Reorientation of Impurity-Fluoride Interstitial Complexes in Rare-Earth-Doped CaF_2 †

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Measurements of dipole relaxation by the method of ionic thermocurrents have been made on $CaF_2:Gd^{3+}$ and peaks at 140 and 60.5 K have been observed. Analysis yields reorientation energies and τ_0's of 0.395 eV and 1.2×10^{-13} sec for the upper peak and 0.167 eV and 2×10^{-13} sec for the lower peak, respectively. Opportunity is taken to correct the previously reported parameters for the low-temperature peak in $CaF_2:Er^{3+}$. The correct values are 0.147 eV and 3×10^{-13} sec.

In a recent letter[1] a study of the dielectric relaxation of impurity-defect dipoles in $CaF_2:Er^{3+}$ which involved the use of ionic thermocurrent (ITC) techniques[2] was reported. Two relaxation peaks were observed, one at 138 K and one at 54 K for nominal heating rates of $\beta = 0.2$ and 0.1 K sec^{-1}, respectively. Computer fitting of these peaks according to the first-order kinetics applicable to dipole reorientation in a dilute system yielded values for the activation energy E_d and the reciprocal of the frequency factor τ_0 of 0.380 eV and 2×10^{-13} sec for the upper peak and 0.167 eV and 3×10^{-15} sec for the lower peak. The magnitudes of τ_0 and E_d for the upper peak compare favorably with values obtained on CaF_2 doped with other rare earths using both ITC[3] and EPR[4] methods and it is concluded that this peak is associated with the relaxation of Er^{3+}-F^- (int) complexes in which the F^- occupies the nearest-neighbor (nn) interstitial position with respect to the Er^{3+} ion.[5] The origin of the lower-temperature peak, which had not been observed previously, is less certain. However, for reasons stated in Ref. 1, it has been tentatively ascribed to the relaxation of a complex in which the F^- occupies a next-nearest-neighbor (nnn) interstitial position.

In further experiments on $CaF_2:Fe^{3+}$, it was discovered that there was a small systematic error in the heating rate used in the ITC measurements below 80 K. The purpose of this paper is to report in brief form the new results obtained on $CaF_2 Gd^{3+}$ and to correct the previously reported values of τ_0 and E_d for the low-temperature peak in $CaF_2:Er^{3+}$.

Measurements of ITC were made over the range 40–160 K on a crystal of CaF_2 containing 0.01-mole% GdF_2. The crystals had been annealed previously in HF to reduce the extent of compensation of the Gd^{3+} by O^{2-}. The ITC spectrum of the crystal was quite analogous to the one[1] obtained on $CaF_2:Er^{3+}$ except that the amplitude of the low-temperature peak was smaller by nearly an order of magnitude. Although ultraviolet excitation had no appreciable effect upon the low-temperature peak, quenching from 425 K resulted in a substantial enhancement relative to the high-temperature peak. The last observation suggests that the two peaks in Gd-doped CaF_2, like the ones in Er-doped CaF_2, may be associated with two forms of the F^- (int)–rare-earth impurity complex, e.g., nn and nnn complexes. In this interpretation the nnn form is less stable relative to the nn form and a potential barrier exists which prevents the F^- (int) from readily transferring between them.

Values of τ_0 and E_d obtained from a computer fit of the two ITC peaks are listed along with the peak temperatures T_p and heating rates β in Table I. Also listed are the corrected parameters for $CaF_2:Er^{3+}$ as a result of using the proper heating rate for the low-temperature peak. It is gratifying that the corrected τ_0 is much more nearly the normally expected value for atomic motion than the one previ-

TABLE I. Parameters for the relaxation of dipolar complexes in doped CaF_2. T_p is the ITC peak temperature, β the heating rate, τ_0 is the reciprocal of the relaxation time, and E_d the activation energy. The uncertainty ranges for τ_0 and E_d were obtained from the least-squares computer fit.

