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Investigation of NaCl-AgCl Trapping Centers by a Metbod of Thermo-Optical Bleaching

CH. BLUSHCHIK, F. N. ZAITOV, KH. A. MIAGI
AND K. IU. EL'KEN

Tartar State University

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TO investigate trapping centers in a crystal, a method could be applied which is based on the measurement of the change $\Delta\varkappa$ of the absorption coefficient of the trapping centers as a function of the temperature T when the crystal is excited by heat at a constant rate β. The theory and some of its applications are explained in the following[1-3]. The dependency of $\Delta\varkappa(T)$ was investigated under conditions such that electrons released from the trapping centers by optical excitation were small compared to the thermal excitation during the measurement of $\Delta\varkappa$. Perhaps conditions can be treated such that the optical system which releases electrons from the trapping centers will be of a secondary nature. This discloses a supplementary method for investigation of trapping centers. Usually the probability of direct optical ionization of the trapping centers for the release of electrons is smaller than that of the optical release of electrons from trapping centers of thoroughly warmed crystals[4].

Let us suppose a crystal contains a single type of electron trapping center; the change of the numbers of electrons n of the thermally excited crystal would then be proportional to the condition of continuous illumination of the light flux B, and determined by the equation

$$-\frac{dn}{dT} = \beta_0^{-1}(p + \alpha B p^*)\, n\, \frac{\sigma_p n}{\sigma_p n + \sigma_3(N - n)}. \qquad (1)$$

Here σ_r and σ_t are the effective crosssections of recombination and trapping N, the number of trapping levels, $p = p_0 \exp(-E_T/kT)$ and $p^* = p_0^* \exp(-E_T^*/kT)$ — the laws of probability of thermal ionization of the trapping centers of the stable and excited states. (It would be convenient to designate the value of E_t as the thermal ionization energy of the trapping center, although this is not strictly correct. See, for example, Ref. 2. Since $\Delta\varkappa = An$, the coefficient A is slightly dependent on the temperature ($A \sim T^{-0.5}$). Equation (1) determines not only $n(T)$ but also the dependence of $\Delta\varkappa(T)$.

If $p \gg \alpha B p^*$, which has been previously pointed out[3], the tempertaure T_k at which $n = 0.5\, n_0$, is connected with the thermal ionization energy of the trapping centers by the relation

$$T_k = \frac{E_T}{k}\left\{\ln\left[\frac{p_0}{\beta_0}\,\delta_k\left(1 + \frac{2\sigma_3 N}{\sigma_p n_0} - \frac{\sigma_3}{\sigma_p}\right)^{-1}\right]\right\}^{-1} \qquad (2)$$

If $p \ll \alpha B p^*$, then most of the electrons would be liberated from the trapping centers due to optical bleaching. It is easily shown that, in this case,

$$T_k = \frac{E_T^*}{k}\left\{\ln\left[\alpha B\,\frac{p_0^*}{\beta_0}\,\delta_k\left(1 + \frac{2\sigma_3 N}{\sigma_p n_0} - \frac{\sigma_3}{\sigma_p}\right)^{-1}\right]\right\}^{-1}. \qquad (3)$$

Thus, when B is small (the region of thermal bleaching) $T_k \neq T_k(B)$. When B is large (the region of optical bleaching) $T_k^{-1} = kE_T^{-1}\ln B + \text{const}$.

For measuring the bleaching curve $\Delta\varkappa(T)$ it is necessary to maintain control of the light flux for the investigation. It is possible to determine E_T. from the rate of the thermal bleaching, which is dependent on $\Delta\varkappa(T)$.[2,3] From the rate of the optical bleaching, which is dependent on $\Delta\varkappa(T)$ as well as T_k for B, it is possible to determine the thermal ionization energy E_T of the excited trapping centers.

A method of thermo-optical bleaching was used by us in the investigation of trapping centers of single crystals of NaCl-AgCl. Simultaneous experiments were made of the spectral absorption of the trapping centers $\Delta\varkappa(\lambda)$ and thermal curve $I(T)$.

