6. Optical transmission spectroscopy on CaF_2

In experiments with air cleaved crystals performed by N. Bouchaala [Bou97] in our group, it was found that no isolated point defects could be detected after 1 to 3 keV electron irradiation. Even at the lowest achievable sample temperature of 190 K during irradiation, only a very broad band centered at 2.3 eV was observed, but no *F*-center peak (compare to Fig. 2.9). Another broad structure at 6 eV appeared during irradiation, which was tentatively attributed to oxygen.

The main concern of this chapter, devoted to an optical absorption study of electron irradiated CaF_2, is to find out whether isolated *F*-centers can be produced by low energy electron irradiation under available experimental conditions. i.e. at temperatures of 150 K or above. This information is needed to decide whether the lack of *F*-center emission in the UPS spectra from electron irradiated CaF_2 is simply due to the absence of this species in the crystal, or whether it is determined by other factors.

Optical absorption spectroscopy has been used as a tool for the investigation of bulk defects like *F*-centers and defect aggregation in CaF_2 [AOr76]. Early optical spectroscopy investigations on the formation of calcium colloids in additively colored and with 0.5 MeV electrons irradiated CaF_2 have been performed by Alcala and Orera [OAl76], [OAl78]. The relation between colloid size and position of the respective absorption band was calculated by these authors on the basis of Mie's theory with corrections taking into account the optical constants of calcium and the pressure exerted on the colloids by the surrounding lattice [OAl77]. In this way, the size evolution of calcium colloids during annealing of additively colored crystals was followed by measuring the shift of the absorption band. Recently, the same method was used in our group to investigate colloid formation after irradiation with low energy electrons (0.5 to 3.0 keV) [Gün94], [Bou97].

The new experimental setup designed for this thesis provides two technical improvements compared to the one formerly used: the minimum temperature that can be reached is 150 K instead of 190 K, and it is now possible to cleave crystals in UHV. Therefore, it can be tested whether isolated *F*-centers can be observed at lower irradiation temperatures, and whether the feature at 6 eV is different for air and UHV cleaved crystals, i.e. indeed related to oxygen. Another aim of the work presented in this chapter is to check whether a reaction of the oxygen stored in the bulk of the crystals after exposure to air (see chapter 5.4) with the calcium metal produced during electron irradiation has an influence on the optical extinction.

The crystal used for this investigation was cleaved in air and transferred into UHV. After bakeout of the vacuum chamber, the crystal was cooled to 155 K and irradiated for 30 min with 2.5 keV electrons at a current density of 60 µA/cm^2. The spectra shown in Fig. 6.1 were measured during heating at a rate of 2 K/min. The last spectrum was taken at a temperature of 320 K. After this experiment was finished, the crystal was again cooled to 155 K and cleaved in UHV. Care was taken to remove a sufficiently thick peace of the crystal (2 mm) to ascertain an oxygen free surface. The experiment was repeated under the same conditions as mentioned above. The spectra measured from the UHV cleaved crystal during heating are shown in Fig. 6.2.

