FIG. 3. The emission current plotted as a function of rotation of the analyzer. The scales are proportional to intensity and angle but have not been calibrated. (a) Copper $\langle 111 \rangle$; (b) tungsten $\langle 110 \rangle$.

and center of the dark area as shown in Fig. 2. (The projected diameter of the probe hole, in this case, was 30 Å.) These five plots are the averages of four separate runs in which a smooth curve was drawn through any variations which could be attributed to random noise. However, no significance is attached to the structure in the curves. The emission current for the 10° and 13° plots was adjusted to 10^4 counts/sec while for the other three it was maintained at 300 counts/sec. This latter figure represented the maximum total current it was possible to draw without danger of rupturing the tip. The associated large shot noise was augmented by thermal migration of the prominent surface atoms since the tip was held at room temperature. The random noise is

shown in Fig. 2 for the two count rates used. Figure 3 shows the effect of varying the alignment of the analyzer. The scales have not been calibrated in angle or intensity. In the case of the copper $\langle 111 \rangle$ direction, as the analyzer was rotated away from the straight-through direction the threshold in the energy distribution plots approached the Fermi energy.

These results show that the upper limit of the conduction band in the $\langle 111 \rangle$ direction of copper is 0.4 ± 0.05 eV below the Fermi level. This is in good agreement with the calculations of Burdick.[5] It also appears that an insignificant amount of diffuse electron scattering was caused by the thermally migrating surface, and that the band structure of the bulk copper persists to the surface monolayer. It is further concluded that the alignment of the analyzer is of great importance to the observation of these effects.

[1]E. M. Hörl, Acta Phys. Austriaca 18, 33 (1964).
[2]R. H. Good and E. W. Müller, Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1956), Vol. 21, p. 176.
[3]F. I. Itskovich, Zh. Eksperim. i Teor. Fiz. 50, 1425 (1966) [translation: Soviet Phys.-JETP 23, 945 (1966)].
[4]A. G. J. van Oostrom, Philips Res. Rept., Suppl. No. 11 (1966).
[5]G. A. Burdick, Phys. Rev. 129, 138 (1963).

KBr:Tl EMISSION IN AN ELECTRIC FIELD

U. Giorgianni, V. Grasso, and P. Perillo
Istituto di Fisica dell'Università di Messina, Messina, Italy

The influence of an electric field ($\sim 10^4$ V_{rms}/cm) on the luminescence of KBr:Tl for excitation in the A band has been investigated. The measured spectrum points out beyond any doubt that there are two different centers responsible for the emission.

The emission spectra of thallium-doped alkali-halide phosphors have been investigated at different temperatures by several authors.[1-4] In general, emission bands can be ascribed to the optical transitions between localized electronic states and their shapes will be due to the interaction with the ions neighboring the impurities. The theoretical analysis of these bands becomes extremely difficult when electronic degenerate states are involved because the electron-lattice interaction will yield a coupling between different levels. This is just the case of the alkali-halide crystals activated by thallium. Particularly we have investigated the luminescence of

KBr:Tl at 80 and 300°K on the entire A-band excitation as shown in Fig. 1.

At 300°K the emission consists of two bands centered at 3.99 and 3.54 eV, while at 80°K the bands are shifted to 4.06 and 3.46 eV, respectively. In the latter case both bands show approximately Gaussian shape. At 300°K the area of the lower energy emission band (E_2) is 1.6 times greater than the area of the higher energy emission band (E_1). At 80°K the E_2 band area is 3 times greater than the E_1 band area. On comparing the areas of the bands at the two temperatures it was noted that the E_1 area is reduced to half when the temperature changes from 300 to
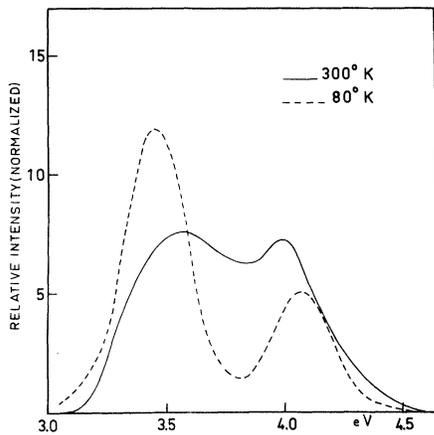
FIG. 1. Emission spectra of KBr:Tl at 300 and 80°K excited by light absorbed in the A band at 2475 Å.