The quantities $\Delta\varkappa(T)$ and $\Delta\varkappa(\lambda)$ were measured on the SF-4 and SF-2M spectrophotometers. Curve $I(T)$ was recorded with the aid of an electron multiplier, amplifier, and self-recording potentiometer EPP-09. In all runs, $\beta_0 = 0.14$ deg./sec.

In accordance with literature[5-8], we found the F– and M– bands (460 and 720 mμ) in x-rayed single crystals of NaCl-AgCl 0.3 *M*%, and additional absorption bands at 275, 315 and 345 mμ which were absent from the above mentioned source of x-rayed unactivated trapping centers.

Strong flourescence was emitted when the bands were excited (see Refs. 9-10). After initial heating to 200 °C, the bands at 276 and 345mμ started to disappear, and the band at 315 mμ remained broad. Excitation of this band produced a green flourescence of $\lambda_m = 540$ mμ, which was dependent on the transition from the excited level to the ground state. The temperature for half maximum of $\Delta\varkappa_{315}(T)$ (the band at 315 mμ) was $T_k^{\varkappa} = 530$ °K. The thermal ionization energy corresponding to this band of trapping centers can be calculated with the help of the half-life relationship obtained by Lushchik.[3] It was found that $E_T = 1.3$ ev. Liberation of the electrons from the trapping centers can be related to be dependent on the intensity of the fluorescence of the unifirmly heated crystal. The temperature at half-maximum causes a brilliant green fluorescence at $T_k^{\pm} = 505$ °K. Determination of $T_k^{\varkappa}$ and $T_k^{\pm}$ depends upon the effective thermal quenching of the trapping centers.

In the thermal bleaching curve for the phosphor NaCl-AgCl 0.3*M*% we observed three maxima at 345, 385 and 425°K, in agreement with the literature[2,11,12]. It was thought that the liberated electrons from the trapping level corresponding to the band at 315 mμ would appear in thermal emission with decreased sensitivity it was possible to see a sharp peak in the thermal emission at $T_m = 480°$ K. The large difference of T_m of this peak of the $T_k^{\varkappa}$ for the band at 315 mμ is probably due to strong thermal quenching of the luminescent ionic Ag^+. Thus, activating trapping centers of NaCl-AgCl and in KCl-TlCl (see Refs. 1, 12) can also appear in thermal emission.

In NaCl-AgCl 0.001 *M*% the temperature of half-maximum for the absorption coefficient of the *F*-band is $T_k^{\varkappa}=425°$ K. At this same temperature we have observed the most intense peak of thermal emission, which corresponds to the liberation of electrons from the *F*-level. The energy of the thermal ionization of the *F*-centers, determined from the dependence of $\Delta\varkappa(T)$, $E_T = 1.02$ ev is in agreement with prior data[13].

$T_k^{\varkappa} = 395$°K for the 275 mμ band for NaCl-AgCl 0.3 *M*%. The thermal ionization energy was calculated for the trapping centers of this band to be $E_T = 0.94$ ev.

Comparison of the complete absorption spectra of NaCl-AgCl after optical decay of the *F*-band at room temperature indicated that the probability of retrapping electrons liberated from the *F*-level to the activated trapping level measured was at least ten times smaller than the probability of their recombination with the luminescence centers.

In the temperature range where the 275 mμ bands 275 disappears, the 315 mμ band increases as a result of retrapping of electrons in the trapping level. From the comparison of the curves of $\Delta\varkappa_{275}(T)$ and $\Delta\varkappa_{315}(T)$ it follows that the probability of the retrapping A_t is five times smaller than the probability of recombination A_r. These facts confirm the previous conclusion of one of us[14] that $A_t > A_r$ in a regime of strong excitation in alkali-halide phosphors. The problem of the relation of A_t and A_r on weakly excited crystals awaits further experimentation.

