

# Size evolution of low energy electron generated Ca colloids in CaF<sub>2</sub>

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Metal colloids in CaF<sub>2</sub> created by low energy electron irradiation are identified by their optical absorption bands. A mean colloid radius of 18 nm is deduced from a narrow colloid band found in crystals irradiated at room temperature. Absorption data reveal a strong influence of crystal temperature during irradiation on metallization efficiency, mean colloid size, and colloid size distribution. A reversible absorption band shift is observed when turning the electron beam on and off, which may indicate a decrease of colloid size during electron irradiation. © 1995 American Institute of Physics.

High energy ionizing radiation is well known to produce color centers<sup>1</sup> and color center aggregation in the bulk of alkaline-earth halide crystals.<sup>2</sup> This also applies to electrons of low energy. The small penetration depth of low energy electrons, however, leads to a high density of defects on or near the surface.<sup>3</sup>

In this letter we report on the agglomeration of calcium in the bulk of CaF<sub>2</sub>, observed by extinction spectroscopy. This investigation is part of a comparative study including measurements of electron stimulated desorption, surface reflectivity,<sup>3</sup> and displacement,<sup>4,5</sup> as well as scanning force microscopy studies<sup>6</sup> of an irradiated surface. While the primarily created self-trapped excitons (STE)<sup>7</sup> can easily be identified by their UV emission, extinction spectroscopy can distinguish between *F*, *M*, *R*, and *H* centers<sup>1</sup> and calcium colloids.<sup>8,9</sup> The incident electrons excite electron hole pairs which localize within picoseconds as STEs.<sup>7</sup> The STE in the fluorite structure is a nearest neighbor pair of a *F* and a *H* center and the separation of this pair can lead to a stable color center.<sup>10</sup> Diffusion and agglomeration may furthermore result in the formation of defect aggregates and eventually an efficient metallization. The thickness of the surface layer where the metallization occurs is determined by the penetration depth *d* of the electrons. This depth depends on the primary energy *E* approximately like  $d=50 \text{ nm } E^{1.3}$  (*E* in keV),<sup>11</sup> leading to a depth of about 160 nm in our case.

Here, we concentrate on the development of the metal colloid extinction band as a function of the crystal temperature during irradiation with 2.0–2.5 keV electrons. Measurements of wavelength dependent light transmission were performed with two different UHV setups. The transmission measurement allowed a direct determination of the extinction that is approximately equal to the absorption for the small clusters investigated here.<sup>2</sup> For slow scans of the extinction spectra we used the monochromatized light of a high pressure xenon lamp and a single-beam configuration for transmission measurements. For the investigation of fast changes in the spectra, the sample was irradiated with the polychro-

matic light of a *D*<sub>2</sub> lamp and spectra were taken with an optical multichannel analyzer. While the former technique facilitated a discrimination between light from the xenon lamp and STE luminescence radiation by means of a chopper and phase-sensitive detection, the latter apparatus allowed to observe effects of turning on and off the electron beam with a time resolution of 3 s. In both cases the (111) surface was irradiated under UHV conditions with a 10 μA electron beam incident under 45° and focused into a spot of approximately 4 mm diameter. Although experiments have been carried out in different laboratories and with crystals of different origin a very good reproducibility between measurements was obtained.

For the interpretation of the irradiation temperature dependence of extinction spectra it is important to obtain a measure for the fraction of STEs converted into *F*-*H* center pairs. Therefore, we have taken a series of luminescence spectra during irradiation at different temperatures shown in Fig. 1. The observed spectrum and decrease of luminescence yield due to thermally activated separation of the STE into *F* and *H* centers is well in accordance with published data.<sup>12</sup> This indicates that the primary processes for excitation and

