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Low-temperature heat capacities of orthorhombic and cubic PbF_2

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Heat capacities of orthorhombic (α) and cubic (β) lead fluoride (PbF_2) have been measured between 3 and 22 K. For both structures the data can be well fitted to the sum of a Debye term and an Einstein term with exponential temperature dependence. The latter may be attributed to the existence of low-lying vibrational modes in the paraelectric compound. The observed Einstein frequency of 35 cm^{-1} for the orthorhombic structure agrees with that of a Raman-active mode in $PbCl_2$ and $PbBr_2$ of the same structure, which involves the movement of Pb atoms only.

Low-temperature heat capacities of cubic lead fluoride (PbF_2) have been reported by Lawless.[1] Apart from the Debye-type lattice contribution expected for crystalline materials, an Einstein-type term has to be included in fitting the experimental data. The anomalous behavior is attributed to the presence of low-lying vibrational modes in the paraelectric compound. Even though no such modes have been identified by other techniques in cubic PbF_2, good agreement has indeed been obtained in this respect between the calorimetric and the optical or neutron experiments in various compounds, e.g., $LiNbO_3$ and TlBr.[1] Since low-lying vibrational modes are intimately related to such fundamentally important phenomena as ferroelectricity and superconductivity,[2] we have done further calorimetric work on PbF_2 in its orthorhombic (α) and cubic (β) structures as a comparative study. While both structures can be easily retained, their relative stability at ambient and lower temperatures is not yet clearly established.[3,4] Furthermore, their different temperature dependence of dielectric constants[5] suggests different lattice dynamics.

Heat-capacity measurements between 3 and 22 K were made, using the standard adiabatic heat-pulse method and germanium thermometry, on an orthorhombic polycrystal (27.8550 g) and a cubic single-crystal (6.6200 g) sample. The polycrystal sample was prepared by consolidating α-PbF_2 powder under hydrostatic pressure of 0.2 GPa, with argon as pressure medium. It has a specific density of 7.08, compared to the single-crystal value of 8.48. As confirmed by x-ray diffraction, the lower density is due to porosity rather than structural inhomogeneity (i.e., the polycrystalline sample is composed of α-PbF_2 only).

The heat-capacity (C) data are analyzed as follows: For each sample the constant C/T^3 at temperatures below 3.5 K in Fig. 1 indicates that the Debye model is valid in this lower temperature region. Based on the Debye temperature (Θ_D) thus determined and a tabulated Debye function,[6] the Debye-type contribution to the heat capacity (C_D) is calculated for the whole temperature range of the measurements. This contribution alone, however, cannot account for the observed C/T^3 peaks with maxima at about 11 and

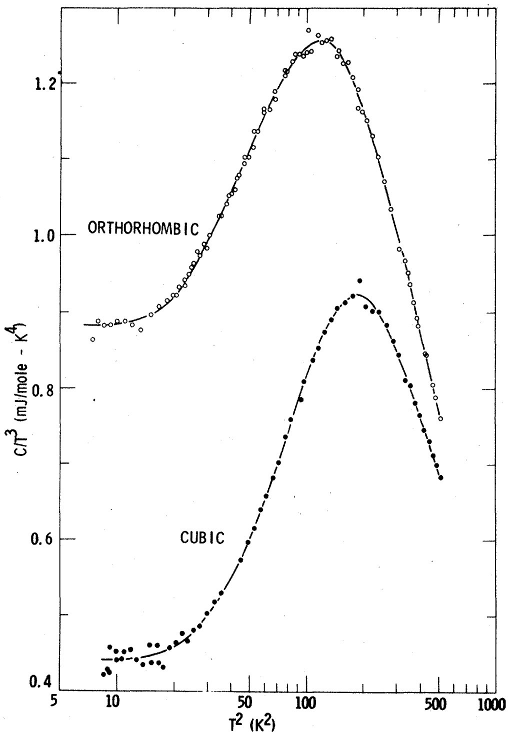

FIG. 1. Temperature dependence of C/T^3 of PbF_2.

