

## Diffusion and Clustering in the $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$ Solid Solution: A Fluorine NMR Study

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An investigation has been carried out by  $^{19}\text{F}$  NMR on the  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  solid solution which is a fast fluoride ion conductor. The results are interpreted on hand of the existence of different fluoride sublattices and exchanges between them at rising temperature. The diffusive character of the mobile  $\text{F}^-$  ions motion is shown above  $T \approx 350$  K. The NMR study has allowed to justify the hypothesis of the formation of clusters of 2:2:2 type in  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$ . Improvement with increasing  $x$  of the electrical conductivity above  $x \approx 0.05$  may result mainly from the higher number of 2:2:2 clusters and consequently from that of the mobile anions. © 1991 Academic Press, Inc.

### I. Introduction

The ideal  $\text{CaF}_2$ -type structure can be described as a cubic packing of  $\text{F}^-$  anions, the  $\text{Ca}^{2+}$  ions occupying alternatively half of the cubic sites. For the very low substitution rates of divalent by trivalent cations ( $x \leq 0.01$ ) the  $\text{M}_{1-x}\text{M}'_x\text{F}_{2+x}$  solid solutions with fluorite-type structure are characterized by the introduction of charge-compensating anions into interstitial sites. The point-defect pairs so created are called either *nn* or *nnn*. The *nn* and *nnn* pairs are respectively of tetragonal ( $C_{4v}$ ) and trigonal ( $C_{3v}$ ) symmetry. Preferential formation either of *nn* or of *nnn* pairs has been related to the size difference between the host and guest cations (1-6).

For higher substitution rates ( $x \geq 0.01$ ) more extended defects, i.e., clusters, are formed. They result from an association among one or several doping cations, vacancies in normal sites, and interstitial an-

ions. Such a clusterization is characterized by a transfer of fluoride ions from normal sites into interstitial ones with the creation of supplementary vacancies in the normal anionic sublattice (2). It results in an enhancement of the electrical performance as a consequence of increasing anionic disorder (6).

Different optimization criteria of the electrical behavior of the  $\text{M}_{1-x}\text{M}'_x\text{F}_{2+\alpha}$  ( $\alpha = 1, 2, 3$ ) solid solutions have been proposed (7, 8): vacancies in the normal anionic sublattice, high polarizability of the cations, significant size difference between the involved cations, etc. The transport properties depend also on the appearance of a short-range order as the substitution rate increases in anion-excess solid solutions. Hence the establishment of straight correlations between the cluster extension with substitution rate and the composition dependence of electrical properties is of a large interest. Recently a model has been

proposed relating in a continuous manner the composition dependence of the electrical properties and the progressive extension of the clusters as  $x$  increases in the  $M_{1-x}^{2+}M_x'^{2+\alpha}F_{2+\alpha x}$  solid solutions (9).

This model, applied to different solid solutions (10, 11), has allowed us to determine the nature of the clusters set up in such materials; so, the existence of single-file monodimensional clusters  $n + 1 : 2n : 1$ , the length of which grows when  $x$  increases, has been proposed for  $Pb_{1-x}Bi_xF_{2+x}$ ; these clusters are based on the association of  $(n + 1)$  vacancies in the normal positions of the fluorite structure,  $2n F'(\frac{1}{2}, u, u)$  and  $1 F''(v, v, v)$  interstitial anions (12). The validity of this short-range model is confirmed by the comparison of the numbers of interstitial anions of  $F'$  and  $F''$  type and the number of vacancies calculated from the model to those experimentally determined by neutron diffraction.

A large number of anion excess fluorite-related solid solutions,  $M_{1-x}^{2+}M_x'^{2+\alpha}F_{2+\alpha x}$ , where  $M$  is Ca, Sr, Ba, or Pb and where  $M'$  represents a trivalent or tetravalent substitute, have been investigated and various defect structures have been proposed (10–15). In contrast, the solid solutions based on the  $CdF_2$  matrix have been much less considered; the study of point defects and the determination of short-range order in these materials have been based essentially on theoretical calculations (5) and optical spectroscopy investigations (16–18).

