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Low-temperature heat capacity of barium fluoride

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Low-temperature heat capacity of barium fluoride can be analyzed in terms of two types of contributions: one following the Debye model [$\Theta_D(0) = 286$ K] and another following the Einstein model ($\nu_E \simeq 1.6 \times 10^{12}$ cps). The $\Theta_D(0)$ value is in good agrrement with that previously determined from elastic-constant measurements. These results are not significantly affected by doping the compound with 0.1 at.% Dy. Also presented is an alternative interpretation of the experimental data based only on the Debye function but with temperature-dependent Θ_D values.

Following an earlier work on PbF_2,[1] low-temperature heat-capacity measurements have been made on barium fluoride (BaF_2). In addition to determining the limiting value of Debye temperature $\Theta_D(0)$ and comparing it with the value obtained from other techniques, the measurements also provide information on possible existence of Einstein-type heat-capacity contributions in this compound. Such calorimetrically identified Einstein modes were first suggested by Lawless[2] in terms of soft phonon modes for many paraelectrics, ferroelectrics, and antiferroelectrics.

To examine possible impurity effect on the Einstein-type heat-capacity contributions, pure and doped (0.1 at.% Dy) BaF_2 samples were used in this study. The deliberately doped material, which was obtained from Optovac, Inc., North Brookfield, Mass., was chosen because rare earths are the most likely impurities to be found in barium fluoride and the defect complexes which result give rise to local modes which will contribute to the heat capacity. This is because rare earths enter the lattice substitutionally for lattice cations and are accompanied by interstitial charge compensating fluorines. Far-infrared studies of Dy-doped barium fluoride by Villermain-Lecolier *et al.* have revealed the existence of the related vibrational local modes.[3,4] Though their interpretation of the modes has been questioned by Miller and Wright,[5] it is clear that many local modes do exist. These defect complexes do exist in the crystal studied in the present work since it was taken from the boule used in recent dielectric relaxation studies of Andeen *et al.*[6] which revealed the presence of significant numbers of dipolar defect complexes. The same techniques were applied to a section of our pure sample, which was obtained from the Harshaw Chemical Co., Solon, Ohio, showing that no rare earths or other aliovalent ions are present at the ppm level.[7]

The samples of pure and doped BaF_2 used in this work weighed about 30 g each. Heat-capacity measurements between 3 and 25 K were made using the standard adiabatic heat-pulse method and germanium thermometry.

The heat-capacity (C) data for the pure BaF_2 sample are shown in Fig. 1 as C/T^3 vs T^2. Below about 5 K, C/T^3 approaches a constant value of 0.249 mJ/mole K^4, which corresponds to a Debye temperature $\Theta_D(0) = 286$ K. This is in good agreement with $\Theta_D(0) = 282$ K reported by Gerlich[8] from elastic constant measurements. The C/T^3 peak in Fig. 1 is then analyzed in a semilog plot of $T^2(C - C_D)/9R$ vs $1/T$ (Fig. 2) where C_D is the Debye-type contribution to

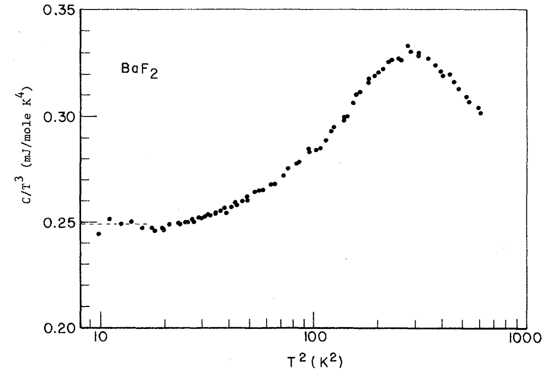

FIG. 1. Temperature dependence of C/T^3 of BaF_2.

