

PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 41, NUMBER 14

15 MAY 1990-I

Thermal-expansion and index-of-refraction variation in lead fluoride between 300 and 850 K

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(Received 5 September 1989)

Diffuse transitions have been observed in alkaline-earth and lead fluorides at temperatures below their melting points. High ionic conductivity saturates above the transition temperature. One also observes lattice melting, a peak in the heat capacity, and an onset of disorder associated with lattice defects. We have observed an anomalous variation in the thermal variation of optical path length and the coefficient of linear expansion. This anomalous behavior occurs at about 705 K and appears to be associated with the formation of defects.

INTRODUCTION

Lead fluoride is a superionic conductor with the fluorite structure. Its ionic conductivity increases continuously up to 705 K, above which it tends to saturate.¹ The high-temperature specific heat exhibits a peak near the temperature where the ionic conductivity begins to saturate.^{2,3} Lead fluoride is generally described as undergoing a continuous (or diffuse) transition from the low-temperature insulating state to the high-temperature conducting state. The phase transition is also known as the Faraday transition. The ionic conductivity arises because of the motion of F^- ions in the nearly rigid host sublattice provided by the Pb^{2+} ions. The superionic behavior of lead fluoride has been attributed to the high degree of disorder (Frenkel defects) in the crystal lattice and to the interaction among the defects.³

Neutron-scattering studies on lead fluoride indicate a knee in the variation of lattice constant with temperature.⁴ The measurements of the linear-thermal-expansion coefficient have been reported for temperatures below 300 K (Ref. 5) and more recently up to 900 K by Roberts and White.⁶ These authors, using push-rod dilatometry, observed a maximum in the values of coefficient of expansion between 700 and 800 K. The behavior of the expansion coefficient near the Faraday transition temperature was briefly reported but not discussed earlier.⁷ Aurora *et al.*⁸ observed an anomalous increase in the ex-

pansion coefficient for the superionic solid barium fluoride near its transition temperature (1235 K). The unusual variation in the expansion coefficient occurs near the temperature where a specific-heat anomaly is observed.

Measurements of the linear-thermal-expansion coefficient, α ,

$$\alpha = d(\ln L)/dT$$

and the temperature variation of the index of refraction, δ ,

$$\delta = d(\ln n)/dT$$

require a more complete picture to be developed. Here, n is the index of refraction of the crystal, L is its length, T is the absolute temperature, and \ln denotes natural logarithm. These measurements are also useful in making necessary corrections to ultrasonic and Brillouin scattering studies. Some solid electrolytes with the fluorite structure are widely used as optical materials in lasers. A knowledge of α and δ is required to design properly the optical-laser components. It can be shown from classical electrodynamics that δ is proportional to α . Temperature dependence of α and δ in ionic materials has been shown to be correlated.⁸ This work was undertaken with the goal of measuring α and δ for lead fluoride and also to test whether there is a peak in α when lead fluoride undergoes a Faraday phase transition.

EXPERIMENT

The experiment was done in two parts. In the first part of the experiment, the optical length coefficient, A [$=\alpha + \eta\delta(\eta - 1)$], was determined. In the second part, the coefficient of thermal expansion, α , was determined. The measurements of α and A were used to calculate the thermo-optic coefficient, δ .

The optical length coefficient, A , was measured using a laser interferometer.⁹ The sample was an unoriented, single crystal, 5.4 mm long. Its refractive index is 1.7621 (Ref. 10) and the crystal was purchased from Optovac. The sample chamber was flushed with dry N_2 gas before it was heated. The measurements were carried out under a dynamic vacuum at a pressure of 30 m Torr. Below 733 K, the decrease in the signal intensity was negligible. This implies that the sample had not significantly oxidized up to 733 K. Above 733 K, however, the signal intensity was rapidly attenuated, signifying the onset of the sample oxidation. The interference fringes were recorded during heating and the temperature was measured using a chromel-alumel thermocouple.

