Brillouin Scattering Investigations of Cerium Fluoride at High Temperature: A Diffuse Superionic Transition

P. E. Ngoepe
Department of Physics, University of the North, Sovenga 0727, South Africa

and

J. D. Comins
Department of Physics and Condensed Matter Physics Research Group, University of the Witwatersrand, Johannesburg P. O. Wits 2050, South Africa

(Received 15 June 1988)

The complete set of acoustic-mode frequencies associated with elastic constants in cerium fluoride have been measured by Brillouin scattering to temperatures of about 1500 K. These frequencies decrease linearly from 300 to about 1150 K. Above 1150 K striking deviations from linear behavior are observed. The results are discussed in terms of anharmonicity and a diffuse superionic transition in which the development of disorder proceeds by means of cooperative mechanism.

PACS numbers: 63.20.Dj, 61.70.Bv, 64.70.Kb, 78.35.+c

The potential application of superionic, or fast-ion, conductors as solid electrolytes in energy-storage devices and for ion-specific electrodes has resulted in substantial interest in such compounds. Studies by Brillouin scattering of acoustic-mode frequencies in certain fast-ion conductors have provided important information concerning the development and extent of sublattice disorder.[1-7] The results have been correlated with other techniques such as neutron and Raman scattering, ionic conductivity, and specific-heat studies.[8] Such work on the simple fluorites, e.g., CaF_2, BaF_2, etc. has resulted in a reasonably satisfactory theoretical understanding.[9,10]

It is important to extend investigations to other compounds whose structure is different, but nonetheless sufficiently simple to be amenable to the current theoretical approaches. Thus, interest in other fluorides has developed to include those rare-earth (M) trifluorides, MF_3, which have the tysonite (D_{3d}^4) structure with trigonal, essentially hexagonal, symmetry.[11,12] These compounds differ from the fluorites in possessing good ionic conductivity at the relatively low temperatures of 300 to 600 K, as demonstrated by ionic conductivity[13-17] and NMR studies[18-23] on LaF_3 and CeF_3. This is caused by significant fluorine-ion mobility and is associated with the motion of vacancies. The theoretical discussion has assumed Schottky disorder based largely on lattice-parameter and dilatation measurements.[19] Studies at higher temperatures have been sparse. The most significant of these are the measurements of the high-temperature enthalpy and the excess heat capacity ΔC_p derived from them.[24-26] These investigations show a significant increase in ΔC_p beginning around 1000 K. Recent theoretical studies by Jordan and Catlow[27] favor Frenkel rather than Schottky disorder which, taken in conjunction with the heat-capacity behavior, suggests the possibility of a diffuse transition to fluorine sublattice disorder at high temperatures, based on Frenkel defects.

Following the successful application of Brillouin spectroscopy to problems of this type, we have initiated such studies on the MF_3 series. In recent measurements of a few selected modes in LaF_3, we observed striking reductions of mode frequencies above about 1150 K which were well correlated with the heat-capacity anomaly discussed above.[6,7] The present investigation of CeF_3 represents the first reported study of an MF_3 compound in which a complete set of acoustic modes associated with all the elastic constants for hexagonal symmetry are determined to temperatures near 1500 K. Some modes are measured to a temperature of 1600 K, this beginning to approach the melting point of 1733 K. Such measurments provide a suitably complete study for comparison with theoretical approaches.

Spectra were excited with the 514.5-nm line from an argon-ion laser. The analysis was carried out with a triple-pass, piezoelectrically scanned, Fabry-Perot interferometer which was electronically stabilized. The signals were detected by a photon-counting system and accumulated by a multichannel analyzer. The birefringence of CeF_3 is negligibly small over the temperature range investigated. Hence a mean refractive index $\bar{n}$ may be used in the equation for the Brillouin frequency shift in the scattered light, namely

$$\Delta\omega_B = (2\bar{n}v\omega_0/c)\sin(\theta/2). \qquad (1)$$

Here v is the velocity of the acoustic phonon, ω_0 is the frequency of the incident light, C is the velocity of light, and θ is the scattering angle chosen to be 90°.