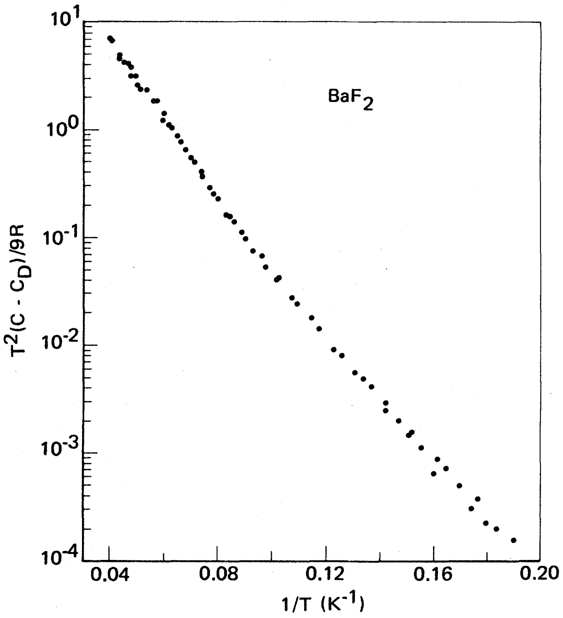

FIG. 2. $T^2(C-C_D)/9R$ vs $1/T$ for BaF_2 based on the Einstein model.

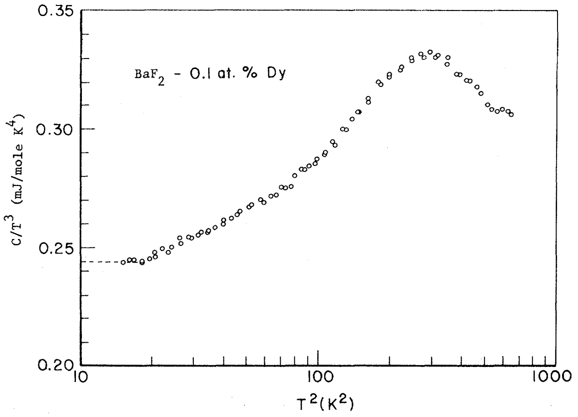

FIG. 3. Temperature dependence of C/T^3 of BaF_2–0.1 at.% Dy.

heat capacity and $C-C_D=C_E$ is the Einstein-type contribution. Such an analysis was carried out by using the large $X=\Theta_E/T$ approximation of the Einstein term,[2] i.e.,

$$C_E=3rRn(h\nu_E/kT)^2\exp(-h\nu_E/kT)$$
$$=3rRn(\Theta_E/T)^2\exp(-\Theta_E/T) \;, \qquad (1)$$

where r is the number of atoms per molecule ($r=3$ for BaF_2), R is the gas constant, n is the fraction of vibrational modes contributing to the Einstein-type heat capacity, ν_E is the Einstein frequency, and Θ_E is the Einstein temperature. For PbF_2 (Ref. 1) a linear fit was obtained, resulting in well-defined values of n and ν_E. For BaF_2, this is not the case. Instead, limiting values of these parameters are calculated and listed in Table I. Similar results have been previously reported for several compounds. For example, in the case of paraelectric $KTaO_3$, Lawless[2] suggested that the low-lying modes soften from 26 to 19 cm^{-1} as temperature decreases from 10 to 3 K.

Instead of being intrinsic to a given solid, low-lying modes could also be induced by impurities. To rule out this possibility for the aforementioned observa-

TABLE I. Calorimetric parameters of BaF_2 and BaF_2-0.1 at.% Dy.

		BaF_2	BaF_2–0.1 at.% Dy
$\Theta_D(0)$		286 K	288 K
Θ_E	20 K	85.6 K	79.6 K
	6 K	66.3 K	48.8 K
ν_E	20 K	59.4 cm^{-1} (1.78×10^{12} cps)	55.3 cm^{-1} (1.66×10^{12} cps)
	6 K	46.0 cm^{-1} (1.38×10^{12} cps)	34.0 cm^{-1} (1.02×10^{12} cps)
n	20 K	0.030	0.029
	6 K	0.008	0.002

