Color centers in alkaline earth fluorides

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Summary

Subsequent to the very extensive investigations of color centers in alkali halides the attention has shifted gradually to these defects in the alkaline earth fluorides CaF_2, SrF_2 and BaF_2. It appeared that F -centers in these compounds have physical properties similar to those in the alkali halides, although some interesting differences have been observed.

In chapter 1 we give a survey of the literature on color centers in alkali halides and alkaline earth fluorides.

In order to identify the F -band in SrF_2 and BaF_2 combined optical and ESR -experiments have been carried out (chapter 3). The F -band in SrF_2 and BaF_2 is situated at 4490 Å, and 6060 Å, respectively. The effective oscillator strength of the F -band in additively colored CaF_2 was found to be 1.3 which is rather high compared to the corresponding values in the alkali halides. This result is due to the additional absorption by M (F_2) -centers.

An extensive study of the behavior of the optical absorption spectrum during photochemical bleaching has been made for CaF_2, SrF_2 and BaF_2 and it was found that new absorption bands are formed which are probably due to coagulates of F -centers (chapter 4). Furthermore, evidence has been obtained for the formation of large coagulates of F -centers in CaF_2 during optical bleaching at 130°C.

A theoretical study of the electronic structure of F -centers in alkaline earth fluorides enabled us to assess the relative merits of different models which had been applied to F -centers in alkaline earth fluorides (chapter 5). At first glance both the point-ion-lattice model and the semi -continuum model have some advantages. The point-ion-lattice model gives a good description of the magnetic properties, while the semi -continuum model describes remarkably well the optical properties. A more detailed inspection of these models, however, has shown that they do not predict a correct trend for the isotropic hfs -constants and the F -band energy. On the other hand the LCAO -model which was not successful in explaining the physical properties of F -centers in alkali halides may in the present case have some advantages above the conventional models mentioned. In fact, the LCAO -model predicts a correct trend for the g -shift, the second shell hfs -constant and the F -band transition energy of F -centers in CaF_2, SrF_2 and BaF_2.

The excess metal in additively colored alkaline earth fluorides initially present as electron excess centers tend to coagulate to metallic precipitates during heat treatments. The coagulation may be enhanced appreciably by the application of F -light (chapter 4). The physical properties of the colloids as measured by ESR (chapter 3) or optical experiments (chapter 6) depend upon the size of the particles. It has been found that the maximum obtainable size of the precipitates is much larger for alkaline earth fluorides than for the alkali halides. Moreover, the grains show regular forms and crystal faces indicating that they are present in crystalline form. It is highly probable that the calcium and strontium crystallites in CaF_2 and SrF_2 formed below 850°C have the FCC -lattice structure, while above 1000°C the BCC -structure is favored. For barium precipitates formed at temperatures below 850°C the crystal structure has been found to be BCC. The Ba -particles formed above 1000°C appear to be precipitated in the molten phase.