

The Symmetry and Basic Structures of LaF_3 , CeF_3 , PrF_3 and NdF_3

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The difference in the screening constants for various fluorine positions has been used to determine the symmetry and basic structures of paramagnetic cerium, praseodymium and neodymium trifluorides. It is concluded that all three belong to the space group $P6_3/mcm$ with $Z=6$, and that CeF_3 has an ordered structure, whereas PrF_3 and NdF_3 are disordered.

Although the structure of the natural mineral thysenite $(\text{La,Ce,Pr,Nd})\text{F}_3$, characteristic of several trifluorides of the cerium group rare earth elements (LaF_3 , CeF_3 , PrF_3 and NdF_3) (Katz & Rabinowitch, 1951) has repeatedly been the subject of X-ray analysis (Ofstedal, 1929; Schlyter, 1953; Mansmann, 1964, 1965; Zalkin, Templeton & Hopkins, 1966; de Rango, Tsoucaris & Zelmer, 1966), it still remains to be elucidated. The difficulty in determining the details of the structure is primarily caused by the low scattering factor of fluorine (compared with lanthanum).

In the present work, the ^{19}F n.m.r. method has been used to determine the fluorine atom locations. To obtain a satisfactory resolution, we have examined the spectra of the paramagnetic analogues of thysenite, *viz.* CeF_3 , PrF_3 and NdF_3 . The samples studied were optically pure monocrystals cut in the form of spheres, of diameter 5–8 mm. Crystal orientation was effected with the aid of an X-ray goniometer. The spectra were recorded at about -100°C on a JNM-4H-100 spectrometer with a broad line attachment.

Spectral angular dependence, recorded when the crystals were rotating around their threefold C axes (perpendicular to the external magnetic field), was used for the analysis. Fig. 1 shows the angular dependences obtained for the position of the components in the ^{19}F n.m.r. spectra of CeF_3 , PrF_3 and NdF_3 , as well as the typical spectra.

Two different groups of lines may be identified in the CeF_3 spectrum. The first group includes three components of equal intensity, their positions being dependent on the rotation angle of the crystal about the c axis (angle φ). The overall intensity of these components (proportional to the absorption band areas) amounts to two-thirds of the intensity of the entire spectrum. The second group includes two lines, and their positions do not depend on φ . The intensity ratio of these two lines is 1:2.

The position of the n.m.r. signal in a spectrum is independent of the rotation angle of the crystal about a certain axis only when that axis is 3-, 4- or 6-fold, and the nucleus responsible for the signal is situated on the axis. Hence, the ^{19}F atoms whose n.m.r. signals are responsible for the appearance of the second group of lines with an intensity of one-third the total are

situated on the crystallographic 3-fold axes. The total number of these atoms is divisible by three, since as mentioned above the intensity relationship between the two components is 1:2. The remaining two-thirds of the fluorine atoms are in structurally equivalent locations (related by the structure symmetry elements), since the three curves of the angular dependences of the first group line positions are identical (the shift in φ being $\pm 60^\circ$).

An X-ray structural analysis (Ofstedal, 1929; Schlyter, 1953) has shown that the smallest elementary cell of the LaF_3 -type structure contains two formula units. The above-cited angular dependence analysis of the ^{19}F n.m.r. spectra indicates that the total number of fluorine nuclei in the elementary cell is divisible by 9 and, consequently, the smallest CeF_3 elementary cell cannot be bimolar. The Ofstedal (1929) analysis shows that the larger cell of the LaF_3 -structure type should contain no less than 6 formula units, and the latest X-ray structural determination results arrive at the same conclusions (Mansmann, 1964, 1965; Zalkin *et al.*, 1966; de Rango *et al.*, 1966). Thus, it follows from the experimental n.m.r. data that the CeF_3 elementary cell contains no more than 18 fluorine atoms of three structurally nonequivalent types, denoted herein as F(1), F(2) and F(3) respectively. In the crystal hexagonal lattice, two F(1) atoms occupy twofold positions; four F(2) atoms fourfold positions; and twelve F(3) atoms twelvefold positions. Cerium atoms are, presumably, situated at the sixfold special positions of the hexagonal elementary cell.

It is apparent from the symmetry of the CeF_3 spectra angular dependence and the 12-fold positions of the F(3) atoms that the F(3) atom positions are linked (apart from the threefold axes) by two vertical mutually perpendicular symmetry planes. One of these planes passing through a threefold axis contains the F(3) atoms, since, as noted above, these atoms give similar angular dependence curves shifted in respect to one another by $\pm 60^\circ$.

It follows from the 12-fold locations of the F(3) atoms that apart from the two vertical symmetry planes, one more horizontal plane perpendicular to the threefold axis should be present. Thus, the CeF_3 -structure symmetry may be assigned to a dihexagonal-dipyramidal

type of symmetry, the possible space groups being $P6/mmm$, $P6/mcc$, $P6_3/mmc$ and $P6_3/mcm$.