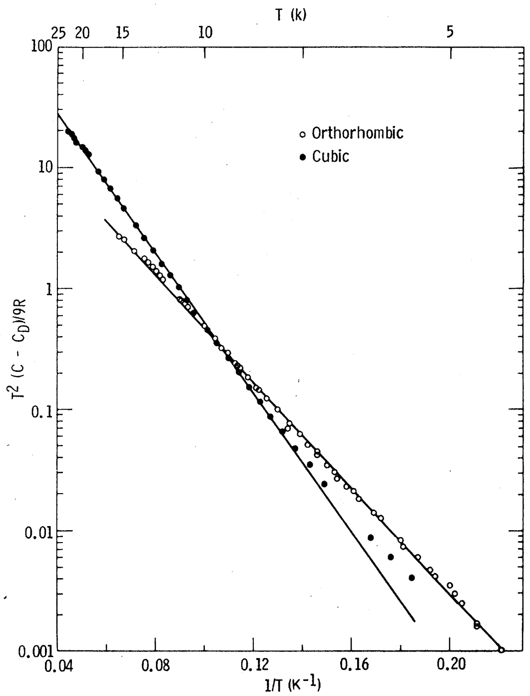

FIG. 2. Semilog fit of $C - C_D$ of PbF_2 vs $1/T$, based on the Einstein model.

13 K for the orthorhombic and cubic structures, respectively. Instead, the difference $C - C_D$ can be well fitted to an exponential term, which is the low-temperature limit of an Einstein-type heat capacity (C_E),

$$C - C_D = C_E = 3rRn\left(\frac{h\nu_E}{kT}\right)^2 \exp\left(-\frac{h\nu_E}{kT}\right) = 3rRn\left(\frac{\Theta_E}{T}\right)^2 \exp\left(-\frac{\Theta_E}{T}\right),$$

where r is the number of atoms per molecule ($r = 3$ for PbF_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. This can be clearly seen in Fig. 2, a semilog plot, where $T^2(C - C_D)/9R$ has a linear dependence on $1/T$ over several orders of magnitude. Consequently, the values of ν_E, Θ_E, and n can be determined. It should be noted that such a relatively simple scheme for data analysis is justified here mainly because (i) the C_E contribution happens to be negligible (<0.6% of C for orthorhombic and <0.07% of C for cubic PbF_2) below 3.5 K, where C_D is proportional to $(T/\Theta_D)^3$, and (ii) the low-temperature limit of the Einstein model also happens to hold well for the temperature range of interest. Otherwise, a more complicated fitting procedure involving the full expressions of C_D and C_E has to be used.[1]

TABLE I. Calorimetric parameters of PbF_2.

	Orthorhombic	Cubic	
		This work	Ref. 1
Θ_D (K)	188	237	225
Θ_E (K)	50.8	66.2	63.0
ν_E (cm^{-1})	35.2	45.9	43.8
n	0.030	0.087	0.072[a]

[a] This is a corrected value by taking into consideration $r = 3$ for PbF_2. In the original paper by Lawless (Ref. 1), n is listed as 0.217.

Table I lists various parameters for comparison. The two sets of results on cubic PbF_2 are in reasonable agreement, considering the magnitude of experimental uncertainties (< ±2% in this work and < ±5% in the work of Lawless[1]). The Θ_D values also agree well with that of 221 ± 3 K calculated from room-temperature elastic-constant data.[7,8] Similarly, the calorimetrically determined Θ_D value for the orthorhombic structure falls inside the range of 185 ±5 K, [9] which we obtained recently through room-temperature sound-speed measurements on seven orthorhombic samples with specific density between 6.92 and 7.38.

There are no available optical or neutron data for direct comparison with the ν_E values in Table I. But it is of interest to note that both orthorhombic $PbCl_2$ (Refs. 10 and 11) and $PbBr_2$ (Refs. 11 and 12) have a Raman-active mode of close to 35 cm^{-1}. As pointed out by Ozin,[10] these modes involve mainly lead atom movement. Accordingly, the low-lying frequency should be approximately invariant on passing from $PbCl_2$ to $PbBr_2$ to PbF_2. Finally, with four molecules per unit cell and therefore a total of 36 vibrational normal modes in orthorhombic PbF_2, one Raman mode would correspond to about 3%. In Table I the n value is indeed of this magnitude.

Note added in proof. In an inelastic neutron scattering study on cubic PbF_2 at 10 K, M. H. Dickens and M. T. Hutchings [J. Phys. C 11, 461 (1978)] observed a strong peak at 7 ±0.5 meV (56 ±4 cm^{-1}) corresponding to the zone-boundary transverse acoustic modes. This is close to the calorimetrically determined ν_E of 45.9 cm^{-1} in Table I.

ACKNOWLEDGMENT

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