JOURNAL DE PHYSIQUE IV
Colloque C7, supplément au Journal de Physique III, Volume 4, juillet 1994

Probing electron induced defects in CaF_2 by photothermal displacement

M. Reichling, R. Bennewitz and E. Matthias

Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Abstract: The surface displacement technique is used to measure the temperature and frequency dependence of the periodic expansion of a CaF_2-surface subject to a modulated focused beam of 1keV electrons. Theoretical models are presented for a prediction of the observed phenomena based on thermal transport and defect lifetime effects. The use of such investigations for the study of thermal and non-thermal transport phenomena in alkaline-earth halides is discussed.

1. INTRODUCTION

The interaction of electrons with CaF_2 has been studied for years and many of the elemantary processes following the primary excitonic excitation by the energetic electrons are now well understood. The formation of self-trapped-excitons (STE) within picoseconds after excitation is either followed by a radiative decay restoring the unperturbed lattice or the separation into an F-H defect center pair [1]. While the temperature dependent lifetime of STEs is well documented, little is known about the decay of F-H pairs, especially the probability for a separation into F- and H-center lattice defects. It has been demonstrated that there exists another crucial parameter for the electron induced F- and H-center formation rate namely the probability for a secondary hole excitation [2]. This process leads to a large separation of the defect pair and enhances the formation of stable defect centers. The lifetime of these species is not well known, however, one can anticipate that it depends strongly on their diffusion properties since diffusion may result in a recombination in the bulk or desorption at the surface.

The question of F- and H-center lifetime and diffusivity recently gained interest in connection with the study of low energy electron induced surface processes [3]. In such experiments the defect production is restricted to a thin (typ. 500Å) surface layer and the accumulation of densely packed F-centers leads to an effective metallization at the surface. For a quantitative interpretation of the processes resulting in the formation of metal colloids and subsequent surface metallization the knowledge of defect center formation and diffusion rates is of great importance.

For the measurements of these properties we propose the application of the surface displacement technique originally developed for the study of thermal transport properties [4]. It is a well known fact that lattice defects in ionic crystals require more space than the regular lattice constituent [5,6]. The main problem of such a procedure is the separation of thermal and non-thermal contributions to the photothermal signal and to define those experimental conditions where this separation is most pronounced. For carrier transport studies in semiconductors the modulation frequency has been shown to be a useful parameter for pronouncing a specific process [7].

In the present paper we continue preliminary studies [8] of electron induced defect transport phenomena in CaF_2 and present first suggestions for models yielding a quantitative understanding of such experiments.

2. BASIC OBSERVATIONS

To types of displacement experiments have been performed. Displacement signal amplitude and phase have been monitored either as a function of the modulation frequency for a fixed temperature or temperature dependent for fixed frequency. For frequency dependent scans in most cases a 1/f-behaviour has been observed that is not useful for the study of lifetime or diffusion properties. For our electron beam diameter of 1.8mm we had to work at low temperatures (<150K) and at low frequencies (<100Hz) to obtain significant deviations from the 1/f-curve. A typical result for 4μA of 2keV electrons impinging on the CaF_2 (111)-surface of a single crystal cooled down to 135K is shown in Fig. 1.

3. THERMAL MODEL

The calculation of the surface displacement amplitude in the center of the deformation h based on a thermoelastic model yields [9, 10]:

$$h=\alpha_{th}\frac{1+\nu}{1-\nu}\frac{P}{4\pi\lambda}\int_0^\infty u\frac{e^{\frac{(au)^2}{8}}}{u^2+\frac{i2\pi f}{\kappa}}du$$

α_{th}: th. exp. coeff.
υ : Poisson ratio
λ : th. conductivity κ: th. diffusivity
a: e^--beam radius P: inc. Power

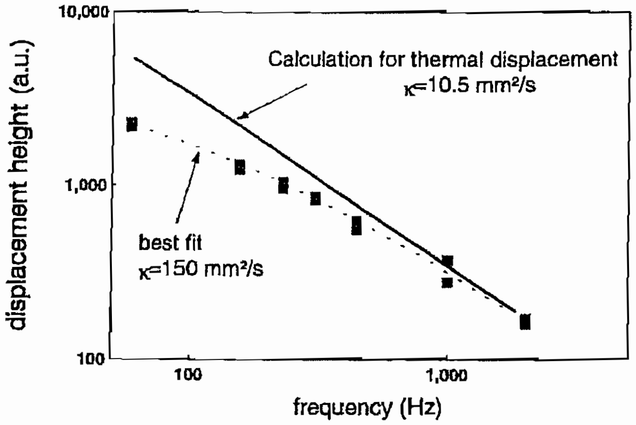

Fig.1: Frequency dependent displacement amplitude at 135K.
■: measurement, solid line: calculation κ=10.5mm²/s,
dashed line: calculation κ = 150mm²/s (thermal model).