New ionic conductors involving a high mobility of the  $F^-$  ion have been recently prepared with the  $CdF_2$  matrix, e.g.,  $Cd_{1-x}M'_xF_{2+x}$ , where  $M'$  is a trivalent substitute ( $M' = In, La, Ce, Nd, Gd, Er, Bi$ ) (19). The  $Cd_{1-x}Bi_xF_{2+x}$  solid solution that involves two cations of high polarizability has the best electrical performance. Clusterization processes based on the composition dependence of transport properties have been proposed;  $Cd_{1-x}Bi_xF_{2+x}$  could adopt a cluster of 2 : 2 : 2 type, analogous to

that previously shown in  $Ba_{1-x}La_xF_{2+x}$  (15).

As neutron diffraction cannot be used for cadmium compounds as they absorb neutrons, an investigation of  $Cd_{1-x}Bi_xF_{2+x}$  by  $^{19}F$  NMR has been achieved. Valuable information relative to the existence of different possible sites for fluoride ions and to thermal variation of their mobility was expected: It aimed at checking the proposed cluster model for the concerned solid solution.

## II. Experimental

### A. Preparation of Samples

The samples of the  $Cd_{1-x}Bi_xF_{2+x}$  ( $0 \leq x \leq 0.35$ ) solid solution have been obtained by synthesis of binary fluorides.  $CdF_2$  is a (Vertron) ultrapure product;  $BiF_3$  is prepared by treating  $Bi_2O_3$  by a 40% HF solution in a Pt crucible; after evaporation in a sand bath, the obtained product is heated at 400°C under an HF gas stream to eliminate eventual traces of water.

Appropriate mixtures of  $CdF_2$  and  $BiF_3$  are heated at 600°C in sealed gold tubes, then quenched from that temperature. An XRD analysis shows the existence of a disordered phase with fluorite-type structure, the characteristics of which are in agreement with those previously determined (20).

### B. Solid State NMR

NMR experiments were performed on a Bruker MSL-200 spectrometer ( $B_0 = 4.7$  T) equipped with a standard variable temperature unit in the temperature range  $-150$  to  $+150^\circ C$ . The single pulse sequence ( $p_x - \tau -$  acquisition) was used. Due to strong dipole-dipole coupling and to substantial chemical shift of the  $^{19}F$  nuclei in our samples the width of the  $^{19}F$  resonance is as large as 40 kHz. This requires the use of very short pulses to obtain a sufficiently

wide flat central portion of the excitation power spectrum. Consequently a  $90^\circ$  pulse width of as short as  $0.7 \mu\text{s}$  was used. The other spectrometer operating conditions were:

- Spectrometer frequency: 188.283 MHz
- Pulse program: Onepulse
  - $90^\circ$  pulse width:  $0.7 \mu\text{s}$
  - Dead time delay (ringdown delay):  $6 \mu\text{s}$
  - Recycle delay time: 15 s
- Spectral width: 1 MHz
- Filter width: 2 MHz

The linewidths characteristic of our samples are very large: 60 kHz. On the other hand, the localization of the  $\text{F}^-$  ions in sites of different nature (normal and interstitial sites) involves RMN parameters (i.e., the  $\pi/2$  pulse length) specific to each type of anion. Consequently, high resolution spec-

tra cannot be obtained by the classical techniques of multiple pulse sequences connected with MAS (spinning speed limited to 7 kHz for the spectrometer used).

### III. Electrical Properties of $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$ (Recalls)

The study of the electrical properties of the  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  solid solution has shown that the temperature dependence of conductivity is in agreement with an Arrhenius type law.

