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STUDY OF V_k CENTERS IN CsI CRYSTAL

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V_k centers have been observed in CsI doped with Na^+ and Tl^+ after X-ray irradiation at LHeT using optical and EPR techniques. It is shown that they are oriented along [100] directions. By studying thermoluminescence two types of thermal migration have been found, one due to linear displacement of the centers along the cubic axis and the other due to 90° rotations. They correspond to two glow peaks at 60 and 90°K respectively.

INTRODUCTION

IN ALKALI halide crystals the free holes which are produced by ionising radiation are spontaneously trapped at low temperature to form a covalent bond between two adjacent halide ions (X_2^- or V_k center). The electrons can either recombine with V_k centres giving rise to the characteristic intrinsic emission or can be trapped at defects already present in the crystal or created by the radiation. These trapping processes allow of the possibility to have stable V_k centers. Their number is a function of the concentration and of the efficiency of the electron traps.

V_k centers have been already observed and studied in detail in several alkali halides of NaCl structure and in a number of other crystals.[1] Their existence in alkali halide crystals with CsCl structure was never explicitly demonstrated though it can be inferred indirectly.

In the case of pure CsI crystals for instance, two intrinsic luminescent components at 290 and 338 nm are observed either under u.v. excitation in the excitonic bands or under ionising radiation (X, β). Since the emissions are the same in both cases the relaxed exciton states produced directly (without the isolated X_2^- ions) must be identical to the metastable states formed by an electron in presence of a pre-existing V_k center.[2] The purpose of this work is to prove directly the existence of V_k centers in CsI and to obtain information on their thermal mobilities.

PRODUCTION AND IDENTIFICATION OF V_k CENTERS

In CsI, defects such as vacancies, interstitials, etc. have never been created in a stable configuration under the most severe ionising irradiating conditions (X, β). Stable V_k centers should therefore be observed in this substance only in doped crystals after irradiation at low temperature. We performed for this purpose optical measurements of absorption spectra after X-ray irradiation at LHeT of CsI doped either with Na^+ or with Tl^+. The results are reported in Fig. 1. Since the optical properties of the band centered at 410 nm are independent of the nature of the impurity, we attribute this band to the u.v. transition $^2\Sigma_g^+ - {}^2\Sigma_u^+$ of V_k centres. We summarise in Table 1 relevant data in connexion with different experimental conditions. It can be observed that Na^+ impurity appears as the most efficient electron trap available yet. Several other bands appear at longer wavelength and their number, position and width are related to the specific impurity introduced in the crystal as an electron trap (720 nm for CsI: Na^+, 500 and 620 nm for CsI: Tl^+).

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Table 1

	CsI : Tl^+	CsI : Na^+
Origin	K. Korth	Teledyne Isotopes
Impurity concentration in the melt	1000 ppm	200–300 ppm
X-ray irradiation time at 10°K (150 kV, 10 mA, anode W)	20 min	1 min
Absorption coefficient α at 410 nm	8.6 cm^{-1}	10.2 cm^{-1}

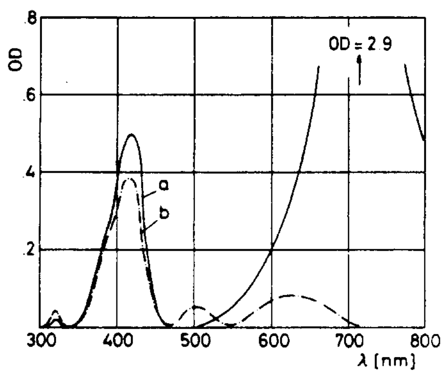

FIG. 1. Optical absorption after X-ray irradiation at LHeT, (a) CsI:Na^+, (b) CsI:Tl^+.