Crystal	Peak	T_p (K)	β (K/sec)	τ_0 ($\times10^{-13}$ sec)	E_d (eV)
$CaF_2:Gd^{3+}$	I	139.8 ± 0.4	0.203	1.2 ± 0.7	0.395 ± 0.01
	II	60.5 ± 0.2	0.105	2 ± 1	0.167 ± 0.005
$GaF_2:Er^{3+}$	I	137.9 ± 0.4	0.203	2 ± 0.3	0.386 ± 0.008
	II	53.6 ± 0.2	0.105	3 ± 2	0.147 ± 0.004

ously reported.

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Heat Conductivity in Cylindrical Samples

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In a previous paper,[1] the authors gave the first exact solution of the nonlinearized Boltzmann transport equation for particles with a linear dispersion law (e.g., phonons) subject to point scattering in an infinite slab. The two faces of the slab were in contact with two heat reservoirs at different temperatures, and from the knowledge of the phonon distribution function, the temperature distribution in the slab and the thermal conductivity were derived as a function of all pertinent parameters. These were the temperature, the scattering cross section, the impurity concentration, the slab thickness, and the sound velocity. Hence, one had a model of heat transport in insulators at low temperatures. The results were compared with experimental data obtained on specimens of prismoidal and cylindrical shapes, and good agreement was found despite the fact that an infinite slab is geometrically very different from either a prism or a cylinder.

It is the purpose of the present comment to show that the solution given in the cited paper is valid not only for the infinite slab, but also for a straight prism or cylinder of any cross section and of finite length, provided that the phonons are specularly reflected at the side walls.

First, a heuristic argument: Suppose that people with identical features are milling around in a room of infinite extension on all four sides. Among them is the reader as an observer. Now mirror walls perpendicular to the floor are erected around the observer, making him a member of a sufficiently large crowd enclosed in the prismatic room so created. Can the observer tell by looking around, whether he is in the finite room or in the infinite room? It is intuitively clear that he cannot tell the difference as long as the dimensions of the en-

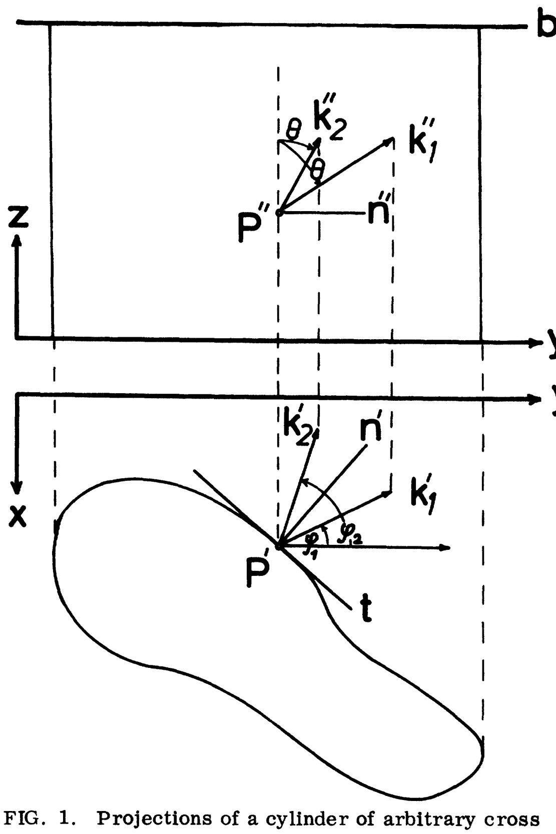

FIG. 1. Projections of a cylinder of arbitrary cross section inscribed into the infinite slab. Bottom: Projection on the x-y plane. Top: Projection on the y-z plane. The slab rests on the x-y plane, and is topped by the plane b. One and two primes denote the x-y and y-z projections of the labeled quantities, respectively. The incident phonon wave vector is $\vec{k}_1$, the reflected wave vector is $\vec{k}_2$ at the point P. The tangential plane at P is t, the normal vector is $\vec{n}$. The figure shows that only the azimuthal angle φ, and not the polar angle θ, is changed in the reflection.