Figures 1a, 1b give the isotherm  $\sigma_{423\text{K}}$  and the variation of the activation energy  $\Delta E_\sigma$  as a function of  $x$  (19):

- A first domain corresponds to low substitution rates ( $0 \leq x \leq 0.01$ );  $\sigma$  drops quickly and  $\Delta E_\sigma$  increases simultaneously.
- A second domain ( $0.01 \leq x \leq 0.05$ ) is

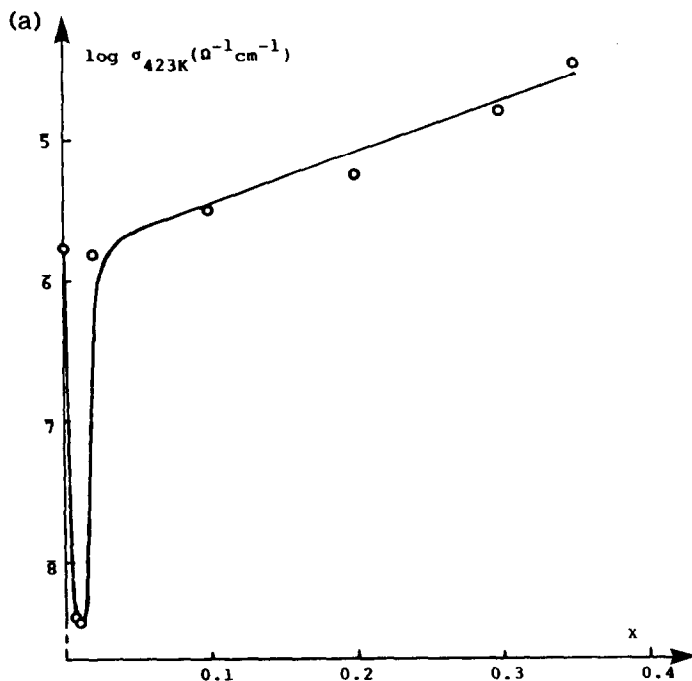
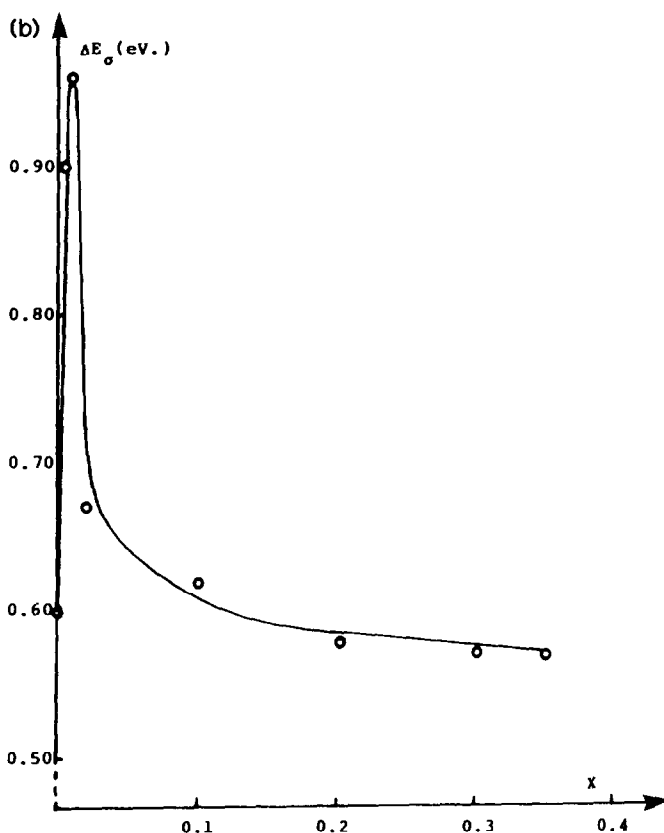


FIG. 1. (a) Composition dependence of  $\log \sigma_{423\text{K}}$  for the  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  solid solution. (b) Composition dependence of  $\Delta E_\sigma$  for the  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  solid solution.



characterized, on the contrary, by a large increase of  $\sigma$  associated with a strong decrease of  $\Delta E_{\sigma}$ .

—Beyond  $x \approx 0.05$ ,  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  shows increasing  $\log \sigma$  and decreasing  $\Delta E_{\sigma}$ , with variations which are quasilinear. The very particular variation of electrical properties for  $x \geq 0.05$  was induced us, by analogy with  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  (15), to propose the existence of 2:2:2 clusters in  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  and to correlate thus short range order and transport properties (19).

#### IV. Results and Discussion

##### A. Limited Substitution Rates

Two formulations corresponding to the values  $x = 0.03$  and  $x = 0.05$  have been studied.

