

DIPOLAR RELAXATION OF Z_1 CENTRES IN Sr^{2+} DOPED KCl CRYSTALS

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ITC measurements performed for electrolytically coloured $\text{KCl}:\text{SrCl}_2$ crystals containing Z_1 centres reveal a slight effect which, according to our calculations, reflects a contribution related to the dipolar moment of the defects in question.

1. Introduction

From among various models proposed for Z_1 centres, appearing in the alkaline earth doped alkali halide crystals (cp. [1]), that proposed by Rosenbeger and Lüty [2] (F centre in vicinity of Me^{2+} -cation vacancy dipole, cp. Fig. 1) is fully supported by the experiment [2, 3]. Among others, it has been shown that under the action of a d.c. electric

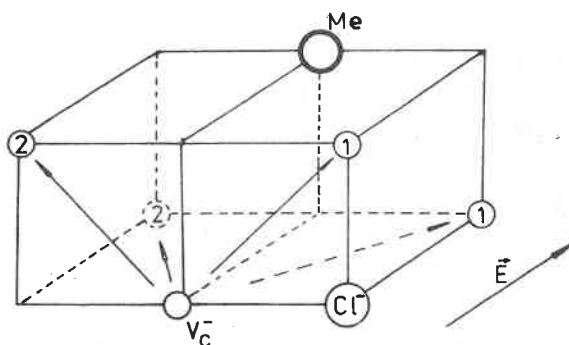


Fig. 1. The Z_1 center models proposed by Rosenbeger and Lüty [2]

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field, Z_1 centres can change their orientation with an activation energy of about 0.4 eV for a KCl:SrCl₂ crystal. Using the latter value and the above Z_1 centre model, appropriate calculations [4] show that on measuring the depolarization currents by the ITC method one should expect the appearance of a new peak localized at the low temperature side of the normal Me^{2+} -cation vacancy (I.V.) dipole peak, induced by the Z_1 centre reorientation shown in Fig. 1 (positions 1). Moreover, by considering the possibility of a quasi-dissociation of the Z_1 centre (Fig. 1, e.g. position 2), one should expect the appearance of another ITC peak on the high temperature side of the I.V. peak. In spite of the dipolar character of the Z_1 centre the appropriate measurements of dielectric polarization [5, 6] and dielectric loss [7–13] have not revealed the existence of the expected dipolar moment related to this defect.

2. Experimental details

In our experiments we have used SrCl₂ doped OH⁻ — free KCl crystals [14] cleaved into slabs of the size of $10 \times 10 \times (10 \text{ to } 15) \text{ mm}^3$. The neighbouring parts of the above slabs were used for measuring the concentration of the I.V. dipoles. The slabs were electrolytically coloured in a dry argon atmosphere at 365°C, by applying a d.c. electric field of 350 V cm^{-1} . The samples used in ITC measurements were always taken from the central part of the coloured slabs. The conversion of the F centres into Z_1 centres was performed at room temperature, by applying F -band light illumination. The samples coated with colloidal graphite were subjected to the ITC measurements in the apparatus described earlier [15].

The polarization was performed at 270 K in a 3.5 kV cm^{-1} field. After quenching to about 100 K, the sample was heated at a constant rate (e.g. 0.1 deg s^{-1}). The background current did not exceed 10^{-15} A .

3. Results

As shown in Fig. 2 the ITC plots for a crystal non-coloured (curve 1) and containing Z_1 centres (curve 2) shows small but reproducible differences on the low and high temperature side of the main I.V. peak, distinctly exceeding the experimental error. These differences, in particular that on the low temperature side, can be ascribed (according to the results of our calculations [4]), to the depolarization current related to the reorientation of Z_1 centres (Fig. 1, positions 1). Earlier attempts to reveal the dipolar character of the Z_1 centres by the ITC method failed [5, 6], possibly due to the large I.V. dipole concentration in respect to the concentration of Z_1 centres. The pertinent figures taken from these papers are $\sim 670 \times 10^{-6} \text{ m.f.}$ for I.V. dipoles and but $10 \times 10^{-6} \text{ m.f.}$ for Z_1 centres. In our case the concentration of the I.V. dipoles in the original samples was lower ($170 \times 10^{-6} \text{ m.f.}$ on assuming n.n. state) and hence the concentration ratio $c_{Z_1}/c_{\text{I.V.}}$ was 0.05 (higher than in the former case, $c_{Z_1}/c_{\text{I.V.}} = 0.01$). In spite of this fact the concentration of the original I.V. dipoles engaged in building Z_1 centres amounts here to about 5% and consequently does not contribute to the lowering of the I.V. peak in an appreciable way.

For this reason, it is indispensable to obtain samples with appropriate dopant concentration and original F centre concentration in which the $c_{Z_1}/c_{I.V.}$ ratio will be much higher. This permits the observation of the shape of the Z_1 centres peak, the eventual drop under the I.V. peak and the appearance of the peak related to the quasi-dissociation of Z_1 centres.

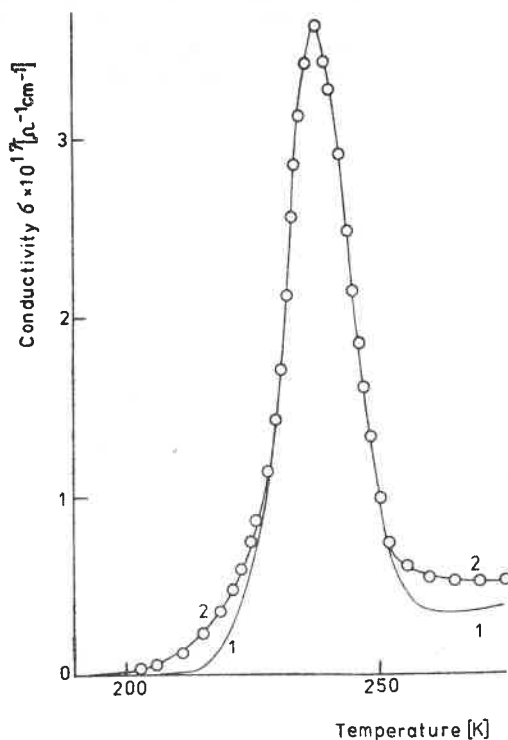


Fig. 2. ITC plots for a sample of $KCl:SrCl_2$: curve 1 — “as received” (non-coloured), curve 2 — after electrolytic colouration and $F \rightarrow Z_1$ transformation

It should be noticed here that electrolytic colouration induces in samples the appearance of some homocharge effects, giving rise to the appearance of some additional ITC peaks. The above effects decay, however, with storage time and are totally removed during F -band light illumination ($F \rightarrow Z_1$ transformation) making ITC measurements fully reliable.

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