The phonon propagation directions, together with the modes used, are given in Table I: **K** is the unit vector parallel to the phonon propagation direction; **u** is the

TABLE I. Combinations of elastic constants of a hexagonal crystal in the various phonon propagation and polarization directions.

K	**u**	Mode	γ_{ij}[a]
$(1,0,0)$	$(1,0,0)$	L	c_{11}
$(0,0,1)$	$(0,0,1)$	L	c_{33}
$(0,1,1)/\sqrt{2}$	$(0,u_2^3u_3^3)$	QL	γ_{13}
$(0,1,1)/\sqrt{2}$	$(0,u_2^4u_3^4)$	QT	γ_{14}
$(0,1,1)/\sqrt{2}$	$(1,0,0)$	T	γ_{15}
$(-1,\sqrt{2},1)/2$	(u_1^5,u_2^5,u_3^5)	QL	γ_{16}
$(-1,\sqrt{2},1)/2$	(u_1^6,u_2^6,u_3^6)	QT	γ_{17}
$(-1,\sqrt{2},1)/2$	$(1,0,1)/\sqrt{2}$	T	γ_{18}

(a) $\gamma_{13}=\frac{1}{4}\{c_{33}+c_{11}=2c_{44}+[(c_{11}-c_{33})^2+(c_{13}+c_{44})^2]^{1/2}\}$;
$\gamma_{14}=\frac{1}{4}\{c_{33}+c_{11}+2c_{44}-[(c_{11}-c_{33})^2+(c_{13}+c_{44})^2]^{1/2}\}$;
$\gamma_{15}=(c_{44}+c_{66})/2$;
$\gamma_{16}=\frac{1}{4}\{3c_{11}+c_{33}+4c_{44}+[(3c_{11}-2c_{44}-c_{33})^2+12(c_{13}+c_{44})^2]^{1/2}\}$;
$\gamma_{17}=\frac{1}{4}\{3c_{11}+c_{33}+4c_{44}-[(3c_{11}-2c_{44}-c_{33})^2+12(c_{13}+c_{44})^2]^{1/2}\}$;
$\gamma_{18}=(c_{44}+3c_{66})/4$.

phonon polarization direction with its components u_k^l being in some cases complicated expressions which are defined in Ref. 28; γ_{ij} are the combinations of elastic constants; and L, QL, QT, and T refer to the longitudinal, quasilongitudinal, quasitransverse, and transverse modes, respectively. Since the phonon velocities along the (1,0,0) and (0,1,0) directions are virtually identical, the hexagonal approximation to the trigonal structure is adequate for discussion of the elastic properties. Hence it follows that $c_{14}\simeq 0$. If we use Eq. (1), and treat $\bar{n}^2/\rho$ as slowly varying, which holds for fluorites,[3] then $(\Delta\omega_B)^2 \propto \gamma_{ij}$. Four samples of CeF_3 were cut and polished to permit a study of phonon propagation along the directions **K** given in Table I. To avoid contamination of the crystals, they were encapsulated in quartz capsules under ultrapure argon. The orientation of the samples was preserved by use of a matched recess ultrasonically cut into the base of the capsule. They were then mounted in an optical furnace and accurately aligned with respect to the laser beam.

Figure 1(a) describes light scattering from acoustic phonons propagating in the high-symmetry directions (1,0,0) and (0,0,1). The variation in the square of the acoustic-mode frequencies, $(\Delta\omega_B)^2$, corresponding to the elastic constants c_{11} and c_{33}, is shown as a function of temperature. Scattering from transverse phonon modes was too weak to be observable. Between temperatures of 400 and 800 K, it was not possible to measure c_{33} because of the overlap of Brillouin peaks from adjacent orders. Similar measurements were carried out for acoustic modes in the $(0,1,1)/\sqrt{2}$ and $(-1,\sqrt{2}, 1)/2$ propagation directions. The former yielded the quasilongitudinal mode, γ_{13}(QL), and pure transverse mode, γ_{15}(T); the quasitransverse mode, γ_{14}(QT), yielded very weak Brillouin peaks. The $(-1,\sqrt{2},1)/2$ direction resulted in $(\Delta\omega_B)^2$ for the modes γ_{16}(QL), γ_{17}(QT), and γ_{18}(T). All modes displayed essentially similar behavior to those shown in Fig. 1(a), namely a linear decrease in $(\Delta\omega_B)^2$ with increasing temperature followed by a marked reduction above about 1150 K. This may be compared with that of the heat capacity. In Fig. 1(b), the excess heat capacity ΔC_p determined as the difference between the experimental[25] and Debye heat capacities for CeF_3 shows an obvious increase at correspondingly high temperatures.