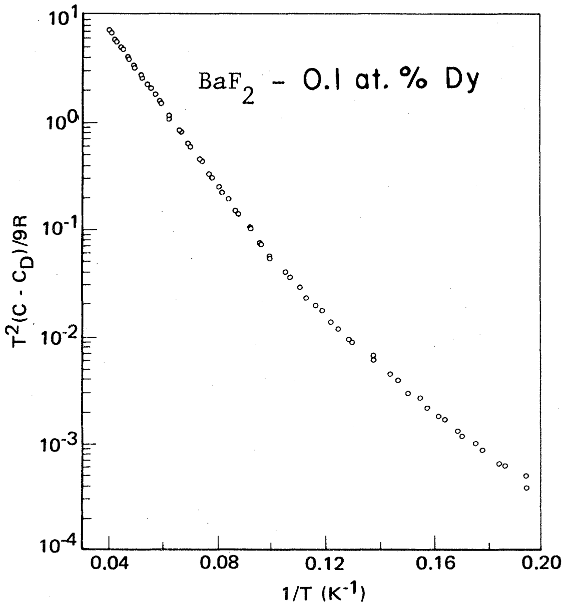

FIG. 4. $T^2(C-C_D)/9R$ vs $1/T$ for BaF_2–0.1 at.% Dy based on the Einstein model.

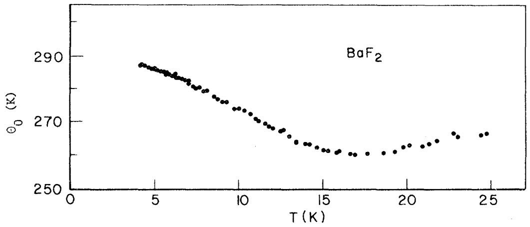

FIG. 5. Debye temperatures of BaF_2 based on Debye function.

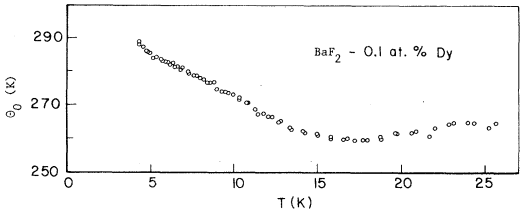

FIG. 6. Debye temperatures of BaF_2—0.1 at.% Dy based on Debye function.

tions in BaF_2, heat-capacity data for the BaF_2 sample doped with 0.1 at.% of the heavy element Dy are useful: the general features of Fig. 3 (C/T^3 vs T^2) and Fig. 4 [$T^2(C-C_D)/9R$ vs $1/T$] are very much similar to those of Figs. 1 and 2, respectively. The various fitting parameters thus obtained for this doped sample are also listed in Table I, showing no significant difference from those for pure BaF_2.

The connection between the reported soft transverse acoustic-phonon modes[9] and the observed excess specific heat of this work in BaF_2 is not yet clear. However, it is of interest to note that the value of $\nu_E = 1.78 \times 10^{12}$ cps at 20 K in Table I is just below the room-temperature broad peak frequency in Hurrell and Minkiewicz's density-of-states histogram.[10]

In a recent article, Burns[11] suggests that it may not be necessary to interpret the heat-capacity anomalies as typified by Fig. 1 by the Lawless approach.[2] Rather, one can simply view the "extra" heat capacity as arising from the differences between the more realistic density of states and that of the Debye solid. Qualitative agreement between experimental and calculated results were obtained on $SrTiO_3$.[11] The calculations were based on a shell model fit to neutron-diffraction data of the phonon modes measured at 90 K. Since there is a lack of low-temperature measurement of phonon spectra for BaF_2, a direct check of this straightforward harmonic lattice-dynamics approach is not possible. On the other hand, as this approach suggests, one can convert heat-capacity data to $\Theta_D(T)$ values using a standard Debye function table.[12] This is done for the pure BaF_2 sample. As shown in Fig. 5, $\Theta_D(T)$ varies from 260 to 290 K, with the minimum occurring at about 17 K where C/T^3 exhibits a maximum. Similar results are obtained and shown in Fig. 6 for the Dy-doped BaF_2 sample.

A final comment on the Θ_D values: in Ref. 8, Gerlich pointed out that the heat-capacity value at 13.79 K (0.25 cal/mole deg), as reported by Pitzer, Smith, and Latimer[13] in 1938 corresponded to a very low Θ_D value of 169 K, and suggested that "the discrepancy (from his value of 282 K at 0 K) may be due to a rapid rise of the Debye temperature in the range 14—0 K." It appears that he made an error in converting C to Θ_D in that he did not account for the three atoms per BaF_2 molecule (i.e., $r=3$ as used in Eq. 1). Having this correction made, the reported heat-capacity value yields a Debye temperature of 240 K. The difference between this value and the value of 263 K in Fig. 5 is rather acceptable, considering the quality of the sample and thermometry of the earlier measurements.

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