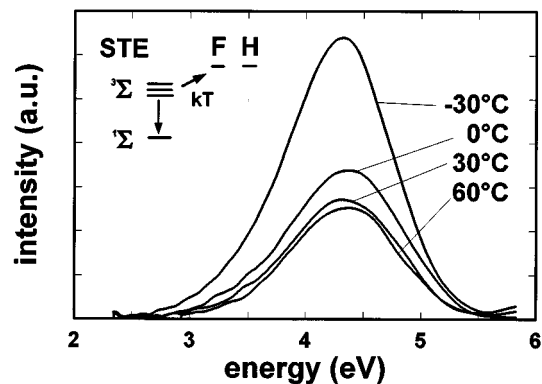


FIG. 1. Recombination luminescence of the self-trapped exciton in CaF<sub>2</sub> during electron irradiation at different temperatures. The inset illustrates the competing channels for deexcitation of the metastable self-trapped exciton state: recombination luminescence and separation into a pair of an *F* and an *H* center.

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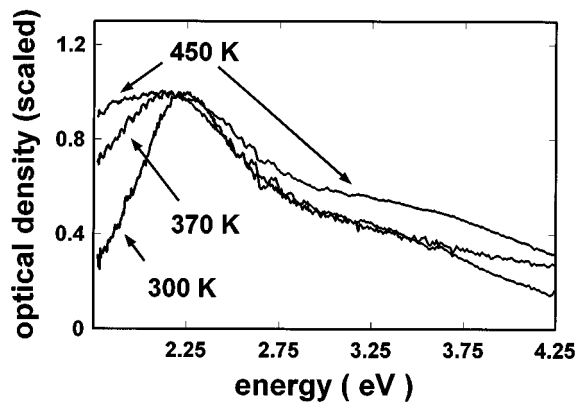


FIG. 2. Optical absorption spectra of  $\text{CaF}_2$  taken after irradiation at different temperatures. The curves are normalized to one at the absorption maximum (see Table I).

defect creation in our case are the same as for high energy radiation. However, a quantitative analysis of the temperature dependence and an extraction of the activation energy from these data is not feasible since the measured fluorescence intensity is influenced by the emerging metallization.<sup>6</sup>

Figure 2 shows typical extinction spectra taken after irradiation at different temperatures. The broadband extinction is identified as the calcium colloid band observed earlier by Orera and Alcalá.<sup>8</sup> For a better comparison of spectra the curves have been scaled to one at their maximum. The specific irradiation conditions and measured maxima for the optical density are listed in Table I. Data analysis first reveals a strong increase in efficiency for the metallization process within a temperature interval of 150 K. This reflects the expected anticorrelation to the temperature dependent decrease of STE recombination luminescence, however, also bulk diffusion properties have to be taken into account for a complete interpretation.

Second, the maximum of the extinction curve is shifted towards lower energies with increasing temperature. Calculations for the relation between the peak position and colloid radius have been performed based on the theory proposed by Orera and Alcalá.<sup>8</sup> The results are displayed in Fig. 3. We find a mean colloid radius growing from 18 nm at room temperature to 32 nm at 450 K (Table I and Fig. 3). Third, in Fig. 2 a strong broadening of the band is observed at higher temperatures. The width of the extinction band at half maximum for colloids of these radii is predicted by the calculations not to deviate significantly from 0.9 eV, and the width of our spectrum observed at room temperature is close to this value. Hence, the broadening of the extinction band for higher temperatures is interpreted as a broadening of the col-

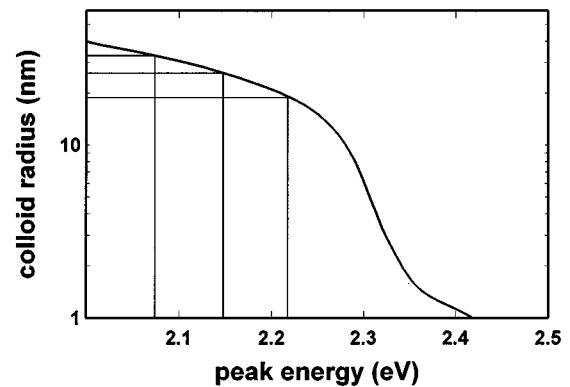


FIG. 3. Relation between colloid radius and extinction peak position for Ca colloids in  $\text{CaF}_2$  calculated from the theory of Orera and Alcalá (Ref. 8). The peak positions of the spectra from Fig. 2 are marked.

loid size distribution. From the asymmetric broadening below 2.25 eV photon energy in Fig. 2 we conclude that higher temperatures predominantly result in the formation of larger colloids and the lower limit of colloid size is that found at room temperature.

