276	70[c]	55
	AgCl	0.348[b]	0.51[b]	2.0	280	120[e]	165
	AgBr	0.241[b]	0.33[b]	1.69	210	200[f]	376
	ZnO	0.27[f]	...	0.85	920	80[f]	152
Electrons	CaF_2	≤ 0.12	≤ 0.17	≤ 1.8	668	236	...
Holes	CaF_2	≤ 0.21	≤ 0.35	≤ 2.4	668	100	...

[a]Calculated using the formula of Petritz and Scanlon.
[b]Reference 14.
[c]C. Seager and D. Emin, Phys. Rev. B 2, 3421 (1970).
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(a) The observation of a p-type μ_d and p-type μ_l when $i_d \geq 0.3 i_l$ suggests the existence of an acceptor center with a depth approximately 1.2 eV, obtained from the slope of i_d in Fig. 1 (a).

(b) With increasing T, the n-type μ_l decreases as i_l rises. This rise in p-type photocurrent is maintained after the annealing. Thus photoemission of free holes from filled acceptors or very deep traps cannot be excluded at the lower temperatures. The n-type signal in the region 25–50 °C, in the steady state following the annealing, means $n\mu_n^2 > p\mu_p^2$, e.g., if one uses the maximum values of μ_n and μ_p in that range of T obtained from Fig. 2, one can conclude only $n > 0.25p$. The effect of ionizing radiation at room temperature in increasing the absorption at $3000 < \lambda < 4000$ Å as well as the bleaching of this band by switching light is well known in rare-earth doped CaF_2.[4,10] In our additively colored samples, the increase in the absorption by the additional complex centers thus created is always accompanied by a rise in the measured value of μ_n (increase in n/p). Also, there is some evidence of "bleaching" of μ_n by switching light. However, Fig. 2 shows that the switching light can release holes from acceptors or traps with a lifetime $\tau \gg 10^6$ sec at 20 °C ($E \geq 1.2$ eV). Also, the existence of deep electron traps filled by the x-ray irradiation cannot be ruled out. Consequently, it is not possible to distinguish between the electron and hole transfer models for the photochromic process from the present measurements.

(c) Because of two-carrier effects, all measured mobilities are lower limits, and $\mu(T)$ cannot be fitted to any theoretical expression. Nevertheless, an upper limit on the magnitude of m^* and m_p can be estimated for electrons and holes in CaF_2, using the highest values of μ at $T=\frac{1}{2}\theta_{LO}$, under the assumption of polaron motion which is reasonable in view of the large value of α, as discussed above, but which cannot be proved at present.

The theoretically derived expressions for the mobility using the large-polaron model (continuum approximation, or "heavy" electron moving in a wide band) are normally considered to apply only where $\alpha < 1$.[6,7] Such expressions have been derived by Howarth and Sondheimer,[11] by Petritz and Scanlon,[12] and by Garcia-Moliner.[13] However, all these expressions yield mobilities which do not differ by more than a factor of 2 or 3 from the experimentally determined values for materials where $\alpha < 5$ at $T=\frac{1}{2}\theta_{LO}$. Examples are given for six polar crystals in the upper-half of Table I, where the polaron mass has been determined independently by cyclotron resonance.[14] Values of μ calculated by the formula of Petritz and Scanlon

$$\mu = \frac{e}{2m^*\omega_{LO}\alpha}\left(\frac{8}{3\pi^{1/2}}\right)\chi(Z)\left(\frac{e^Z-1}{Z^{1/2}}\right),$$

where $Z=\theta_{LO}/T$ and $\chi(2)=0.72$, give the closest fit at this temperature. Using this formula, we calculate upper limits for m^* in CaF_2 of $0.12m$ and $0.21m$, respectively, for electrons and holes as shown in the lower half of Table I. An error of a factor of 2 in the accuracy of the Petritz and Scanlon formula would raise these limits at most by a factor of 1.6. The polaron masses calculated using the expression $m_p = m^*(1-\frac{1}{6}\alpha)^{-1}$, yield, respectively, $m_p \lesssim 0.17\,m$ and $m_p \lesssim 0.35\,m$ for electrons and holes, values lower than those calculated by Bennett[8] for electrons.

The low values of effective masses m^* imply the existence of broad conduction and valence bands. This is of interest since no calculation of the band structure of CaF_2 has been done to date.

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X-Ray Photoelectron Spectroscopy of Solids; Evidence of Band Structure

T. Novakov

Shell Development Company, Emeryville, California 94608

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X-ray photoelectron spectra of solid Cu_2O, CuCl, CuO, CuS, and $CuSO_4$ were measured. In all cases, satellites having various degrees of complexity are seen adjacent to the (Cu) $2p$ photolines. A multiple-excitation mechanism is proposed for the explanation of these satellites. The satellites are formed when the emission of a $2p$ photoelectron takes place in parallel with a valence-band–conduction-band excitation. These photolines are thus emitted with kinetic energies lowered by the amounts of allowed interband transitions.

I. INTRODUCTION

X-ray photoelectron spectroscopy is successfully being applied to elucidate problems of molecular structure by measuring the electron core-level binding energies.[1] Both solids and gases are studied. Binding energies are known to depend on the charge of the atom in the molecule.[1,2] Valence-electron structure has also been investigated, mostly in the case of free gaseous molecules. The same technique has been extensively used to study Auger-electron emission from both atoms and molecules.[3] Most of the work done in this field, however, relates to chemical problems.

In this paper, some photoelectron experiments will be described, which seem to have a direct relation to electronic properties of solids. The method of photoelectron spectroscopy is basically very simple. The solid whose photoelectron spectrum is to be investigated is irradiated by a "monochromatic" x ray, for example, by Mg $K\alpha$($h\nu$ = 1253.6 eV) or Al $K\alpha$($h\nu$ = 1486.6 eV) radiation. These radiations have an intrinsic width of about 1 eV, which sets the limit on the linewidth. The emitted photoelectrons are analyzed by a high-resolution electron spectrometer.

From the conservation of energy it follows that

$$h\nu = E^f - E^i + E_{\rm kin} + \phi \ ,$$

where E^f and E^i are the total final and initial energies of the system. $E_{\rm kin}$ is the kinetic energy of the ejected electron and ϕ is the contact potential difference between the sample surface and the spectrometer. If there are several final states possible then there will be, at least in principle, a corresponding number of photoelectron lines emitted from a given subshell.

For a simple one-electron process, E^f would correspond to a vacancy in the level, and the difference $E^f - E^i$ would be equal to the electron binding energy of that level. In this case, a single photoline is seen. In other cases, complex lines may appear in the spectrum. In this investigation, we were looking particularly for cases of line splittings and line satellites. Less attention has been paid to the absolute energies of photolines and therefore all our quoted binding energies are nominal.

II. EXPERIMENTAL TECHNIQUE

The experiments described in this work have been performed with the Varian IEE-15 electrostatic spectrometer, utilizing Al $K\alpha$ radiation. The analyzer part of the spectrometer was set to transmit electrons of a preset energy. Typically, this energy may be between 30 and 100 eV. The scanning of the spectrum is done by stepping a positive bias voltage applied to the sample. Provision, however, was made that the immediate vicinity of the sample was in a field-free region, although at a positive potential with respect to the rest of the spectrometer. The advantage of this mode of operation is that the spectrometer contribution to the