LETTERS TO THE EDITOR

X-RAY DETERMINATION OF THE THERMAL EXPANSION OF CERIUM TRIFLUORIDE

THE crystal structures of LaF_3 and its isotypes CeF_3, NdF_3 and PrF_3 have been the subject of apparently conflicting reports[1-6]. These rare earth trifluorides have the structure of a naturally occurring mineral tysonite, crystallizing in the space group P_3Cl of trigonal system[3].

The polymorphism, structure and the unit cell parameters of these compounds at room temperature have been recently reported by Sobolev *et al.*[7] and Spedding *et al.*[8] have published the high temperature enthalpies of a number of rare earth trifluorides. The only substance of this group, for which the data on thermal expansion are available, is LaF_3. Sher *et al.*[9] made detailed investigations of thermal expansion on LaF_3 as determined by X-ray method and also, using a dilatometer. They followed Anderson and Proctor[6] in reporting the value of the *c*-parameter in terms of the double hexagonal cell. Klein and Croft[10] also reported the expansion coefficients of LaF_3 from 111–299° K using X-ray method. The data on the lattice parameters reported by the latter authors are in agreement with those reported by Zalkin and Templeton[3]. A perusal of literature shows that there is no data available on the precision lattice parameters and coefficients of thermal expansion of CeF_3 and other crystals of this type at different temperatures. A programme has therefore been drawn in this laboratory to undertake a complete X-ray study of these crystals with a view to obtaining detailed information on the temperature variation of the lattice parameters, the cofficients of thermal expansion, the positions and thermal parameters of atoms in the unit cell and the Debye temperatures. The present note gives the results of the work done on the lattice thermal expansion of CeF_3 in the high temperature range.

The powder sample of CeF_3 used in this investigation was kindly supplied by Dr. L. H. Pierce of Florida State University. The X-ray powder photographs at eight different temperatures were taken employing a high temperature symmetrical back reflection focusing camera and CuK radiation. The details of the experimental techniques were described earlier by Suryanarayana[11]. Unambiguous reflections recorded in the Bragg angle region between 69° and 83° were used to evaluate the lattice parameters employing Cohen's[12] least squares method in combination with an error function $\varphi \tan \varphi$. Independent measurements and calculations were made on each film and the average values obtained therefrom are given in Table I.

TABLE I
Values of the lattice parameters of CeF_3 at different temperatures

Temp. in °C	*a* in Å	*c* in Å
31	7·1306	7·2805
74	7·1339	7·2879
115	7·1380	7·2911
171	7·1436	7·2971
212	7·1483	7·3034
267	7·1551	7·3084
310	7·1593	7·3115
340	7·1646	7·3162

The errors in the values of the parameters as calculated by the method of Jette and Foote[13] are ± 0.0005 Å and ± 0.001 Å in '*a*' and '*c*' respectively. The values of the two principal coefficients of expansion α_a and α_c at different temperatures were evaluated from the temperature/parameter plots by the method suggested by Deshpande and Mudholkar[14] and the following expressions were obtained for their temperature variations:

$$\alpha_a = 11 \cdot 77 \times 10^{-6} + 76 \cdot 12 \times 10^{-10} t + 54 \cdot 10 \times 10^{-12} t^2$$

$$\alpha_c = 13 \cdot 35 \times 10^{-6} + 85 \cdot 14 \times 10^{-10} t + 6 \cdot 87 \times 10^{-12} t^2$$

where t is the temperature in °C. The results are shown in Fig. 1.

The values of the two coefficients at 30° C are $\alpha_a = 12 \cdot 05 \times 10^{-6}/°$ C and $\alpha_c = 13 \cdot 61 \times 10^{-6}/°$ C. The mean coefficients of expansion over the range 30–350° C were found to be $\bar{\alpha}_a = 16 \cdot 55 \times 10^{-6}/°$ C and $\bar{\alpha}_c = 15 \cdot 39 \times 10^{-6}/°$ C. The results on the thermal expansion of CeF_3 at room temperature are compared in Table II with those obtained on LaF_3 by other investigators.

Though there are differences among the reported values of the coefficients of expansion of LaF_3, they agree in regard to the anisotropy, *i.e.*, $\alpha_a > \alpha_c$ at room temperature. The present results on CeF_3 show the opposite, that is, the value of α_c at room temperature is less than that in the perpendicular direction. However, our

