Photoconductivity of KBr Containing *F* Centers*

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The quantum efficiency or number of conduction-band electrons produced per absorbed photon in the region of the L bands at 21°K in KBr was found to be nearly unity. Photoconductivity measurements indicated that the L bands are due to electronic transitions to energy levels which are in the conduction band and that the K band is composed of two or more overlapping optical-absorption bands, of which the higher energy ones are due to electronic transitions to the conduction band. The temperature dependence of the L-band photoconductivity below 45°K can be explained by the temperature dependence of the mobility.

I. INTRODUCTION

THE F band in the alkali halides is accompanied by weaker optical-absorption bands, whose absorption maxima are proportional to the F-band height. These bands,[1] named K, L_1, L_2, and L_3, are shown by the solid curve of Fig. 1 for KBr. The F center is an electron trapped in a negative-ion vacancy. Optical excitation of this electron to the first excited state gives rise to the F band while excitation of this electron to higher states is considered to be the cause of the remaining bands.[2,3] The temperature dependence of the photocurrent due to F-band irradiation shows that an electronic transition to a bound state causes the F band.[2] An investigation of the photocurrent produced by irradiation in the K and L bands would indicate whether these transitions are to bound or unbound states. Inchauspé[4] measured the photocurrent due to irradiation between 3.2 and 5.8 eV in additively colored KBr at 80°K. He suggested that ionization of the F center produced this photocurrent. Later Lüty[3] discovered the L bands in a variety of the alkali halides. Because the spectral dependence of the photocurrent measured by Inchauspé corresponded to the optical absorption in the L-band region, Lüty suggested that the L bands arise from transitions to the conduction band. To verify this idea, Wild and Brown[5] measured the photocurrent due to irradiation in the L_1 band in KCl at 10°K. They found that the quantum efficiency or the number of conduction-band electrons produced per absorbed photon was 0.04 for the L_1 band. This low value indicated that the L_1 band was not due to an electronic transition to the continuum.

By means of photoconductivity measurements, we have shown that in additively colored KBr, the L bands and the high-energy tail of the K band arise from transitions to states above the bottom of the conduction band.

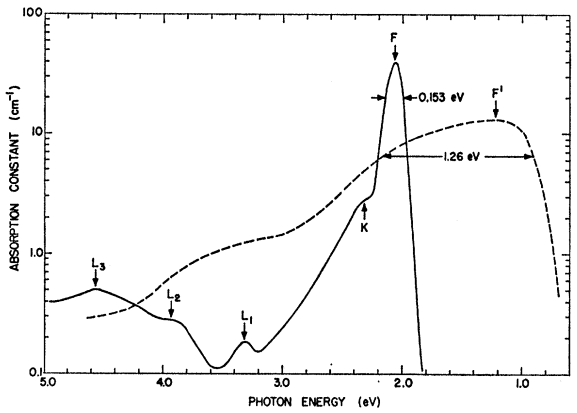

FIG. 1. The solid line is a plot of the absorption constant versus photon energy for a KBr crystal containing 4.2×10^{17} F centers/cm³ measured at 7.5°K by Spinolo. The dotted line is the F' band for a KBr crystal normalized to contain 4.2×10^{17} F' centers/cm³ at 7.5°K. The actual optical-absorption measurements were made on a crystal containing 7.9×10^{15} F' centers/cm³. The half-widths are shown for both the F' and F bands.

II. EXPERIMENTAL PROCEDURE

The additively colored KBr crystals and the equipment used for the measurements are described in the previous paper.[6] A hydrogen lamp was used in place of the tungsten lamp as radiation source in the ultraviolet region of the spectrum and a calibrated Cs_3Sb photocell[4] replaced the radiation thermocouple. The measurements of the temperature dependence of the photocurrent were made in a cryostat similar to that described by Tippins and Brown.[7] The crystal, which was isolated from the cryogenic fluid, was cooled by helium exchange gas.

