Comments on the "Dielectric Loss in Fluoride Crystals"

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In the preceding paper by Barsis and Taylor[1] some questions have been raised as to the validity of the physical model used in a paper by Chen and McDonough.[2] The data quoted in their paper are questionable for the following reasons. The interstitial motion energy quoted in Table I has been obtained from conductivity data which are less reliable than dielectric loss-peak measurements. For example, their data are in disagreement with a recent paper by Popov.[3] It is well known that conductivity measurements sense the integrated contribution from all types of charged defects, whereas the dielectric relaxation peaks selectively examine a species with a particular relaxation time, analogous to the comparison of magnetic susceptibility with electron spin-resonance data. It is also well known that oxygen diffusion and fluorine vacancy motion cannot be discounted in conductivity measurements in this class of material. The association energy 0.4 eV, quoted in the second column of Table I, also lacks self-consistancy. It seems to be fairly independent of the physical properties of the host lattice. The lattice and dielectric constants increases going from CaF_2 to BaF_2 should all contribute to the decrease in the association energy. The magnitude of 0.4 eV is also large compared to results of divalent ions in NaCl, where the classic experiments of Etzel and Maurer[4] indicate a value of 0.3 eV for the divalent cation and Na vacancy-pair association. The 0.12-eV value of Chen and McDonough (CM) is smaller than 0.3 eV, as one would expect since CaF_2 has a higher dielectric constant compared to NaCl, and the $Y^{3+} - F^-$ interstitial in CaF_2 has a larger dipole length than that of the Ca — Na vacancy system in NaCl.

Extreme care must be taken in the interpretation of the relaxation-peak heights based on a simple model and nominal impurity concentration. Segregation effects in Bridgman crystal growth can vary the impurity concentration over a wide range. The exact dipole moment has not been determined independently and is therefore not known. A linear dependence between the impurity concentration and the number of free dipoles may be a good approximation only in the very-low-concentration range. For high concentrations, one should expect increasing dipole-dipole interaction and cooperative effects. There is experimental evidence of this nonlinear behavior.[5] For very low-impurity concentrations (0.001%), the experimental data can be fitted well with a single relaxation time. These absorption peaks are not present in the undoped material. The activation energies obtained from these relaxation peaks are dependent on the type and size of the impurities present, as found by Chen and McDonough (see Refs. 6, 7, and Table I). These results, together with the correlation of the Mössbauer[6] studies with dielectric measurements of CaF_2: Fe, favor the model suggested by CM. This model is also supported by the recent electron-paramagnetic-resonance work of Twidell,[8] and the earlier electron-paramagnetic-resonance results of O'Conner and Chen.[9] The question of the concentration dependence of the relaxation peak can only be resolved by a systematic study. In this regard, CaF_2: Y is a most appropriate material because of the high solubility of Y in fluorite.

TABLE I. Activation energies associated with trivalent impurity in CaF_2.

Trivalent ion	Ionic radius (Å)	Activation energy (eV)
Y	0.93	1.16
Fe	0.64	1.04
Co	0.63	0.94–0.96
Sm	1.04	1.37
U	1.11	1.7

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