In the present work, measurements of $\Delta\varkappa(T)$ were completed in the regime of thermal bleaching ($p \gg \alpha B p^*$). Data on the regime of optical bleaching ($p \ll \alpha B p^*$) will be given in a later work.

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*For convenience, we shall call E_T the energy of thermal ionization of the capture centers, although this is not strictly accurate (see, e.g., Ref. 2).

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The Effect of Uniform Compression on the Superconducting Properties of the α- and β-Modifications of Bi_2Pd

N. E. ALEKSEEVSKII AND I. I. LIFANOV
Institute of Physical Problems
Academy of Sciences, USSR

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IT has been pointed out in a previous communication that the compound Bi_2Pd exists in two forms[1], of which the α-modification has a monoclinic lattice and goes over into the superconducting state at $T_c = 1.70$ °K., while the β-modification with a tetragonal lattice, becomes superconducting at $T_c = 4.25$ °K. It seemed of interest to determine the displacement of T_c under uniform compression for both forms of this compound. For this we used our previously-employed method of measuring the mutual inductance at audio frequency.[2] The pressure was developed in a beryllium bronze bomb by the change in volume of water upon freezing, following the method suggested by Lazarev[3]. The construction of the apparatus was such as to permit placement in the measuring coil, at the time of the experiment of either the specimen in the pressure bomb, or an ebonite ampule in which was placed a similar specimen not subjected to uniform compression. The amount of pressure developed in the bomb was determined from the displacement of the critical temperature for tin. To accomplish this, two completely identical samples of tin were inserted along with the Bi_2Pd samples in both the beryllium bronze bomb and the ebonite ampule; the difference in their respective transition temperatures determined the pressure in the bomb. This was generally ~ 1700 kgm/cm^2. The temperature was determined from the helium vapor pressure. In Fig. 1 are presented the transition curves for compressed and uncompressed specimens of β-Bi_2Pd and tin (along the vertical axis are given the readings in volts of a cathode voltmeter connected to the output terminals of the mutual induction measurement system[2]). A certain non-reproducibility in the transition curves for β-Bi_2Pd, observed when the pressure

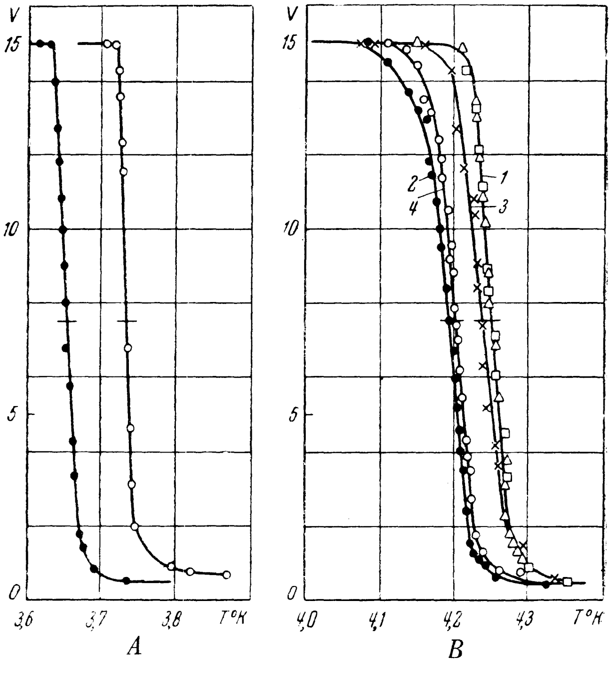

FIG. 1. Transition curves into the superconducting state: *a* — Sn in bomb with β-Bi_2Pd specimen: ○ no pressure in bomb, ● — ice pressure in bomb; *b* — β-Bi_2Pd: sample: △ — in beryllium bronze bomb, no pressure, □ – in ebonite sample, ○— ice pressure reapplied; β-Bi_2Pd specimen in bomb with Sn sample: ice pressure in bomb, × — pressure removed.