Comment on Jahn–Teller Distortion of Ag$^{2+}$ Ions in SrF$_2$ and CaF$_2$ by Odd Modes

Hans Bill

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

(Received 11 May 1972)

Observation of the Ag$^{2+}$ in CaF$_2$ and SrF$_2$ has been reported by Fedder. The present comment suggests an alternate interpretation of the electron-paramagnetic-resonance (EPR) results given in his paper by attributing them to the O$^-$ ion incorporated into CaF$_2$ and SrF$_2$.

Fedder$^1$ reports observation of the Ag$^{2+}$ ion in CaF$_2$ and SrF$_2$ by electron paramagnetic resonance (EPR) and optical-absorption spectrometry. In a subsequent theoretical part the author explains the experimental results in terms of covalent bonds between the Ag$^{2+}$ ion and two F$^-$ neighbors. An off-center Jahn–Teller effect acting upon the Ag$^{2+}$ is given as the cause for the formation of the AgF$_2$ cluster.

The present comment proposes an alternate interpretation of the experimental results given by Fedder by attributing them not to Ag$^{2+}$ but to the ion O$^-$ incorporated into the crystals. The reasons for this interpretation are as follows.

(i) Crystals prepared as given in Ref. 1, except for total absence of any silver in any state of the treatment, exhibit the same EPR spectrum as reported in Ref. 1.

(ii) The O$^-$ ion reported in Ref. 2 exhibits the same EPR spectrum as the spectrum described in Ref. 1. We have correlated the presence of O$^-$ and the observed EPR spectrum by doping some crystals with an isotopic mixture $^{16}$O: $^{18}$O = 4:1.

The resulting EPR pattern shows in this case besides the features of the $^{16}$O (e.g., prominent hfs interaction with two F$^-$ ions) the characteristic hyperfine splitting due to one $^{18}$O nucleus. Comparison of the known intensity ratio $^{16}$O/$^{18}$O of the oxygen used in doping with the intensity of the corresponding EPR spectra shows that one nucleus of oxygen is involved in each center:

(iii) No hyperfine structure due to the Ag$^{2+}$ nucleus is reported in Ref. 1. As the hyperfine interaction takes place through core polarization, which is likely to be only weakly affected by the quite strongly polar CaF$_2$ crystal (the calculations in Ref. 1 yield a 90% Ag$^{2+}$ part of the total ground-state wave function), one would expect to observe a hfs of the order of the one observed in similar crystals. We have investigated the ion Ag$^{2+}$ in SrCl$_2$, a crystal isomorphous to CaF$_2$. The experimental results yield tetragonal hfs interaction with the Ag nucleus ($^{109}$Ag = 42 G, $^{109}$Ag = 32.7 G) of magnitude comparable with the one observed for Ag$^{2+}$ in the alkal halides.