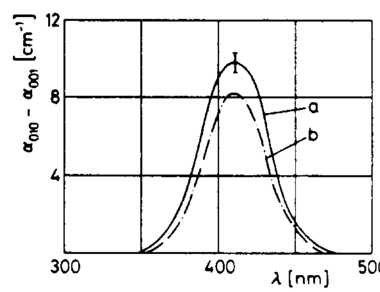

FIG. 2. Dichroic absorption spectra (α[010] − α [001]) for V_k centers obtained by bleaching with [001] polarized light propagating along [100] direction. (a) CsI : Na^+ $\lambda_{bleaching}$ = 406 nm, (b) CsI : Tl^+ $\lambda_{bleaching}$ = 606 nm.

To further prove the identification of the 410 nm band with V_k center absorption we have shown its dichroism by bleaching with light propagating along the [100] direction and polarized along the [001] direction. We report in Fig. 2 the dichroic spectrum $\alpha_{010} - \alpha_{001}$ in this region. The band is centered at 410 nm (3.02 eV) and its half width is 0.35 eV. Up to now no i.r. transition have been found for V_k centers in this material.

We have also performed EPR measurements to show that X_2^- molecular ions are effectively created in CsI : Na^+ and in CsI : Tl^+. The resonance spectrum of non aligned V_k centers is given in Fig. 3. The eleven prominent lines suggest indeed an interaction with a total nuclear spin of 5 (nuclear spin for ^{127}I is 5/2, natural abundance 100 per cent). It is possible to show by EPR that after polarized bleaching performed under the same conditions as described in Fig. 2 one obtains a V_k center system almost completely aligned in a specific direction.[3]

It is worthwhile to mention also that in CsI : Na^+ having aligned V_k centers in a [100] direction the intrinsic recombination luminescence at 290 and 338 nm produced by optical excitation of the traps exhibits a partial plane polarization having essentially a σ character with respect to the axis of the parent V_k center. (Polarization $P_e = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp}) = 0.2$).

THERMAL MIGRATION OF V_k CENTERS

The thermoluminescence of doped CsI crystals X or β irradiated at LHeT shows two peaks having their maxima at 60 and 90°K for a heating rate of 1.4°K/min. The ratio of the maximum intensities depends on the impurity concentration and on the irradiation dose. The emission spectrum of both bands is centered at 420 nm for CsI : Na^+ and is identical to the emission attributed to the radiative recombination of localised excitons in the neighbourhood of defects associated with this impurity.[4] For CsI : Tl^+ the location of the emission is specifically related to the nature of this impurity (560 nm). The glow peaks are reported in Fig. 4. We may note that in similar experiments of thermoluminescence in NaCl structure alkali halides only one glow peak is observed which corresponds to the rotational mobility by 60° jumps.[5]