The quantum efficiency is usually determined from a measurement of the photocurrent which is expressed by the following form of Hecht's equation[8] for the case of $w \ll l$:

$$I_\lambda = eN_\lambda(1-r_\lambda)(1-e^{-K_\lambda l})(w/l)\eta_\lambda. \quad (1)$$

In this expression N_λ is the number of photons incident per second on the crystal, I_λ the photocurrent produced by these photons, e the electronic charge, r_λ the re-

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[1] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962), Chap. III.
[2] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), Chap. IV, pp. 111 and 134–135.
[3] F. Lüty, Z. Physik **160**, 1 (1960).
[4] N. Inchauspé, Phys. Rev. **106**, 898 (1957).
[5] R. Wild and F. Brown, Phys. Rev. **121**, 1296 (1961).
[6] R. S. Crandall, preceding paper, Phys. Rev. **138**, A1242 (1965).
[7] H. Tippins and F. Brown, Phys. Rev. **129**, 2554 (1963).
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flectivity of the crystal, K_λ the absorption constant, l the crystal thickness, w the *schubweg*, and η_λ the quantum efficiency. The subscript λ refers to the wavelength of photoexcitation. The *schubweg*, which must be determined from additional measurements, is the product of the electric field E, electron mobility μ, and conduction-band lifetime τ. A measurement of the photocurrent as a function of the applied electric field determines the *schubweg*. At sufficiently large electric fields, the *schubweg* is comparable to the thickness of the crystal and the photocurrent saturates. The theory of Hecht enables the unit *schubweg*, or the product $\mu\tau$, to be determined from such measurements.[8] This method has been applied by Wild and Brown[5] to determine the *schubweg* and consequently the quantum efficiency of the L_1 band in KCl at 10°K. Warm-electron effects[9] may, however, simulate photocurrent saturation at low electric fields where the *schubweg* is not yet comparable to the thickness of the crystal.

In lieu of measuring the *schubweg*, we determined the quantum efficiency of the L and K bands in terms of the quantum efficiency of the F' band. To apply this procedure we made the assumption that the *schubweg* is independent of the source of electrons. Equating the *schubweg* determined from excitation in the L_3 band to that determined from excitation in the F' band, we obtain from Eq. (1)

$$\eta_{L_3}=\frac{I_{L_3}}{I_{F'}}\frac{N_{F'}}{N_{L_3}}\frac{(1-e^{-K_{F'}l})}{(1-e^{-K_{L_3}l})}\eta_{F'}. \tag{2}$$

The symbols have been defined above; the subscripts refer to excitation in the peaks of L_3 and F' bands. After η_{L_3} was determined in terms of $\eta_{F'}$ by the use of Eq. (2), η_λ for the spectral region between the L_3 and F bands was determined in terms of η_{L_3} by use of this same equation with η_{L_3} replacing η_{F_3}. For the determination of η_λ in terms of η_{L_3}, a crystal containing only F centers was used to avoid difficulties due to overlap of the F' band with the L_2, L_3, and K bands.

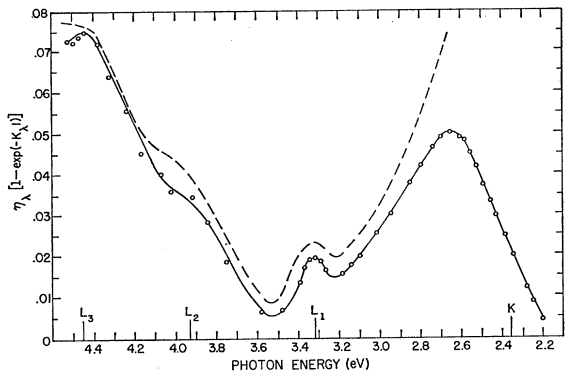

FIG. 2. The solid line is a plot of the product of quantum efficiency η_λ and the quantity $(1-e^{-K_\lambda l})$ versus photon energy at 21°K in KBr crystal 5. The dotted line is a plot of $(1-e^{-K_\lambda l})$, where the absorption constant K_λ was measured by Spinolo at 10°K. Because the quantity $(1-e^{-K_\lambda l})$ is well approximated by $K_\lambda l$, the dotted line represents the absorption constant K_λ.