To ensure that the observed spectra result from extinction by bulk colloids and are not due to surface effects we removed the surface metallization from one crystal *ex situ* by rinsing the surface with de-ionized water. The effectiveness of such a cleaning process is well known from literature<sup>13</sup> and was checked by scanning force microscopy in our case. The spectrum did not change due to the applied procedure.

The *F*-center absorption band which is expected at 3.3 eV in  $\text{CaF}_2$  could be observed only as a weak shoulder on the metal band. This differs significantly from results for LiF or NaF where strong *F*-center absorption has been observed.<sup>14</sup> One explanation could be that the transition from an agglomerate of *F* centers to a metal colloid is more likely in  $\text{CaF}_2$  than in LiF. Calcium ions in  $\text{CaF}_2$  form an fcc structure with a nearest neighbor distance very close to that in metallic calcium.<sup>15</sup> Hence, essentially no movement of the Ca ions is required for colloid formation. On the other hand, in LiF the lithium ions have to change their structure from fcc to bcc in order to form the lithium metal and there is a big difference between the nearest neighbor distances of lithium atoms in metal and lithium ions in LiF. In addition, one should consider that the mobility of *F* centers affects the growth process of colloids and the hitherto unknown mobility in  $\text{CaF}_2$  might be significantly different from that in alkali halides.

A comparison of the optical extinction spectra during and after irradiation with electrons is shown in Fig. 4. As the main observation we note that the extinction band is shifted

TABLE I. Scaling factors, dosages, colloid production efficiencies, and mean colloid radius for the spectra shown in Fig. 2. The mean colloid radius was determined by the graph in Fig. 3.

Temperature	Maximum of optical density	Irradiation dosage	Maximum optical density per dosage	Mean Colloid radius
300 K	0.084	2.25 mC	0.0373/mC	18 nm
370 K	0.178	1.55 mC	0.115/mC	25 nm
450 K	0.4	0.75 mC	0.53/mC	32 nm

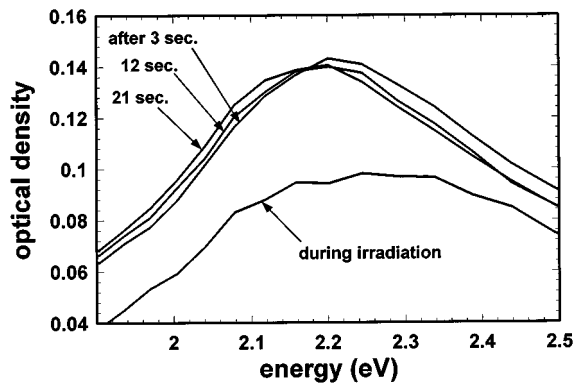


FIG. 4. Temporal evolution of the absorption band of calcium colloids in  $\text{CaF}_2$  when turning off the electron beam after irradiation for 10 min.

towards higher energies during irradiation. This shift is reversible and has a typical time constant of 5 s after switching on the electron beam and 100 s for shifting back after turning the electron beam off. The origin of the observed shift might be an absorption of electrons by the colloids. According to the model of Orera and Alcalá<sup>8,9</sup> based on the Mie theory for small particles, this would imply a reduction of the mean colloid radius during electron irradiation by a factor of 3. Since the penetration depth of electrons in metals is one order of magnitude smaller than in insulators,<sup>16</sup> colloids of more than 10 nm radius absorb most of the energy of low energy electrons impinging on their surface. This additional energy during irradiation might cause a shrinking of colloids by metal evaporation.

However, the change in optical properties may also be due to other reasons like a deviation from spherical shape or

changes in dielectric properties induced by the injected electrons. Which of the mechanisms is the reason for the observed shift will be investigated by further systematic studies that are in progress.

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