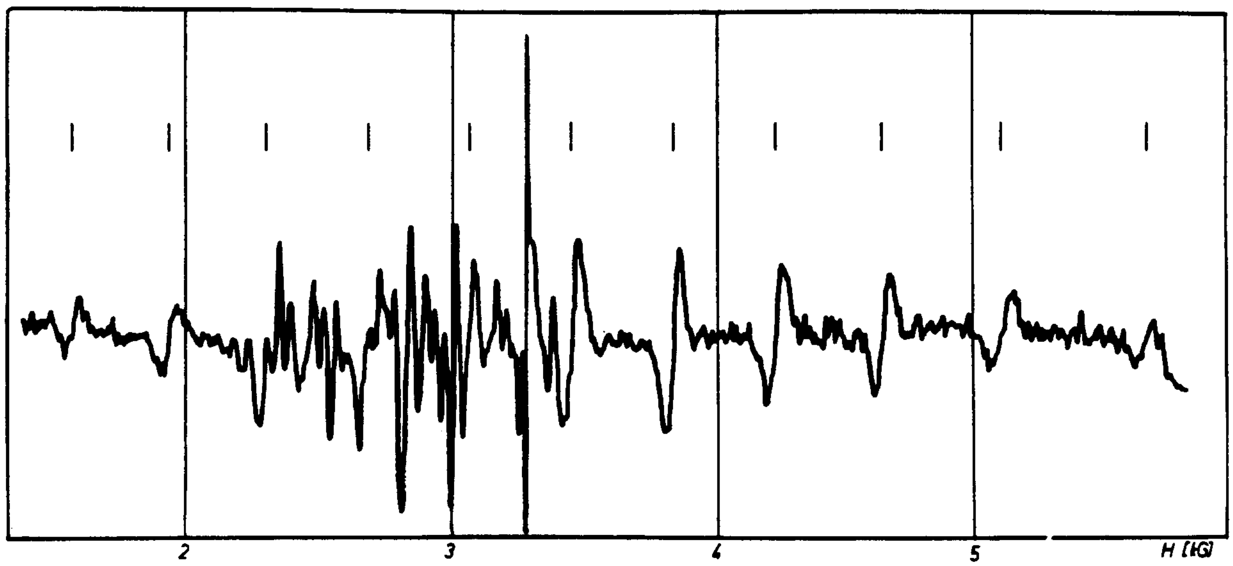

FIG. 3. EPR spectrum of unaligned V_k centers in CsI : Tl^+. $H \parallel [100]$, $\nu = 9.523$ GHz.

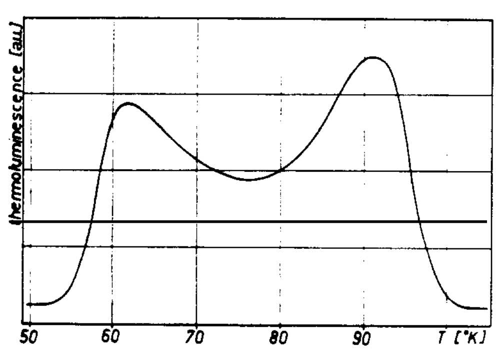

FIG. 4. Glow curve for CsI : Na^+ after 1/4 min irradiation β at LHeT.

The thermoluminescence properties can be explained by a double migration of thermally activated V_k centers followed by a radiative recombination with the trapped electrons. Similar measurements performed with an aligned V_k center system show a net polarisation of the first glow peak which disappears on the low temperature side of the second glow peak. On the other hand, optical absorption and EPR spectra measured at LHeT after thermal annealing at 70°K present only a global reduction of their intensities. This important result means that the remaining V_k centers have conserved their alignmentproperties along the [100] directions. We conclude then that the first glow peak corresponds to a linear migration of V_k centers (0° jumps). Similar experiments show that the second glow peak corresponds to migration of V_k centers by 90° jumps with reorientation.

After thermal annealing at 120°K all the V_k centers have disappeared. Their destruction has occurred either radiatively (glow peaks) or by capture on unknown sites as observed by the appearance of new optical absorption bands (e.g. 380 nm in CsI : Na^+). This gives rise to several other glow peaks for $T > 120$°K.

Let us note that this double thermal mobility has already been observed in other crystals with CsCl structure like SrF_2, BaF_2 and NH_4Cl.[1] There is also preliminary evidence that the same mechanism of double mobility is common to V_k centers in all alkali halides with CsCl structure.[3,6]

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REFERENCES

1. KABLER M.N., *Point Defects in Solids* (Edited by CRAWFORD J.H., Jr. and SLIFKIN L.M.), Vol. 1, p. 327, Plenum Press, New York, (1972).
2. LAMATSCH H., ROSSEL J. and SAURER E., *Phys. Status Solidi (b)* **48**, 311 (1971).
3. PILLOUD J.J., Private communication.
4. LAMATSCH H., ROSSEL J. and SAURER E., *Phys. Status Solidi (b)* **46**, 687 (1971).
5. KELLER F.J. and MURRAY R.B., *Phys. Rev.* **150**, 670 (1966).
6. SIDLER T., PELLAUX J.P., NOUAILHAT A. and AEGERTER M.A., to be published.

Les centres V_k ont été observés dans CsI doté en Na^+ et Tl^+ après irradiation X à 4°K par des méthodes optiques et RPE. Les centres V_k sont orientés selon les directions [100]. L'étude de la thermoluminescence a révélé deux types de migration thermique, une première due à un déplacement linéaire des centres et une deuxième par rotation de 90°. On leur attribue deux pics de thermoluminescence à 60 et à 90°K respectivement.