The data for the acoustic-mode frequencies in conjunction with the relationships given in Table I were sufficient to allow the $(\Delta\omega_B)^2$ corresponding to the additional individual elastic constants c_{13}, c_{44}, and c_{66} to be calculated as a function of temperature. In order to test the reliability of the calculations, the behavior of $(\Delta\omega_B)^2$, corresponding to c_{11}, was calculated from modes γ_{13}(QL), γ_{15}(T), γ_{16}(QL), γ_{17}(QT), and γ_{18}(T), and is displayed in Fig. 2. A comparison of measured and calculated values for c_{11} shows a most satisfactory degree of agreement if we consider the large number of modes used and the complexity of the relations shown in Table I. Furthermore, the values of the mode frequencies agree well with the previously published data of Hart[29] and Laiho, Lakkisto, and Levola[30] for relatively low temperatures ($T < 600$ K). The observed initial linear decrease in mode frequencies and elastic constants shown in Figs. 1(a) and 2 is attributable to lattice expansion and is accounted for by the quasiharmonic theory of Garber and Granato.[31] In previous studies of fluorites,[1-5] the marked deviation from linear behavior at high temperatures has been used to define a transition temperature T_c; for CeF_3, $T_c \simeq 1150$ K. The pronounced decreases in the mode frequencies and elastic constants above T_c together with the increase in ΔC_p strongly sug-

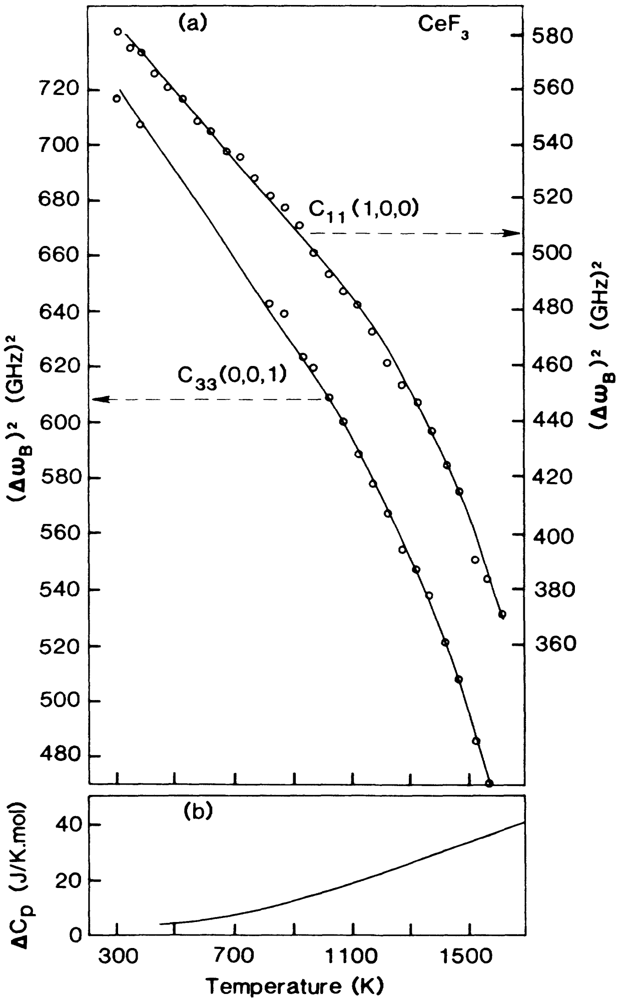

FIG. 1. (a) The behavior of the square of the acoustic-mode frequencies $(\Delta\omega_B)^2$ as a function of temperature for modes related to the elastic constants c_{11} and c_{33}. The phonon propagation directions are also indicated, being (1,0,0) and (0,0,1), respectively. (b) ΔC_p, the difference between the experimental and Debye heat capacities for CeF$_3$ as a function of temperature as determined from the data of Ref. 25.