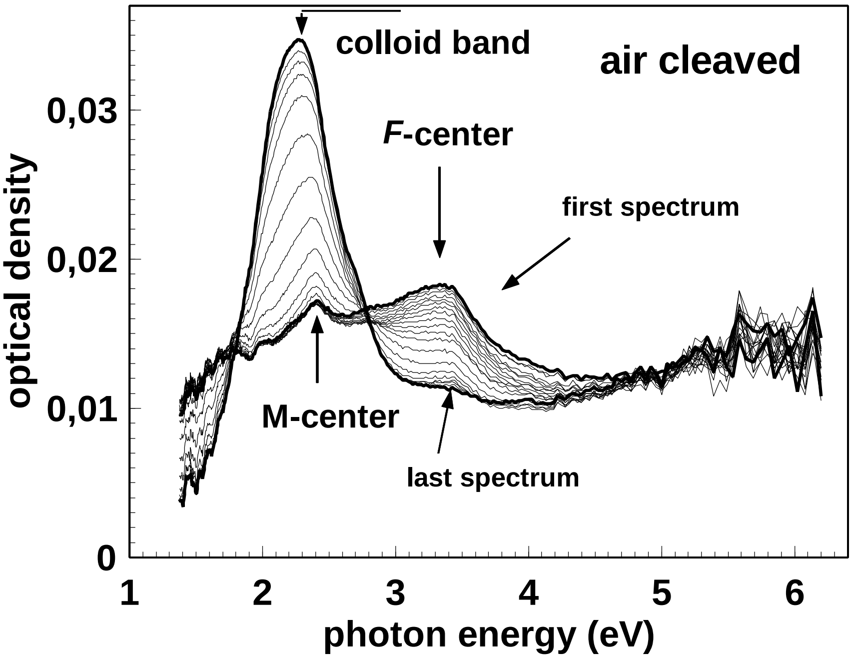

Fig. 6. 1 Series of optical spectra taken during heating after irradiation at 155 K. The crystal was cleaved in air. The two bold lines mark the first and the last spectrum. At low temperature, the most prominent peaks are the *F*-center at 3.3 eV and the M-(=F_2) center at 2.38 eV. At high temperature, the colloid band is the most prominent, indicating that small centers have aggregated to form metallic clusters. The broad feature at 6 eV remains unchanged during heating. Irradiation was done with 2.5 keV at 155 K, the dosis was 0.108 C/cm^2 (60 µA/cm^2, for 30 min).

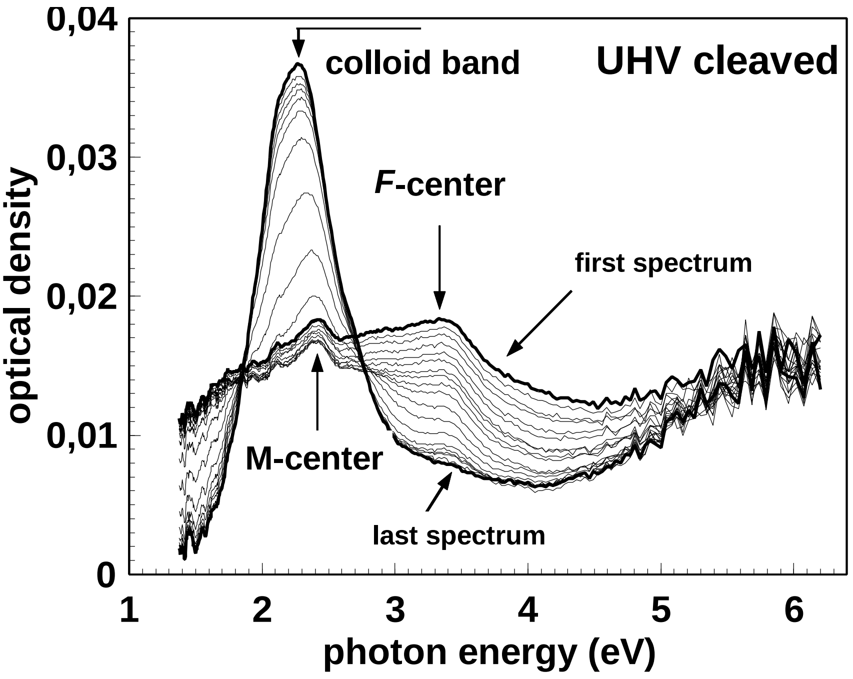

Fig. 6.2 Series of optical spectra obtained from an UHV cleaved crystal during heating after irradiation at 155 K. The two bold lines mark the first and the last spectrum. The features observed are the same as for the air cleaved crystal, however, the broad band at 6 eV seems to be even more pronounced. Irradiation was done with 2.5 keV electrons at a sample temperature of 155 K, dosis was 0.108 C/cm^2, (60 µA/cm^2, for 30 min).

After irradiation at 155 K, the *F*-center and the M-center bands are clearly distinguishable, in contrast to the observations made after irradiation at 190 K, were only a broad band centered around 2.3 eV formed (compare Fig. 2.9). However, when comparing these results with those obtained by UPS, one has to keep in mind that the present investigation was performed on bulk crystals, while the low-temperature UPS measurement were done on thin films to avoid charging problems. *F*-center aggregation may be different in the absence of the electron beam induced electric field inside the crystal (compare chapter 7.4). The broad feature centered at 6 eV does not depend on air or UHV cleavage. This structure is therefore probably not induced by oxygen.