Proceeding from the symmetry of the n.m.r. spectra angular dependence, in our case it is hard to distinguish a mirror from a glide plane. Therefore, the final choice of the space group was made on the basis of detailed calculations. We have calculated the local field magnitudes for the various structure models and compared the resultant angular dependences of the n.m.r. spectra with the experimental. We find that of the four possible space groups only $P6_3/mcm$ corresponds to the CeF_3 structure. Moreover, the F(1) atoms are situated in twofold positions (*a*), F(2) atoms in fourfold positions (*c*), Ce atoms in sixfold positions (*g*) and F(3) atoms in 12-fold positions (*k*).

The above conclusion does not agree with the X-ray structural determinations of the symmetry of LaF_3 (Mansmann, 1964, 1965; Zalkin *et al.*, 1966; de Rango *et al.*, 1966). Inasmuch as the determination of the symmetry of CeF_3 on the basis of n.m.r. spectra was not hampered by any side effects, preference should apparently be given to the latter.

Calculations of the local field by the trial and error method for F(3) served to obtain the approximate coordinates $x=0.29$; $y=0.0$; and $z=0.56$. From the ^{19}F n.m.r. spectra recorded at $H_0 \parallel C_3$ (Fig. 2), one may directly determine the distance between the F(3) atoms. The spectrum line belonging to F(3) is a doublet. Using the Pake (1948) formula $\Delta H = 6 \mu_{\text{F}} r^{-3}$, we have calculated the maximum distance $r[\text{F}(3)-\text{F}(3)]$ from the doublet splitting ΔH . Found for LaF_3 : $-r = 2.52 \text{ \AA}$, for CeF_3 -2.60 \AA , and for PrF_3 -2.71 \AA .

The angular dependences of the ^{19}F n.m.r. spectra for PrF_3 and NdF_3 are on the whole similar to that for CeF_3 , and differ in that each of the three curves with an overall intensity of two-thirds for CeF_3 is split into two in the case of PrF_3 and NdF_3 (Fig. 1). The nature of the spectra symmetry (found for CeF_3) is, on the other hand, fully preserved: there is a threefold axis and three mutually perpendicular planes; all F(3) atoms are in structurally equivalent positions. F(1) and F(2) atoms are located on *c* axes; but F(3) atoms no longer remain in the symmetry planes passing through the threefold axes, and this leads to a splitting of the curve for F(3). F(3) atoms lie out of the symmetry planes so that the F-M bond forms an angle of $\pm 5^\circ$ with the plane in PrF_3 , and $\pm 10^\circ$ in NdF_3 .

Inasmuch as all three structures are basically similar, and all the symmetry elements found in CeF_3 are present in PrF_3 and NdF_3 , it may be concluded that the latter two also belong to space group $P6_3/mcm$, the elementary cell contents being 6 formula units. Since the twelve atoms of F(3) are situated in locations of type (1), which are 24-fold, one may assume from the results obtained that there is a statistical distribution of 12 atoms along the 24 positions. Fig. 3 shows a projection on the *ab* plane of a six-molar cell corresponding to the n.m.r. data.

The conclusion concerning the statistical distribution of fluorine atoms among positions whose number is twice that of the atoms is corroborated by other evidence. Despite the high fusion point of the crystals (1000°C), a high mobility of fluorine atoms, unusual for ionic crystals, is observed in the n.m.r. spectra at 0°C .

