in the equilibrium position and the saddle point both relations $U_H \gtrless U_D$ are possible. Similar ideas are explicitly or implicitly contained in semiclassic treatments by LE CLAIRE [10] and EBISUZAKI et al. [11, 12].

From the experimental value of the Gorsky relaxation strength $\Delta_E = 2\%/\text{at.-\%}$ H ($\pm 10\%$) at 298 °K the dipolemoment tensor $P_{ij} = P\,\delta_{ij}$ can be determined [13] if the proper value for the orientation dependent factor Ω is known [Eq. (19) in Ref. [13]]. For this, actually a complicated averaging procedure, taking into account the spectrum of grain orientation distributions would be required. Since the exact averaging procedure has not yet been worked out, we used $\Omega = 1.8$, which is the average between the two extreme values, yielding $P = 3.5$ eV. This value of the dipolemoment tensor may be compared with $P \approx 4$ eV, as calculated from the critical temperature of H in Pd [14].

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The Pyroelectric Effect in Lithium doped Cadmium Sulfide

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Herrn Prof. Dr. Nikolaus Riehl zum 70. Geburtstag gewidmet

(Z. Naturforsch. **26 a**, 923—925 [1971]; received 9 February 1971)

CdS crystals highly doped with Li, showing the tap-effect [1] have pyroelectric constants considerably higher than those reported by MINKUS[2] for pure CdS crystals. The differences of the surface charges during cooling and heating can be explained by considering the exponential temperature dependence of the electric conductivity of the crystals.

In 1968 PARK and LITTON [1] reportet that Li-doped CdS crystals, after cooling in darkness to the temperature of liquid nitrogen, emit flashes of light when tapped with a pointed metal object. They therefore called this phenomenon tap-effect. As preliminary experiments showed, the mechanical vibration caused by tapping is not a prerequisite for the emission of light. Even lightly touching certain surfaces of the crystal with the pointed metal object suffices. This results in an electric discharge followed by luminescence. It was assumed that the cooling leads to high surface charges. Therefore the pyroelectric properties of these Li-doped CdS crystals were investigated.

To measure the surface charge, the crystal is insulated by mica foil placed between the electrodes of a capacitor. One electrode is the copper block of the cryostat to be heated and cooled. The other electrode is made of quartz glass which is coated with a layer of transparent conductive SnO_2. The CdS crystals are so orientated that the planes which are orthogonal to the *c*-axis are parallel to the electrodes. The charge induced in the electrodes is measured with an electrometer (Keithley 610 C) and registered on a pen recorder. The charge measured by the electrometer as a function of the temperature when the crystal is in darkness is shown in Fig. 1. Cooling is represented by the continuous line, heating by the dotted line.

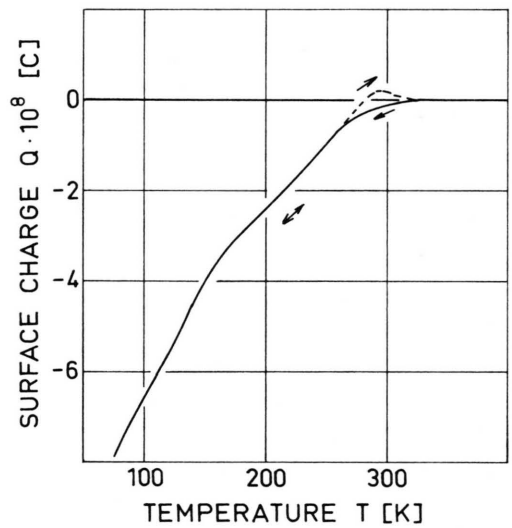

Fig. 1. Measured surface charge as a function of temperature, ——— cooling, — — — heating.

Above 320 K no charge is registered. Below 260 K the cooling curve is identical to the heating curve. In the intermediate range there are differences between both curves. It can be shown that the conductivity which increases exponentially with temperature is the reason for the difference. At temperatures rising above 260 K the conductivity leads during the time of measurement to a rapidly increasing compensation of the surface charge caused by the pyroelectric effect.

Reprints request to Prof. Dr.-Ing. H. NELKOWSKI, II. Physikalisches Institut der Technischen Universität Berlin, *D-1000 Berlin 12*, Straße des 17. Juni 135.

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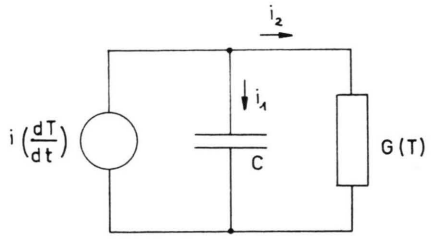

Fig. 2. Equivalent circuit of the crystal.