The linear-expansion coefficient was measured by using the arrangement described elsewhere.⁹ The lead fluoride sample was a parallel-face cylinder, 3.7225 mm long and 8 mm in diameter. It was sputter deposited with a platinum film, 1000 Å thick. The pressure in the sample chamber was 4.7×10^{-5} Torr. In order to achieve good thermal contact between the sample and the thermocouple, the thermocouple junction was embedded in a barium fluoride crystal. The lead fluoride crystal was placed near the barium fluoride crystal. Both lead and barium fluoride crystals were placed on a common surface. The thermocouple, when placed in direct contact with the sample, was found to disturb the optical alignment. Barium fluoride was used with a thermocouple because lead fluoride crystals were very hard to obtain. In equilibrium we did not expect any significant error in temperature.

RESULTS

The results for the optical length coefficient are shown in Fig. 1. A least-squares fit of the values of A between

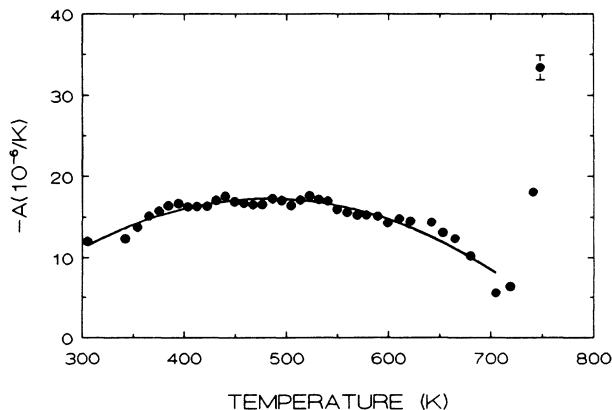


FIG. 1. The variation of the optical length coefficient of lead fluoride with temperature is shown here. The solid line is a second-degree fit through the data below 705 K. The error bar shows the maximum error in the measurements.

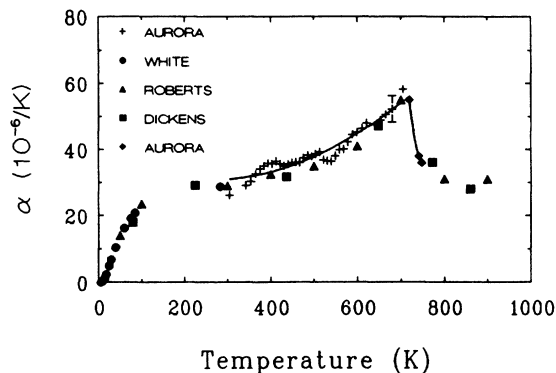


FIG. 2. The variation of the coefficient of linear expansion is shown in this figure. The figure shows the results obtained in this work along with other works for comparison. The solid lines are second-degree fits through our data below and above the transition temperature.

300 and 705 K yielded the expression

$$10^6 A = 25.49 - 0.1775T + 18.40 \times 10^{-5} T^2 .$$

The standard error of the fit was 0.40 which yielded an error of 3.1–4.5 %.

The values of α were obtained by taking an average of the results obtained in three runs and are shown in Fig. 2. A least-squares fit through the values of α up to 705 K yielded the relation

$$10^6 \alpha = 37.97 - 0.05839T + 1.160 \times 10^{-4} T^2 ,$$

with a standard error of 1.12.

These fitted curves for α and A can be used to obtain an expression for δ , using the relation

$$A = \alpha + n\delta / (n - 1)$$

which yields

$$10^6 \delta = -5.40 - 0.0515T + 2.94 \times 10^{-5} T^2 .$$

DISCUSSION

It is seen in Fig. 1 that the absolute value of the quantity A decreases with temperature. It has a small value near 705 K and it increases at higher temperatures. The lowest value of $-A$ occurs at the temperature where the specific heat exhibits anomalous behavior. Therefore, it is clear that the transition to the highly disordered state is accompanied by an anomalous variation in the optical length coefficient.