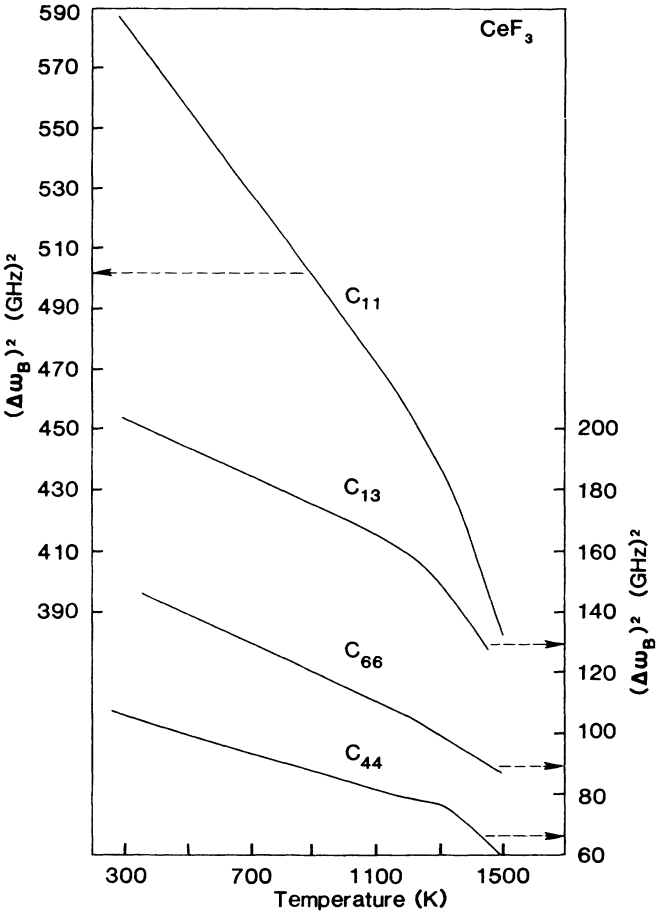

FIG. 2. The behavior of the calculated $(\Delta\omega_B)^2$ corresponding to the individual elastic constants c_{11}, c_{13}, c_{44}, and c_{66} as a function of temperature.

gest the development of a diffuse transition to a disordered superionic state by analogy with the previous studies on fluorites and UO$_2$.[3,32] As discussed previously,[6] contributions of anharmonic interactions beyond those accounted for in quasiharmonic theory may well make a contribution to the reduction in mode frequencies. However, the current evidence from studies of such transitions favors defect generation as the dominant mechamism.

There are certain additional features worthy of mention. The high-temperature behavior of c_{44} appears anomalous in comparison with the other elastic constants. The near constancy in dc_{44}/dT just above T_c has also been observed in LaF$_3$.[28] The reductions in mode frequencies in CeF$_3$ are very similar to those of LaF$_3$, but the reported heat-capacity anomaly is larger by approximation 20% in the latter compound at 1600 K. The reasons for this discrepancy are not clear.

In conclusion, the present results provide the behavior of acoustic-mode frequencies and associated elastic constants in a tysonite-structure rare-earth fluoride to temperatures of 1500 K and above in some cases. They show strong evidence in support of a diffuse transition to a superionic state involving fluoride sublattice disorder above $T_c \simeq 1150$ K.

---

[1] R. T. Harley, W. Hayes, A. J. Rushworth, and J. F. Ryan, J. Phys. C **8** L530 (1975).

[2] Cao-Xuan An, Phys. Status Solidi (a) **43**, K69 (1977).

[3] C. R. A. Catlow, J. D. Comins, F. A. Germano, R. T. Harley, and W. Hayes, J. Phys. C **11**, 3197 (1978).