[9] E. Conwell, J. Phys. Chem. Solids 8, 234 (1959).

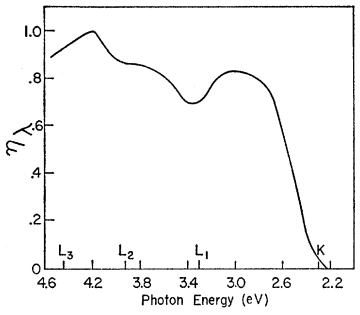

FIG. 3. The quantum efficiency η_λ is plotted versus photon energy at 21°K for KBr. The curve was obtained by dividing the solid by the dotted curve in Fig. 2. The structure between 2.8 and 4.5 eV is presumably caused by errors in measuring the optical density.

III. RESULTS

Two determinations of the quantum efficiency of the L_3 band yielded an average value of $\eta_{L_3}=0.99\pm0.13$ at 21°K and 0.95 ± 0.12 at 81°K. We assumed that the quantum efficiency $\eta_{F'}$ of the F' band is unity and that the peak heights of the L_3 and F bands are proportional. Their proportionality constant[3] is $(K_{L_3}/K_F)=1.27\times10^{-2}$ at 80°K. The L_3-band height was determined at 80°K and assumed to be the same at 21°K. The assumption that $\eta_{F'}$ is unity is well justified because Pick[10] found that the efficiency of ionizing F' centers at low temperatures is unity. The F' band which is shown in Fig. 1 is presumably due to a transition of one of the F'-center electrons to the conduction band.[11] The ratio of the number of F to F' centers was about 50, thus ensuring that the F' band at the peak of the L_3 band was less than 2% of the L_3 maximum. In Fig. 2, we plot the quantum efficiency per incident photon

$$\eta_\lambda(1-e^{-K_\lambda l}) \tag{3}$$

versus photon energy at 21°K. The photocurrent measurements represented by the solid line were made on crystal 5[6,12] containing only F centers. The optical absorption $(1-e^{-K_\lambda l})$, represented by the dotted line, was measured on a heavily colored crystal by Spinolo[13] at 7.5°K. These curves were made to coincide at the peak of the L_3 band by normalizing the factor $K_\lambda l$ at this wavelength. Figure 3 shows the quantum efficiency η_λ versus photon energy. This curve was obtained by dividing the two curves shown in Fig. 2. We believe that the structure in η_λ between 2.8 and 4.5 eV is caused by errors in the optical density. Thus η_λ is nearly unity throughout this region. The spectral dependence of η_λ at 4.2°K was the same as that shown in Fig. 3 for 21°K.

Figure 4 shows the temperature dependence of the photocurrent for excitation at 280 and 500 mμ for a crystal containing 1.0×10^{16} F centers/cm^3. The applied

[10] H. Pick, Ann. Physik 31, 365 (1938); 37, 421 (1940).
[11] F. Seitz, Rev. Mod. Phys. 18, 384 (1946).
[12] R. S. Crandall, Ph.D. thesis, University of Illinois, 1964 (unpublished).
[13] G. Spinolo (private communication).

