JOURNAL OF SOLID STATE CHEMISTRY **30**, 385–386 (1979)

NOTE

F-Center Luminescence in Relation to Crystal–Chemical Parameters

Some 10 years ago we proposed a very simple model to correlate the thermal quenching temperature of luminescent centers with the ionic radii of the host lattice constituents (*1*). This model explains many experimental facts and makes prediction of efficient luminescent materials possible. In recent years an experimental proof of the model was found in the ordered perovskite structure (*2*) and a quantitative confirmation was given by model calculations (*3, 4*) following Struck and Fonger (*5*).

It may be questioned whether this model is also applicable to color centers. Bartram and Stoneham (*6*) have shown that the Dexter–Klick–Russell model (*7*) is able to explain why *F* centers are sometimes luminescent and sometimes not: In RbCl, for example, the *F* center luminesces, but in LiCl it does not. The essential point in this model is that the parabolas in the configurational coordinate model should have small offsets relative to each other in order for luminescence to occur. This was also the starting point in our model. We will show here that the absence or presence of luminescence in *F* centers can be correlated to the ionic size of the constituents and the crystal structure of the host lattice. In fact such a relation was mentioned in Ref. (*6*), but it was not discussed any further.

Alkali Halides with Rock-Salt Structure

In the alkali halides we consider the six metal ions around an anion vacancy containing one electron. It is well known that this center expands considerably upon excitation (see, e.g., Ref. (*8*)). This is due to the more diffuse character of the excited-state wave function. In passing we note that this situation is comparable, but opposite to the s^2 ions where excitation results in contraction (*1*). In the s^2 ions, however, electrons of metal ions are excited; in the *F* center the electron of a negatively charged defect is excited. The expansion of the *F* center may be ascribed to a weakening of the bonds between the metal ions and the central electron. This will be most pronounced for the case of a small metal ion and a small vacancy, i.e., for the relatively strong bonds. As a consequence the offset (equal to the expansion) will be largest for the smaller metal ions.

The metal cluster is surrounded by a shell of anions. According to our model these should be small to counteract the expansion (*1*) and, preferentially, the angle vacancy–metal ion–anion should be 180° (*2*). The latter condition is satisfied in the rock-salt lattice.

Our conclusion is that luminescence from *F* centers in rock-salt alkali halides is to be expected if the metal ions are large and the anions small. This is exactly what has been found (see Ref. (*6*)): *F* centers luminesce in all rubidium and potassium halides, only in NaF and NaCl, and not in the lithium halides.

Alkali Halides with CsCl Structure

The previous arguments can be extended to other structures. Consider first the CsCl structure. For luminescence the metal ions should be large, which is characteristic of this crystal structure. Further this structure also shows the 180° angle vacancy–metal ion–anion. In fact all cesium halides show luminescent *F* centers.

0022–4596/79/120385–02$02.00/0

Printed in Great Britain

Alkaline Earth Fluorides

The compounds MeF_2 (Me = Ca, Sr, Ba) have fluorite structure. Because of the higher metal charge, the bonds will be considerably weakened upon excitation, which means large offset. Although fluorine is a suitable anion for luminescence to occur, in the fluorite structure the 180° angle is not available. In fact the F center does not luminesce in the fluorite lattice. In MgF_2 with rutile structure the situation is somewhat more favorable, since the 180° angle is available. No convincing evidence for F-center luminescence in MgF_2 has been given in the literature (*6*).

Alkaline Earth Oxides with Rock-Salt Structure

F-center luminescence has been reported for MgO, CaO, and SrO (*6*). The oxygen ion is very suitable to restrict the expansion in comparison with the lower-charged halides. The 180° angle condition is fulfilled in this crystal structure. It should be realized that in this case the F center consists of a vacancy containing two electrons, so that upon excitation the weakening of the bond will be less than that in the alkaline earth fluorites.

The M center

The M center consists of two F centers and can be compared with the hydrogen molecule as far as its electrons are concerned. Upon excitation the M center is expected to expand along its axis. The nearest neighbors along this axis are the host lattice anions. Because of their negative charge they will counteract this expansion effectively. It should be expected that the smaller the anions and the smaller the cations, the more effective this counteraction. The latter holds because small cations cause the distance between the M center and the neighboring anions to be small. These criteria for the occurrence of luminescence are different from those for the F center. As far as we are aware, an extensive investigation of M-center luminescence in several lattices has not been performed. It is interesting that the M center shows luminescence in LiCl, whereas the F center does not luminesce in this host lattice (*9*). It is also known that the excited state of the M center shows a smaller offset than that of the F center (see, e.g., Ref. (*10*)).

We conclude that, surprisingly enough, very simple parameters can be used to predict with good approximation whether an F center will luminesce or not.

References

1. G. Blasse, *J. Chem. Phys.* **51**, 3529 (1969).
2. J. Th. W. de Hair and G. Blasse, *J. Solid State Chem.* **19**, 263 (1976).
3. K. C. Bleijenberg and G. Blasse, *J. Solid State Chem.*, **28**, 303–308 (1979).
4. K. C. Bleijenberg and P. A. Breddels, to be published.
5. C. W. Struck and W. H. Fonger, *J. Lumin.* **10**, 1 (1975); **14**, 253 (1976).
6. R. H. Bartram and A. M. Stoneham, *Solid State Commun.* **17**, 1593 (1975).
7. D. L. Dexter, C. C. Klick, and G. A. Russell, *Phys. Rev.* **100**, 603 (1955).
8. W. Beall Fowler, *in* "Physics of Color Centers" (W. Beall Fowler, Ed.), Chap. 2, Academic Press, New York (1968).
9. W. Beall Fowler (Ed.), "Physics of Color Centers," Appendix B, Academic Press, New York (1968).
10. A. M. Stoneham, "Theory of Defects in Solids," Oxford Univ. Press, London/New York (1975).

G. Blasse

Physical Laboratory
State University
P.O. Box 80.000
3508 TA Utrecht, The Netherlands

Received March 5, 1979