The values of α (Fig. 2) are seen to be in good agreement, within the experimental errors, with those obtained from the lattice-parameter measurements, neutron-scattering measurements, and those measurements obtained by dilatometry. The values of α obtained by neutron scattering are also in agreement with the low-temperature work. The scatter in the present results is due to the difficulty in accurately measuring the sample temperature without disturbing the interference pattern.

Below 600 K, α increases slowly with temperature and may be understood in terms of the lattice anharmonicity.

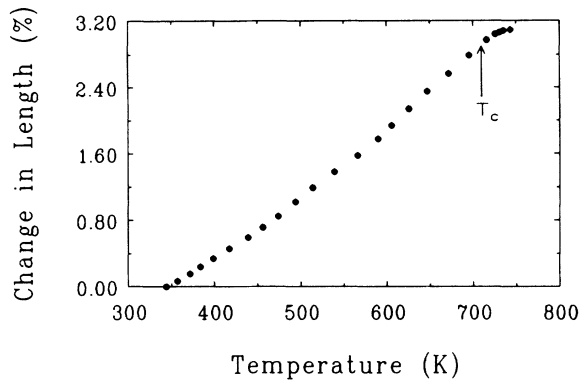


FIG. 3. This figure shows the variation of percent change in the crystal length ($100\Delta L/L$) as a function of temperature. The change in length was calculated from a knowledge of the fringe shift at any given temperature. T_c is the transition temperature.

For temperatures above 600 K, α increases rather rapidly. The large variation in α begins in the region where the defect concentration also increases rapidly.¹² The defects interact via the long-range Coulomb force and also produce a lattice distortion. The defect interaction has been described as being responsible for the knee in the lattice parameter of lead fluoride. Catlow *et al.*¹³ have shown that the defect interaction is responsible for the anomalous behavior of the elastic constants of PbF_2 . Therefore, it can be assumed that the large variation in α is also due to the interaction of defects. There is an indication of a peak in the thermal evolution of α near 705 K where a specific-heat anomaly is also observed. Due to inadequate data above 700 K, the existence of a peak in α cannot be conclusively established in our work.

From our measurements, we are also able to calculate the increase in length of the crystal at any temperature within the range of the experiment. The change in crystal length as a fraction of the original length ($=\Delta L/L$) up to any temperature is shown in Fig. 3 as a percentage. The length increases with temperature and exhibits a knee near the transition temperature where the expansion

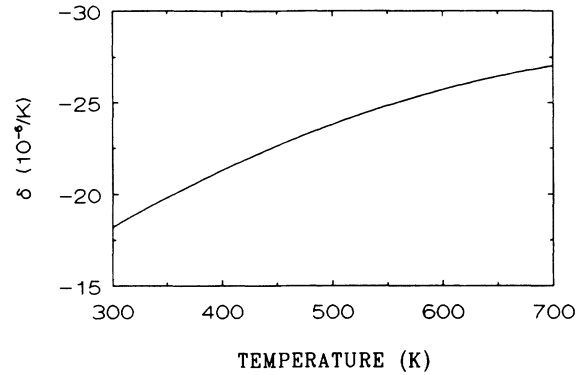


FIG. 4. The variation of the thermo-optic coefficient, δ , is shown below the transition temperature. The expressions for least-squares fits for the linear expansion coefficient and the optical length coefficient were used for this curve.

coefficient shows a possible peak.

The values of δ are shown in Fig. 4. In calculating δ , the least-squares fits were used for α and A . The value of δ is seen to increase gradually up to 700 K.

CONCLUSION

The present results are in good agreement with the available data. In addition, the results indicate that the transition to the highly disordered phase affects the dilatometric and optical properties of lead fluoride.

ACKNOWLEDGMENTS

We thank R. B. Foster and K. Vickers of Texas Instruments for sputter depositing the platinum on the crystals and for the loan of some equipment. We thank the University of Arkansas for the research grant and the physics Laser Lab for the use of their facilities. One of us (T.S.A.) wishes to thank Philadelphia College of Pharmacy and Science for research support.

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