This brief investigation shows that isolated *F*- and M- center do exist after irradiation with 2.5 keV electrons around 155 K. The broad background that is also observed after irradiation a t 155 K may be due to a number of different defects, some possible examples are listed in table 6.1 along with their absorption band positions. Upon heating, most of the background disappears, indicating recombination of defects or aggregation into clusters. Pairs of *F*- and H-centers or V_K- and I-centers (no optical transition reported) can recombine into the undisturbed lattice.

Defect	position of absorption band (eV)
F-center	3.3 [CHH69]
M-center	2.38, 3.39 [Hay74]
M^+-center	2.25 [Hay74], 3.44, 4.13 [Col73]
R-center	1.83, 1.86, [BHH72]
V_K-center	1.65, 3.87 [BHK70]
H-center	4.02 [BHK70]

Tab 6.1. Table of some absorption energies of stable defects in CaF_2. The first four are fluorine deficiency defects that contribute to the broad band around 2.3 eV and may finally aggregate to colloids.

The irradiation induced feature at 6 eV that was previously tentatively assigned to oxygen impurities appears in the spectra of the UHV cleaved crystal as well. It was assumed that this feature arises from a reaction of the neutral oxygen stored in the lattice during exposure to air with Ca metal produced during electron irradiation, $Ca + O \rightarrow Ca^{2+}O^{2-}$. In this picture, the 6 eV peak would be caused by the new formed O^{2-}. However, if this was the case, the feature should not be observable in the spectra from the UHV cleaved crystal, therefore the oxygen origin can be ruled out. The size evolution of the calcium colloids during heating from 155 to 320 K is determined from the peak positions in Fig. 6.1 and 6.2 according to the algorithm presented in [Bou97]. The results are shown in Fig. 6.3.

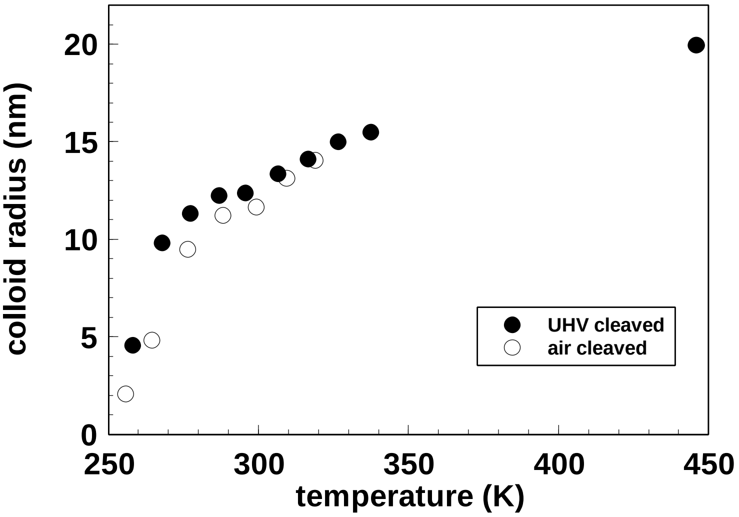

Fig.6.3 Development of the colloid radius during heating for air and UHV cleaved crystals. Irradiation was done with 2.5 keV electrons at a dosage of 0.108 C/cm^2. Temperature during irradiation was 155 K.

In the investigations performed by Bouchaala [Bou97], it was shown that the final colloid radius after heating is determined by the sample temperature during irradiation (compare Fig. 2.11). The final colloid radius after irradiation at 155 K is about 14 nm at 320 K for both UHV and air cleaved crystals. It is concluded that oxygen adsorbed during exposure of the surface to air does not affect *F*-center aggregation into colloids.

The UHV cleaved crystal was subsequently heated to 450 K, were further colloid growth to of 19 nm radius was observed. The final colloid size observed after irradiation at 155 K (14 nm) and heating was still smaller than that after irradiation at 190 K (23 nm), in contrast to the trend visible in Fig. 2.11.