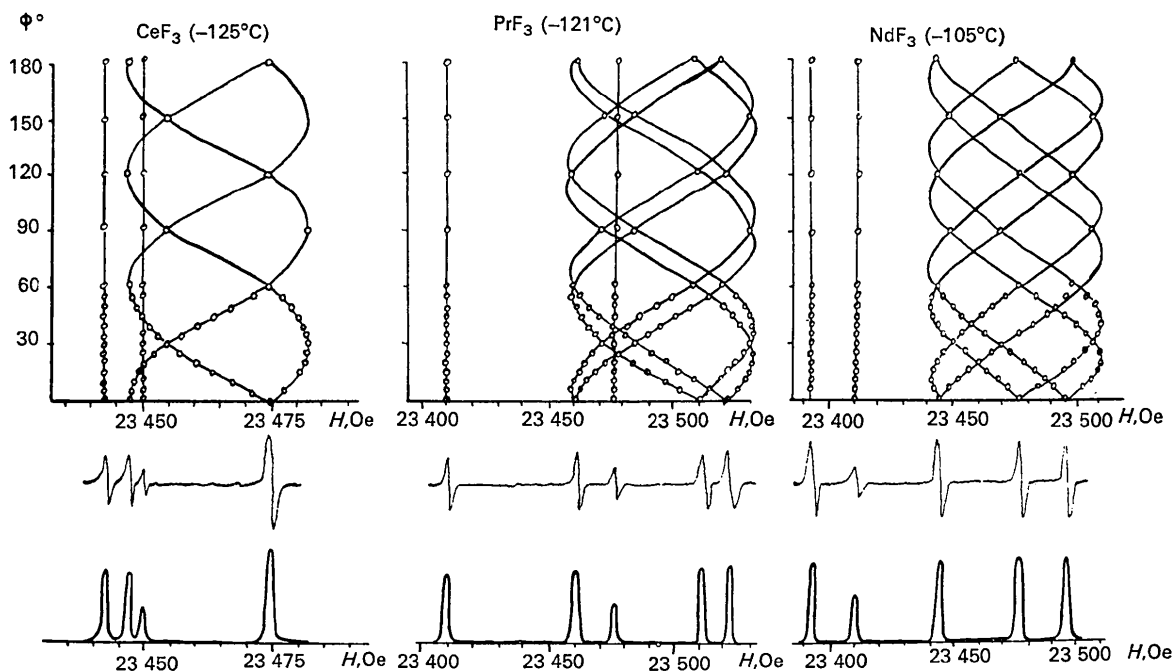


Fig. 1. Angular dependences of the positions of the components in ^{19}F n.m.r. spectra of CeF_3 , PrF_3 and NdF_3 . ϕ angle readings start from z -axis direction. Cited below are the spectra recorded at $\phi = 0^\circ$.

Statistical distribution of atoms in the structures of La, Ce, Pr and Nd trifluorides makes harder still the interpretation of their structures and is, apparently, one of the reasons for the conflicting X-ray results.

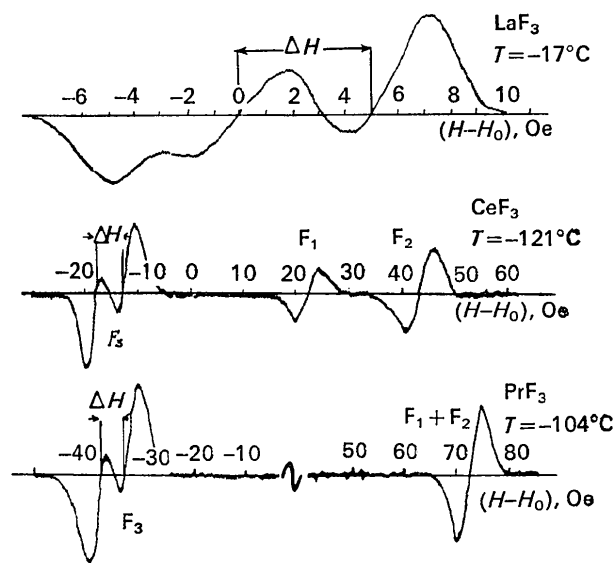


Fig. 2. ^{19}F n.m.r. spectra for LaF_3 , CeF_3 and PrF_3 recorded at $H_0 \parallel C$.

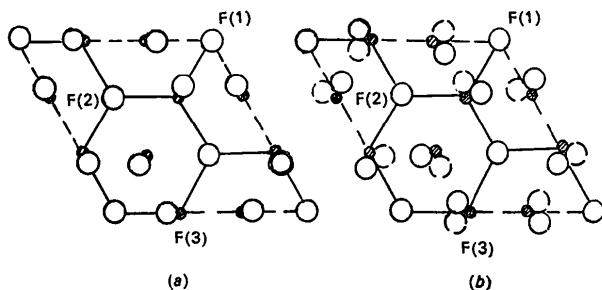


Fig. 3. Projection on the ab plane of a 6-molar cell corresponding to the n.m.r. data: (a) for CeF_3 and (b) for PrF_3 and NdF_3 .

This conclusion explains, for example, the result obtained by Andersson & Proctor (1968) showing the main tensor axis of the electric field gradient (EFG) on the nucleus of ^{131}La to be directed at a certain angle to the plane (001). This led him to the correct conclusion concerning the absence of a horizontal symmetry plane at the positions of the lanthanum nuclei. However, this inference was assigned to the LaF_3 structure as a whole, thereby contradicting the above-cited ^{19}F n.m.r. results.

With a statistical distribution of fluorine atoms among all possible positions, the symmetry of each specific lanthanum position does not have a horizontal symmetry plane; the latter exists only in the statistical sense. Unfortunately, Anderson & Proctor (1966) did not examine the temperature dependence of the EFG tensor axis orientation. At high temperatures ($\sim 300^\circ\text{C}$), when the diffusion rate of the fluorine atoms along the statistically vacant positions becomes sufficiently great, an average EFG possessing a horizontal symmetry plane would act on the ^{131}La nuclei. This conclusion is favoured by the drastic change observed in the asymmetry parameter of the EFG tensor on the lanthanum nuclei above room temperature (Lee, Sher, Anderson & Proctor, 1966).

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