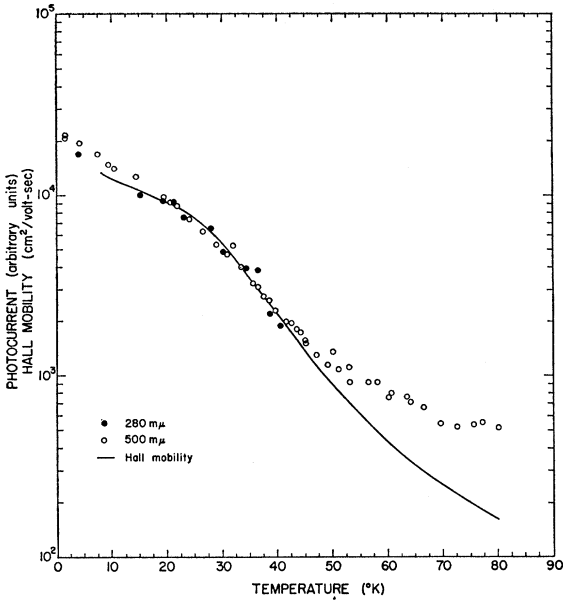

FIG. 4. The solid line is the Hall mobility measured by Ahrenkiel in a KBr crystal containing 1.0×10^{16} F centers/cm^3. The open circles represent photocurrent due to 500-mμ excitation and the solid circles represent photocurrent due to 280-mμ excitation.

electric field was 50 and 34 V/cm, respectively. These values are below the critical field of 90 V/cm where warm-electron effects occur at 4.2°K.[14] The Hall mobility values obtained by Ahrenkiel[15] for a KBr crystal containing 1.0×10^{16} F centers/cm^3 are shown on the same figure. Referring to Eq. (1), we note that the photocurrent in Fig. 4 is proportional to the product $\eta\mu\tau$. A comparison of the mobility curve with the data for $\eta\mu\tau$, indicates that within experimental error the product $\eta\tau$ is independent of temperature below 45°K. Above 45°K the product $\eta\tau$ increases. This increase is presumably due to an increase in conduction-band lifetime τ with increasing temperature.[12] Below 10°K, the slight increase in $\eta\tau$ may be due to changes in τ with temperature or due to experimental error.

IV. DISCUSSION

We found that the product $\eta_\lambda\tau$ is constant, within the experimental error, between 45 and 4.2°K for $\lambda=500$ and 280 mμ, the wavelength of the L_3 band. Because η_{L_3} is unity at 81 and 21°K, we expect it remains unity between these temperatures; therefore τ is constant between 45 and 21°K. If we assume τ remains constant below 21°K,[12] we conclude that η_{L_3} is unity below 21°K. Since η_λ was approximately constant between 2.8 and 4.5 eV at 4.2°K, we conclude that it, like η_{L_3}, is near unity below 21°K.

The conclusion, that η_λ in the region of the L bands is nearly unity at 4.2°K, is difficult to reconcile with the measurement of $\eta_{L_1}=0.04$ in KCl at 10°K.[5] The results in KCl may be subject to error because of the unknown effects caused by the use of high electric fields for photocurrent measurements.[12]

At photon energies less than 2.8 eV, the quantum efficiency decreases rapidly to a value of 0.05 at the K-band maximum. If the photocurrent at photon energies less than 2.8 eV were due to the K band of constant quantum efficiency, the solid and dotted curves in Fig. 3 would have the same form.[16] If we assume that the K band is composed of two or more overlapping absorption bands, we conclude that the transitions to the conduction band produce the absorption band represented by the solid line in Fig. 3, and electronic transitions to bound states are responsible for the remainder of the K band.

We may summarize with the following conjectures:

(1) The L bands are due to electronic transitions to energy levels which are in the conduction band.

(2) The K band is composed of two or more overlapping optical-absorption bands. The band comprising the high-energy tail of the K band is due to electronic transitions to the conduction band. The remaining bands are due to electronic transitions to bound states.

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[15] R. K. Ahrenkiel and F. C. Brown, Phys. Rev. **136**, A223 (1964).
[16] This band was found by photoconductivity measurements in a variety of KBr crystals. A similar band was detected in RbCl at 4.2°K. Its maximum height occurs at 2.62 eV.