*a.  $\text{Cd}_{0.97}\text{Bi}_{0.03}\text{F}_{2.03}$  composition.* The  $^{19}\text{F}$  NMR spectrum at various temperatures is given in Fig. 2 for  $\text{Cd}_{0.97}\text{Bi}_{0.03}\text{F}_{2.03}$ . A large peak, called  $p_1$ , the thermal variation of which is very weak in the temperature range considered (143–393 K) is shown. The relative variation of the second moment ( $M_2$ ) of the spectra recorded at 143 and 393 K is only  $\approx 1\%$  and no characteristic chemical shift of the interstitial positions can be detected.

Above  $T \approx 360$  K, a new peak, called  $p_m$ , appears in the middle of the spectrum. It grows slightly with increasing temperature.

The  $p_1$  peak corresponds obviously to fluoride ions located in the normal positions of the fluorite-type structure. As its thermal variation is very small, these fluoride ions can be considered as fixed in  $\text{Cd}_{0.97}$

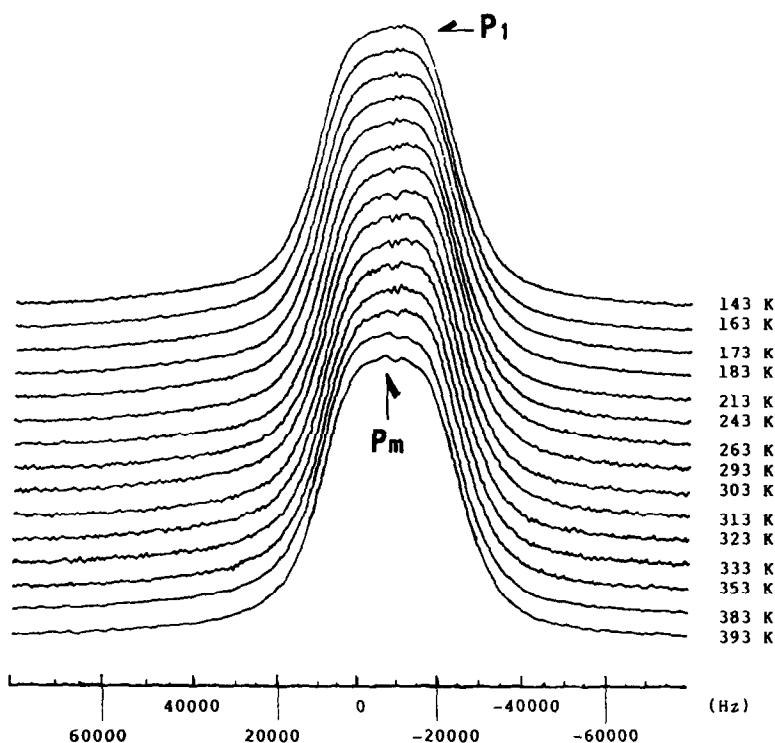


Fig. 2. Thermal variation of the  $^{19}\text{F}$  NMR spectrum for the  $\text{Cd}_{0.97}\text{Bi}_{0.03}\text{F}_{2.03}$  composition.

$\text{Bi}_{0.03}\text{F}_{2.03}$ , at least up to 393 K. The peak  $p_m$  on the contrary, represents fluoride ions mobile above  $T \approx 360$  K.

It seems that the  $p_m$  and  $p_1$  peaks correspond to  $\text{F}^-$  ions with the same chemical shift. Hence, the  $\text{F}^-$  ions belonging to  $p_m$  could represent the locally nonassociated interstitial ions located in the centers of the elementary cubes of the structure; it has been shown by optical spectroscopy investigation that, in  $\text{CdF}_2:\text{Eu}^{3+}$ , for very small  $\text{Eu}^{2+}$  concentrations, the number of tetragonal centers responsible for  $nn$  pairs is far less important than the number of cubic centers (16, 17).

