In our calculations,[2] we have used Eq. (3c) (simplified Kwok's expression) to explain the phonon conductivity of As-doped Ge sample for $T < T_R$ $(= 4\Delta/6K_B)$. It is observed that the contribution of the ω^2 term is negligibly small. In a recent communication the results of the phonon conductivity of As-doped Ge [4] is calculated by considering the Kazakov–Nagaev[5] theory of heat transfer in solids. These calculations also suggest that one can neglect the ω^2 term of Eq. (3c) without any appreciable change in the inverse of the relaxation time and hence the phonon conductivity. The only difference with or without using the ω^2 term observed is a slight modification in the value of the adjustable parameter H. These calculations clearly suggest that elastic phonon-scattering processes are effectively proportional to the phonon frequency to its fourth power.

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Dielectric Loss in Fluoride Crystals

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The dipole-reorientation model used by Chen and McDonough to explain dielectric relaxation measurements in BaF_2, CaF_2, and SrF_2 is shown to be inconsistent with previous ionic-conductivity and electric-elastic relaxation measurements and the nominal-impurity-doping levels in their samples.

Recently, Chen and McDonough[1] (CM) reported measurements of the dielectric relaxation in BaF_2, CaF_2, and SrF_2 single crystals doped with YF_3. They attributed the observed relaxation to yttrium-impurity–fluorine-interstitial dipole reorientation and analyzed their data using a dipole-association model in the manner described by Lidiard.[2] We wish to point out that this interpretation of the dielectric loss peak is inconsistent with the nominal-doping levels in their samples and with previous anelastic-anelectric relaxation and ionic-conductivity measurements.

In BaF_2 (0.01% YF_3), the maximum dissipation observed by CM at 178 °C, corresponds to a dipole concentration, formed of F^- interstitials in the nearest-neighbor octahedral site to the Y^{+3} ion, of approximately 1.0%. This calculated dipole concentration exceeds the nominal Y^{+3} concentration they reported by 100 times. In dielectric measurements on BaF_2 (0.01% GdF_3), the authors[3] obtained a loss peak with similar relaxation times[4] to those reported by CM. We did not ascribe this peak to a simple dipole relaxation because of the large disparity between our calculated and measured values of $\tan\delta_{max}$. Furthermore, the theoretical maximum value of the dipole contribution to the dissipation, computed from our observed value of ω_p (which agrees with the values of CM), and conductivity data obtained on the same material,[3] is approximately 1000 times less than the free-carrier contribution at 175 °C. Chemical and spectrographic analysis of specimens we used showed that the residual concentration of oxygen and other unwanted impurities was insufficient to change the conductivity significantly, say by charge compensation or vacancy or impurity conduction. A similar problem was encountered by Southgate[5] who made elastic relaxation measurements on $CaF_2 - YF_3$ and conductivity measurements on the same material. The parameters of the loss peak determined by CM agree with those determined by Southgate, implying that the same loss mechanism has been observed in both the electric and elastic relaxation measurements. He concluded that an unreasonably high impurity concen-

TABLE I. Comparison of the interstitial-motion energies and the interstitial-impurity (trivalent) association energies determined from ionic-conductivity data, and the corresponding energies in the dipole model proposed by CM.

	Interstitial–motion energy	Impurity–interstitial association energy	CM reorientation energy	CM association energy (eV)
CaF$_2$	1.6[a], 1.55[b]	0.48[b]	1.16	0.12
BaF$_2$	0.79[c]	0.44[3c]	0.86	0.06
SrF$_2$	1.01[d]	0.4[c,d]	1.01	0.09

[a]Reference 6.
[b]B. Rossing, Ph. D. thesis, MIT, 1966 (unpublished).
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tration was necessary to account for the observed conductivity, on the basis of values for the interstitial jump frequency computed from the loss data. A similar discrepency exists between the dielectric measurements in CaF$_2$ – YF$_3$ by CM and the conductivity measurements made by Ure.[6]

From the available data[3] we have chosen "best" values for the fluorine-interstitial motion energies and the impurity-interstitial association energies determined from conductivity measurements based on the simple dipole model also used by CM. These values and the corresponding values determined by CM are shown in Table I. The association energies shown in column 2 for SrF$_2$ and CaF$_2$ agree with the values computed from the measured value in BaF$_2$ and the ratios of Coulomb energies to within 0.1 Ev. Although the reorientation energies shown in Table I are in fair agreement[7] with the motion energies, and the relaxation is present in trivalent-doped material and absent in undoped material,[1,3] a dipole

reorientation mechanism cannot be identified on this basis. Any effect involving the motion of fluorine interstitials may have an activation energy for reorientation approximately equal to the motion energy for free carriers, and would accompany doping with trivalent material. Possibly higher-order complex or interfacial[8] polarization has been observed. The details of the mechanism remain to be illucidated.

Although it is difficult to determine unambiguously from energy changes in the conductivity and from relaxation peaks the mechanisms in the extrinsic range of these materials, we conclude that the relaxation observed by CM cannot be attributed to the simple dipole-reorientation mechanism they propose for the following reasons: (i) The impurity concentrations, calculated from the relaxations we observed by CM, are much too high. This is also true for relaxations we observed in BaF$_2$ samples that were chemically analyzed. (ii) The expected conductivity computed from the parameters of the loss peaks using their model is much higher than the observed conductivity. The authors measured both the conductivity and the relaxation on the same BaF$_2$ specimens. (iii) Based on the measured conductivity, the free-carrier contribution to the loss would be much greater than the expected dipole peak (assuming 100% association) at the frequency of CM's loss measurements and our measurements in BaF$_2$.

References 3 and 9 contain details of the above arguments and a general discussion of the defect model in CaF$_2$, BaF$_2$, and SrF$_2$ deduced from conductivity, electric-elastic relaxation, NMR, and diffusion measurements. The arguments outlined above are not significantly altered by extending the simple-association model to include next-nearest-neighbor and Debye-Huckel interactions.

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