FIG. 2. Relative change of KBr:Tl emission excited in the A band versus photon energy, due to an applied electric field $(2 \times 10^4 \ V_{rms}/cm)$.

80°K, while the E_2 area does not vary appreciably. The decrease of the E_1 band area with temperature, found by us, is in agreement with the results obtained by some authors,[1] and not with those of several others (for instance, Ref. 4) who have found a similar behavior for the lower energy band.

The observed temperature dependence seems to indicate that the level responsible for the high-energy emission is populated at higher temperatures by thermal transition from another excited state. As the above-mentioned disagreement of our results with those of others could be almost entirely canceled by exchanging the energy position of the two bands E_1 and E_2, we think that the emission mechanism is essentially the same in both cases; therefore, it is possible to assume, as in Ref. 4, that the centers responsible for the two emission bands are quite different.

In order to investigate these bands we have studied the effect of an external electric field applied to KBr:Tl crystals when the samples were excited in the A band using the phase-sensitive technique.[5] The samples were mounted in an evacuated chamber between two aluminum evaporated grating electrodes and a sinusoidal electric field $(\sim 2 \times 10^4 \ V_{rms}/cm;$ 80 Hz) was applied in the same direction as the exciting light. The emission modulated by the field was detected by a photomultiplier perpendicularly to this direction. The relative change $\Delta I/I$ versus photon energy is plotted in Fig. 2, where a complex struc-
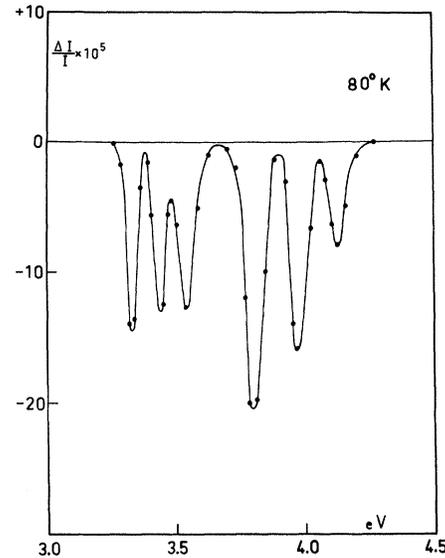
ture is observed. The three peaks (3.33; 3.44; 3.54 eV) show a triplet structure corresponding to that observed in absorption[6] for a transition $^1S_0 \rightarrow {}^3P_1$. This fact seems to indicate that the lower energy emission band must be ascribed to the transition $^3P_1 \rightarrow {}^1S_0$ in the thallous ion. The remaining structure, whose origin is not yet clear, could be connected with the existence of the V_K center.[4] Furthermore, as observed, the relative change of the emission intensity is negative all along the explored energy range, this confirming the zeroth-moment decrease found in A-band absorption.[6] Further discussion with detailed measurements both in emission and in absorption will be reported in the near future.

[1]T. Tamai and E. Matsui, J. Phys. Soc. Japan 16, 1489 (1961).

[2]M. F. Trinkler and I. K. Plyavin, Phys. Status Solidi 11, 277 (1965).

[3]A. Fukuda, S. Makishima, T. Mabuchi, and R. Onaka, J. Phys. Chem. Solids 28, 1763 (1967).

[4]J. M. Donahue and K. Teegarden, J. Phys. Chem. Solids 29, 2141 (1968).

[5]G. Chiarotti, G. Del Signore, A. Frova, and G. Samoggia, Nuovo Cimento 26, 403 (1962).

[6]V. Grasso and G. Saitta, Phys. Rev. Letters 22, 522 (1969).