Figure 2 shows the presumed equivalent circuit of the crystal. Here

$$i(\mathrm{d}T/\mathrm{d}t) = p(T)\ A(\mathrm{d}T/\mathrm{d}t)$$

represents the pyroelectric effect, i. e., the change of the surface charge owing to the temporal change of temperature. $p(T)$ is the pyroelectric constant, i. e. the differential change of the surface charge with temperature per square unit, and A is the area on which the charge appears. The current i divides into i_1 charging the capacitor C, which represents the polar faces of the crystal, and into i_2 flowing through the conductance $G(T)$, which represents the temperature-dependent conductivity of the crystal. On the simplified assumption of a temperature-independent pyroelectric constant and a linear heating and cooling velocity $T = T_0 + a\,T$ (T_0 = starting temperature) we obtain the following differential equation for the charge Q of the capacitor C, i. e. the measurable charge.

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{G_0}{C}\ \exp\left\{-\frac{E}{k\,T_0 + k\,a\,t}\right\} Q = p\,A\,a\,. \qquad (1)$$

There, use is made of the above mentioned exponential temperature-dependence of the conductivity.

The solution of the differential equation is

$$Q = \exp\left\{-\int \frac{G_0}{C}\ \exp\left\{-\frac{E}{k\,T_0 + k\,a\,t}\right\} \mathrm{d}t\right\}\left[\int p\,A \cdot \exp\left\{\int \frac{G_0}{C}\ \exp\left\{-\frac{E}{k\,T_0 + k\,a\,t}\right\} \mathrm{d}t\right\} \mathrm{d}t + H\right]. \qquad (2)$$

H is a constant regarding the initial conditions.

With the constants corresponding to the experimental results $p = 5 \cdot 10^{-12}$ C/K·mm², $a = 40$ K/min, $A = 80$ mm², $C = 200$ pF, $G_0 = 2 \cdot 10^5$ S, $E = 0{,}84$ eV, we obtain the curves for the cooling and heating process as shown in Fig. 3. Within the margins of the approximation good conformity with the experiment is obtained *.

The correctness of this interpretation is confirmed by the ability of compensating the pyroelectric generated surface charge too, if a photo conduction is generated by stimulation of the crystal with light. A discussion of these investigations, however, shall not be carried out here.

* We are very grateful to Mr. G. GSCHWIND for carrying out the calculations.

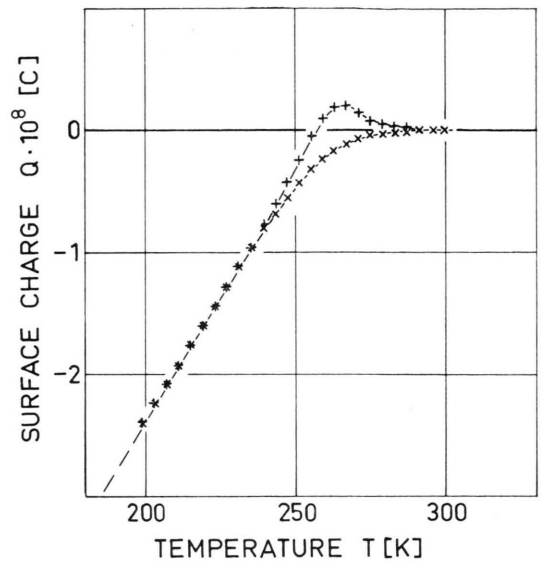

Fig. 3. Calculated surface charge as a function of temperature, —×—×— cooling, —+—+— heating.

To be able to compare different crystals with regard to their pyroelectric properties it is reasonable to specify the pyroelectric constant. This can be got, according to its definition, from the slope of the cooling or heating curve for that region of temperature in which the conductivity is negligible, i. e. for the region in which the cooling and heating curves are identical. This is for temperatures below 260 K. The result is given in Fig. 4. The values of the pyroelectric constant

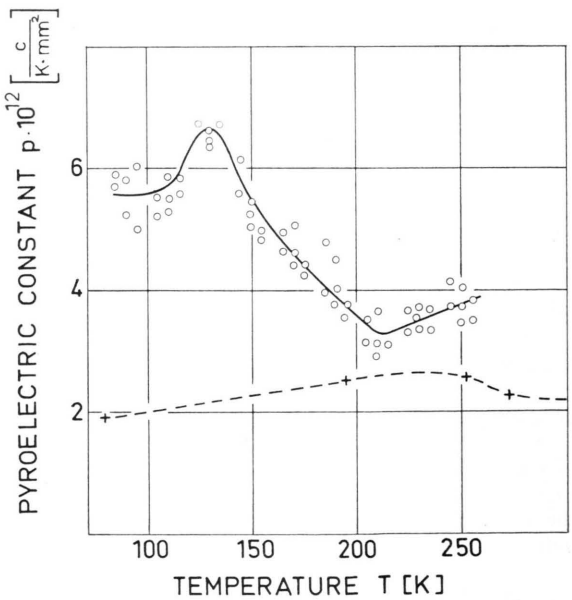

Fig. 4. Pyroelectric constant versus temperature, ——— CdS : Li, — — — undoped CdS (by Minkus).

are between 3 and $7 \cdot 10^{-12}$ C/K·mm². For comparison the result of MINKUS [2] for undoped CdS is also shown. Especially for low temperatures his values are considerably smaller than those of Li-doped CdS. Unfortunately, there are no measurement of Minkus in the region between 100 and 150 K, so that the question remains, whether his crystals show there a maximum of the pyroelectric constant too. At present it is not yet possible to say if the very high pyroelectric constant found for the Li-doped CdS-crystals, is caused by the high concentration of Li in the crystal (~ 1%). If future investigations should confirm this assumption, it would be evident why only these Li-doped CdS-crystals show the tap effect mentioned at the beginning.