[4] C. R. A. Catlow, J. D. Comins, F. A. Germano, R. T. Harley, W. Hayes, and I. B. Owen, J. Phys. C **14**, 329 (1981).

[5] P. E. Ngoepe and J. D. Comins, J. Phys. C **19**, L267 (1986).

[6] P. E. Ngoepe, J. D. Comins, and A. G. Every, Phys. Rev. B **34**, 8153 (1986).

[7] P. E. Ngoepe and J. D. Comins, Cryst. Lattice Defects Amorphous Mater. **15**, 317 (1987).

[8] A. V. Chadwick, Solid State Ionics **8**, 209 (1983).

[9] C. R. A. Catlow and W. Hayes, J. Phys. C **15**, L9 (1982).

[10] A. R. Allnatt, A. V. Chadwick, and P. W. M. Jacobs, Proc. Roy. Soc. London A **410**, 385 (1987).

[11] M Mansman, Z. Kristallogr. **122**, 375 (1965).

[12] A. Zalkin and D. H. Templeton, Acta Crystallogr. B **41**, 91 (1985).

[13] A. Sher, R. Solomon, K. Lee, and M. W. Muller, Phys. Rev. **144**, 593 (1966).

[14] L. E. Nagel and M. O'Keefe, in *Fast Ion Transport in Solids, Solid State Batteries and Devices,* edited by W. van Gool (North-Holland, Amsterdam, 1973), p.165.

[15] A. V. Chadwick, D. S. Hope, G. Jaroszkiewicz, and J. H. Strange, *Fast Ion Transport in Solids,* edited by P. Vashista, J. N. Mundy, and G. K. Shenoy (Elsevier-North-Holland, Amsterdam, 1979), p. 683.

[16] J. Schoonman, G. Overshuizen, and K. E. D. Wapenaar, Solid State Ionics **1**, 211 (1980).

[17] J. R. Igel, M. C. Wintersgill, J. J. Fontanella, A. V. Chadwich, C. G. Andeen and V. E. Bean, J. Phys. C **15**, 7215 (1982).

[18] K. Lee and A. Sher, Phys. Rev. Lett. **14**, 1027 (1965).

[19] M. Goldman and L. Shen, Phys. Rev. **144**, 321 (1966).

[20] A. G. Lundin, S. P. Gabuda, and A. I. Lifshits, Fiz. Tverd. Tela (Leningrad) **9**, 357 (1967) [Sov. Phys. Solid State **9**, 273 (1967)].

[21] E. Ildstad, I. Svare, and T. A. Fjeldly, Phys. Status Solidi (a) **43**, K65 (1977).

[22] F. C. Case and P. P. Mahendroo, J. Phys. Chem. Solids **42**, 385 (1981).

[23] G. A. Jaroszkiewicz and J. H. Strange, J. Phys. C **18**, 2331 (1985).

[24] F. H. Spedding and D. C. Henderson, J. Chem. Phys. **54**, 2476 (1971).

[25] F. H. Spedding, B. J. Beaudry, D. C. Henderson, and J. Moorman, J. Chem. Phys. **60**, 1578 (1974).

[26] W. G. Lyon, D. W. Osborne, H. E. Flotow, F. Grandjean, W. Hubbard, and G. K. Johnson, J. Chem. Phys. **69**, 167 (1978).

[27] W. M. Jordan and C. R. A. Catlow, Cryst. Lattice Defects Amorphous Mater. **15**, 81 (1987).

[28] P. E. Ngoepe, Ph.D. thesis, University of the Witwatersrand, Johannesburg, 1987 (unpublished).

[29] S. Hart, Phys. Status Solidi (a) **17**, K107 (1973).

[30] R. Laiho, M. Lakkisto, and T. Levola, Philos. Mag. A **47**, 235 (1983).

[31] J. A. Garber and A. V. Granato, Phys. Rev. B **11**, 3990 (1975).

[32] K. Clausen, W. Hayes, M. T. Hutchings, J. E. Macdonald, R. Osborn, and P. Schnabel, Rev. Phys. Appl. **19**, 719 (1984).