Results for two different thermal diffusivities are compared to experimental data in Fig. 1. It is found that the best fit to the data can be obtained for a diffusivity of κ = 150 mm²/s a value that is more than one order of magnitude larger than the CaF_2 literature value for thermal conductivity at 135K of κ = 10,5 mm²/s. This discrepancy indicates that a purely thermal model is not appropriate for the interpretation of the experimental result.

4. DEFECT LIFETIME MODEL

The frequency dependent displacement amplitude resulting from a lifetime model is displayed in Fig. 2 for a best fit lifetime of τ = 1.3ms. The displacement height:

$$h=\frac{\Gamma P}{\sqrt{\frac{1}{\tau^2}+(2\pi f)^2}}$$

is found from a simple rate equation:

$$\frac{dn}{dt}=\Gamma P\frac{1+\sin(2\pi f t)}{2}-\frac{n}{\tau}$$

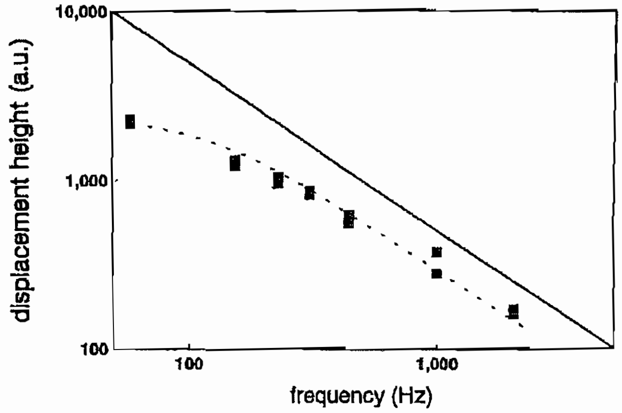

Fig.2: Frequency dependent displacement amplitude at 135K.
■: measurement, solid line: 1/f-curve for comprison,
dashed line: calculation for defect lifetime τ = 1.3ms.

for the density n of defects with lifetime τ. Γ denotes a conversion factor for the creation of the defect species contributing to the surface displacement. Defect diffusion has not been included in this model what might be a plausible assumption in the low temperature region. Quantitative modelling however needs more elaborate models including thermal and defect diffusion as well as lifetime contributions.

5. TEMPERATURE DEPENDENCE

For fixed frequencies the temperature dependence of the displacement signal has been measured. Measurements of the displacement amplitude over the temperature interval 140K - 320K are shown in Fig. 3. In accordance with previously published data [10] it was found that the displacement amplitude does either not vary significantly with temperature or exhibits a tendency towards lower values for increasing temperature. However, the exact temperature behaviour is not precisely reproducible at present.

The temperature dependence of the displacement amplitude calculated by the thermal model is incorporated in Fig. 3 as a solid line. The calculation is based on the temperature dependent thermoelastic constants taken from the literature (c.f. Fig. 4). These constants enter the thermoelastic equation differently with positive or negative temperature coefficients. Therefore, the calculation yields a non-monotonic temperature dependence for the displacement height. From a simple analysis of the thermoelastic equation it is found that the crucial factor for the displacement at high frequencies is the heat capacity ρc while the thermal conductivity λ gains importance in the low frequency region.

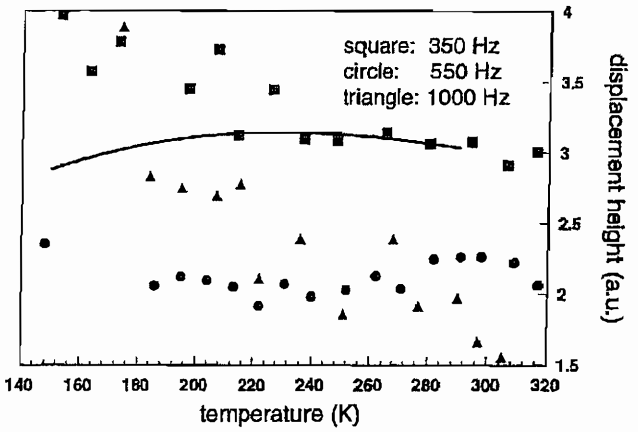

Fig.3: Temperature dependence of displacement amplitude for three frequencies. solid curve: thermal model calculation.

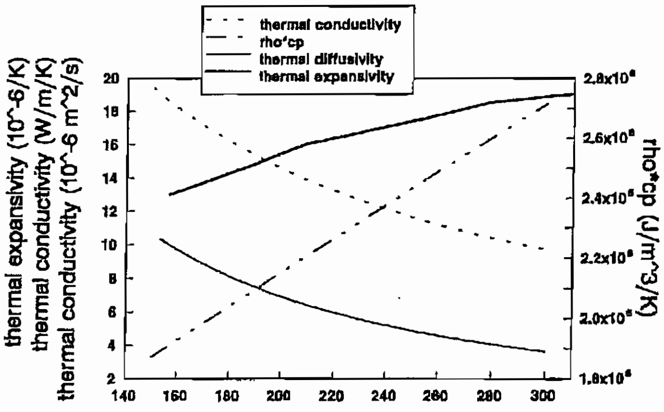

Fig.4: Temperature dependence of important thermoelastic parameters of CaF_2 taken from the literature.