results on CeF_3 agree with those of Sher *et al.* on LaF_3 in that, the rate of temperature variation of α_a is less than that along the basal plane. The present results also show that the values of the two principal coefficients of expansion are equal around 200° C, and above this temperature the value of α_a is greater than that of α_c. Since there is no crystallographic transition in CeF_3[8], the observed anisotropy in expansion might be only due to the interplay of different ionic interactions that are present in this crystal. However, a detailed discussion on the similarities and differences in the behaviour of the expansion characteristics of these substances *vis-a-vis* the structure would be incomplete till such data on other isotypic compounds PrF_3 and NdF_3 become available. This work has been undertaken by the authors.
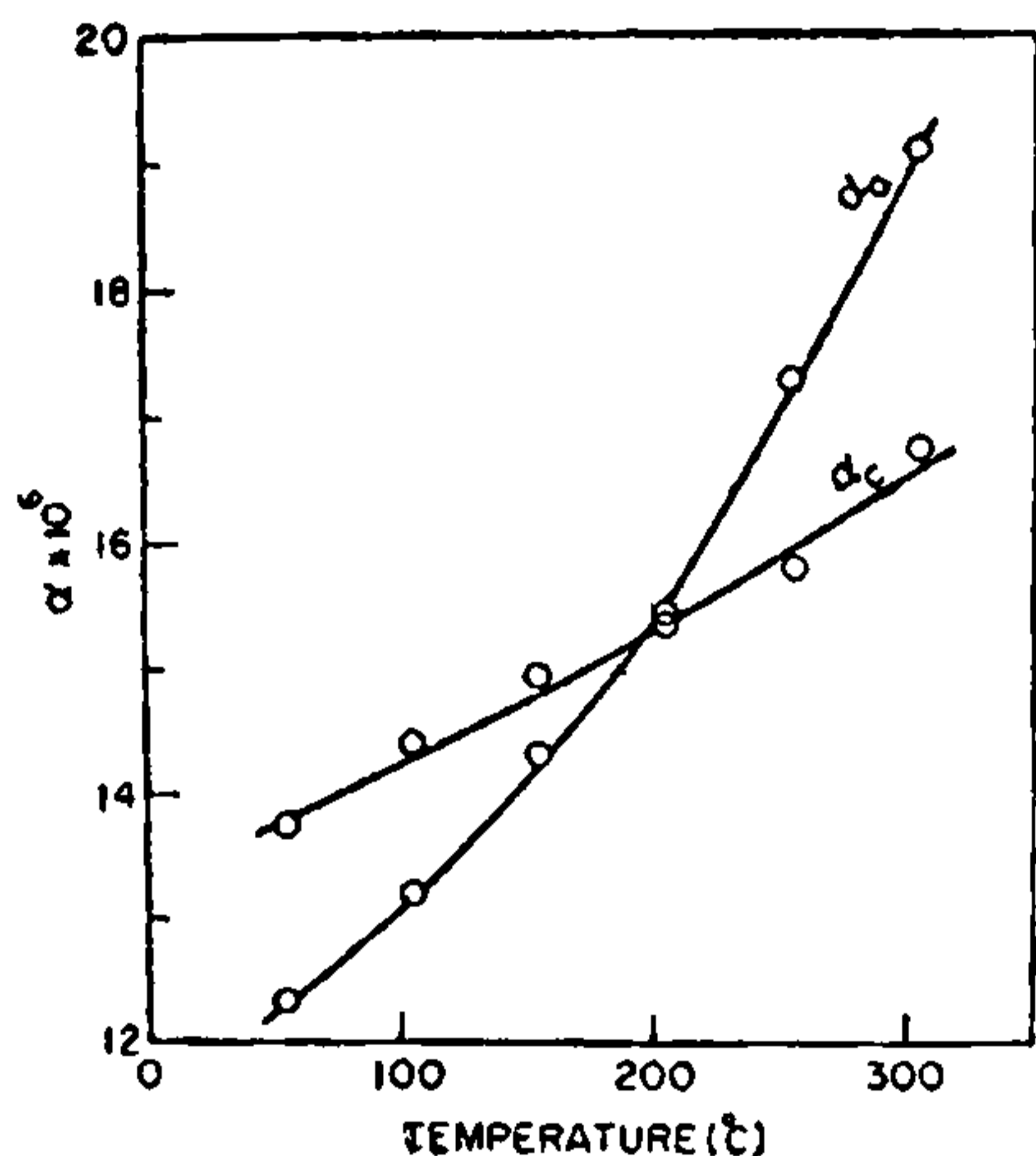

FIG. 1. Temperature variation of α_a and α_c of CeF_3.

TABLE II

Comparison of the values of the coefficients of thermal expansion of LaF_3 and CeF_3 at room temperature

Substance	$\alpha_a \times 10^6$	$\alpha_c \times 10^6$	Reference
LaF_3	15·8	11·0	Sher *et al.*[9]
	20·0	10·0	Klein and Croft[10]
CeF_3	12·1	13·6	Present study

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SMALL ANGLE GRAIN BOUNDARIES IN HEULANDITE CRYSTALS

THE study of the configuration of grain boundaries is important to get additional information about the growth of a crystal. Burgers[1], Bragg[2] and Vogel *et al.*[3] have shown that low angle tilt boundaries are formed by array of edge dislocations. Amelinckx[4] investigated the geometry of dislocation nets and grain boundaries for different crystallographic structures. In the case of small angle grain boundaries it can be shown that $n = n_b + n_c$, where n_a, n_b, n_c are the number of dislocations per microns in the three branches. Recently Loiacono *et al.*[5] have confirmed this in the case of synthetic lead molybdate crystals—Here we are reporting some of the results obtained from the study of grain boundaries in heulandite crystals. Heulandite belongs to Zeolite family of minerals and is a hydrous calcium aluminium silicate. The chemical formula of heulandite is $Ca(Al\ Si_7\ O_{18}).6\ H_2O$. Heulandite is monoclinic and has a very good cleavage along (010) plane. It is found in the mountain regions