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Über die Lumineszenz von ZnS–Ga-Kristallen

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(Z. Naturforsch. **26 a**, 925—927 [1971]; eingegangen am 9. Februar 1971)

Es wird gezeigt, daß das Verhalten der Lumineszenz- und Photoleitfähigkeit von ZnS-Kristallen, die aus einer Ga-Schmelze gezüchtet sind, mit dem Modell der Donor-Akzeptor-Paare beschrieben werden kann. Die grüne und rote Emission wird als Rekombination des angeregten bzw. Grundzustandes des Ga-Ions mit einer Zn-Lücke gedeutet. Auch der Einfluß der Stöchiometrie und Temperatur auf die Anregungs- und Emissionsspektren kann mit dem Donor-Akzeptor-Modell erklärt werden.

Die Zinksulphide gehören zu den am häufigsten untersuchten Luminophoren. Nach ersten Lumineszenz-Modellen [1–3] entstand vor 15 Jahren das Konzept des Donor-Akzeptor-Zentrums [4], das Eigenschaften vereinigte, die bis dahin zu gegensätzlichen Modellen zu gehören schienen (Schön-Klasens und Lamb-Klick). Sowohl SHIONYOA und Mitarbb. [5–7] als auch RIEHL und Mitarbeiter [8–10] haben das Donor-Akzeptor-Paar-Modell erfolgreich für das ZnS:Cu,Koaktivator-System verwendet.

Auch das selbstaktivierte Leuchten von mit A^{III}-Elementen koaktiviertem ZnS wurde mit Hilfe dieses Modells interpretiert (z. B. [11]). Auf Grund von optischen und photoelektrischen Messungen wurde jedoch die Meinung geäußert [12], daß die A^{III}-Elemente, hauptsächlich aber Ga und In, sowohl als einwertige als auch als dreiwertige Ionen in das ZnS-Gitter eingebaut werden können. Demnach erzeugen sie bei Proben mit Zinküberschuß grüne, bei solchen mit Schwefelüberschuß rote Lumineszenz.

In der vorliegenden Arbeit soll über Lumineszenz- und Photoleitfähigkeitsmessungen berichtet werden, die es ermöglichen, zwischen den beiden Vorstellungen zu Gunsten des Donor-Akzeptor-Modells zu entscheiden.

Experimentelles

Für die Untersuchungen wurden aus der Ga-Schmelze gezüchtete stöchiometrische ZnS-Kristalle sowie solche mit Zink- und Schwefelüberschuß verwendet [13, 14]. Die Züchtung aus Ga-Schmelze hat den Vorteil, daß das

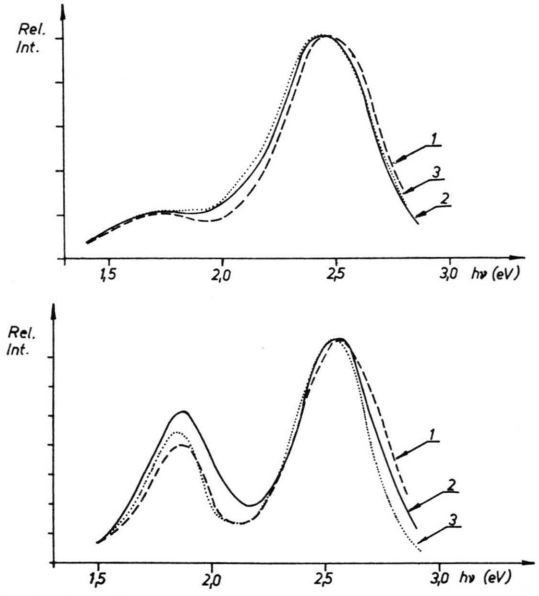

Abb. 1. Emissionsspektrum dreier ZnS: Ga-Proben: a) bei 300 K; b) bei 77 K. Kurve 1: Stöchiometrisch; Kurve 2: Zn-Überschuß; Kurve 3: S-Überschuß.

Sonderdruckanforderungen an Dr. J. SCHANDA, Forschungsinstitut für Technische Physik der Ungarischen Akademie der Wissenschaften, *Budapest*, Ujpest 1, Pf. 76.

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