6. DISCUSSION

All results shown here and also the analysis of the displacement phase of such measurements indicate that the displacement response of a CaF_2 surface subject to electron irradiation cannot be described by a model based solely on thermal energy transport. Therefore, creation, relaxation and diffusion as well as the expansion of defects have to be considered for a model describing electron induced displacement measurements in insulator crystals.

The problem might be complicated by a superposition of effects due to various species, however, it seems to be a good assumption that in an equilibrium situation F- and H-center lifetime and diffusion play the dominant role and contributions from STEs can be neglected. The diffusion range of an STE during its short lifetime is much too small to yield measureable effects. The number density of STEs during continous irradiation of the sample with electrons of energy $E_{incident}$ can be estimated for our experimental conditions:

$$n_{ste} = \underbrace{\frac{j}{eR}}_{\substack{\text{electrons per}\\ \text{unit volume}\\ \text{and second}}} \cdot \underbrace{\frac{E_{incident}}{3E_{gap}}}_{\substack{\text{STEs per}\\ \text{incident electron}}} \tau_{STE} = 2 * 10^{16} \frac{1}{cm^3}$$

$j = 2.5 * 10^{-4}$ A/cm²: current density

$R = 4 * 10^{-6}$ cm: penetration depth

$\tau_{STE} = 1.7 * 10^{-6}$ s: STE lifetime

$E_{gap} = 12$ eV: band gap of CaF_2

This means that under steady state conditions every 10^{-6}th lattice site carries an STE. Even if we assume a relative expansion of 20% of the unit cell with each STE, the integral expansion would be two orders of magnitude below our detection limit. Also F- and H-centers could provide an expansion of the lattice but we cannot predict the magnitude of this contribution: Neither the efficiency of the conversion of the STE into a F-H-pair is known for CaF_2 nor their lifetime. However, conversion factors near unity in combination with lifetimes in the msec regime would yield a measurable displacement.

At the present stage a consistent, quantitative interpretation of the displacement results is not available. An extensive set of sytematic studies over a wide range of temperature and frequency in conjunction with extensive modelling has to be performed to gain more knowledge about this multi-dimensional problem.

7. ACKNOWLEGEMENTS

This work was supported by the Sonderforschungsbereich 337 of the Deutsche Forschungsgemeinschaft

8. REFERENCES

[1] Song K.S. and Williams R.T., Self-Trapped Excitons (Springer Series in Solid-State Sciences 105, Springer-Verlag, Berlin Heidelberg, 1993).

[2] Tanimura K., Katoh T., Itoh N., "Lattice relaxation of highly excited self-trapped excitons in CaF_2", *Phys. Rev.* **B40**(2) (1989) 1282-1287.

[3] Reichling M., Wiebel R., Green T.A., Matthias E., "Low energy Electron Induced Defect Creation and Metallization at a CaF_2 (111)-surface Studied by Modulated Reflectance", Defects in Insulating Materials Vol. 2 (World Scientific, Singapore, 1993) pp. 1318-1320.

[4] Olmstead M.A., Amer N.M., Kohn S., Fournier D., Boccara C., "Photothermal Displacement Spectroscopy: An Optical Probe for Solids and Surfaces", *Appl. Phys.* **A32** (1983) 141-154.

[5] Hayes W., Crystals with the Fluorite Structure (Clarendon Press, Oxford, 1974).

[6] Eshita T., Tanimura K., Itoh N., "Volume Change due to Self-Trapped Exciton and Frenkel Pair in KBr", *J. Phys. Soc. Jap.* **55**(3) (1986) 735-738.

[7] Fournier D., "Competition Between Thermal and Plasma Waves for the Determination of Electronic Parameters in Semiconductor Samples", Photoacoustic and Photothermal Phenomena III (Springer Series in Optical Scienves 69, Springer-Verlag, Berlin, 1992) pp. 339-349.

[8] Reichling M., Wiebel R., Matthias E., "Surface Deformation and Change in Reflectivity During Electron Irradiation: Results for the CaF_2 (111)-Surface", Desorption Induced by Electronic Transitions DIET V (Springer Series in Surface Sciences 31, Springer-Verlag, Berlin, 1993) pp. 295-298.

[9] Wiebel R. and Reichling M., "About the Temperature Rise at a CaF_2 Surface during Electron Stimulated Desorption Experiments", Symposium on Surface Science, Kaprun May 9-15 1993, conference digest.

[10] Reichling M., "Electron-Surface Interaction and Metallization of the CaF_2 (111)-Surface studied by Photothermal Techniques", Radiation Effects and Defects in Solids Vol. 25 (Gordon and Breach Science Publishers S.A. 1993) in print.