*b.  $\text{Cd}_{0.95}\text{Bi}_{0.05}\text{F}_{2.05}$  composition.* The  $^{19}\text{F}$  NMR spectrum is given for various temperatures in Fig. 3 for  $\text{Cd}_{0.95}\text{Bi}_{0.05}\text{F}_{2.05}$ . Below 323 K, the thermal variation of the  $p_1$  peak

is analogous to that previously observed for  $\text{Cd}_{0.97}\text{Bi}_{0.03}\text{F}_{2.03}$ , but above 323 K, a motional narrowing of the line appears, the linewidth at half-height ( $\Delta\nu_{1/2}$ ) decreasing linearly with increasing temperature. Nevertheless, it may be mentioned that the variation of  $\Delta\nu_{1/2}$  represents only approximately 3% of the rigid lattice value between 333 and 413 K.

As for  $\text{Cd}_{0.97}\text{Bi}_{0.03}\text{F}_{2.03}$ , a  $p_m$  peak is observed in the middle of the spectra of  $\text{Cd}_{0.95}\text{Bi}_{0.05}\text{F}_{2.05}$  and increases with increasing temperature. It appears for  $x = 0.05$  at lower temperature than for  $x = 0.03$ .

The larger contribution of  $p_m$  for the  $x = 0.05$  composition and the appearance of this peak at temperatures lower than in the  $x = 0.03$  sample involve a higher mobility of the  $\text{F}^-$  ions in  $\text{Cd}_{0.05}\text{Bi}_{0.05}\text{F}_{2.05}$ , in agreement

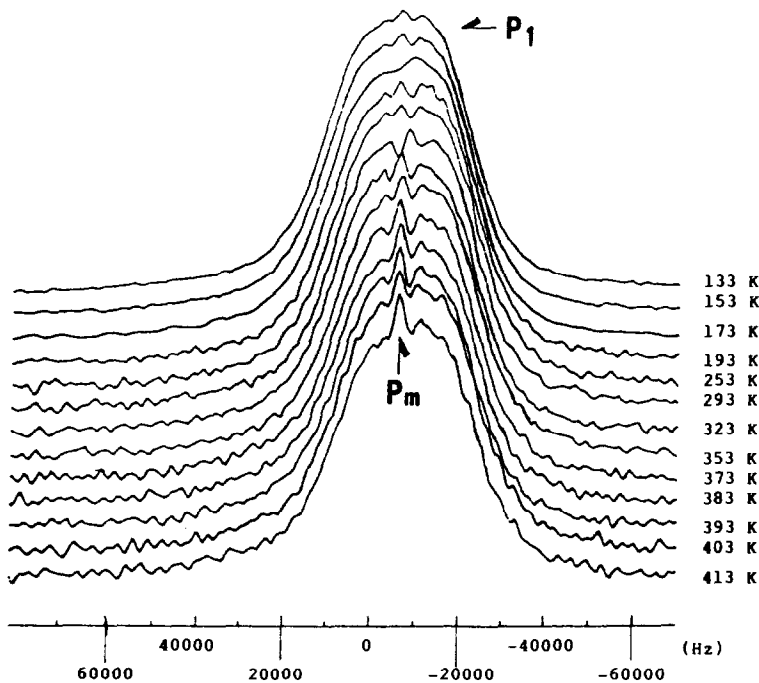


FIG. 3. Thermal variation of the  $^{19}\text{F}$  NMR spectrum for the  $\text{Cd}_{0.95}\text{Bi}_{0.05}\text{F}_{2.05}$  composition.

with the electrical measurements (Fig. 1).

For the sake of comparison, the  $^{19}\text{F}$  spectrum of pure  $\text{CdF}_2$  is given in Fig. 4 for several temperatures. The thermal variation of the  $p_1$  peak is quicker in pure  $\text{CdF}_2$  than for the  $x = 0.03$  and  $x = 0.05$  samples. On the other hand, the  $p_m$  peak appears clearly and its relative area ( $\approx 13\%$  at 400 K) is stronger for pure  $\text{CdF}_2$  than for  $x = 0.03$  and  $x = 0.05$ . The variation of  $p_m$  with  $x$  is in agreement with the composition dependence of the conductivity (Fig. 1) that shows a minimum of  $\sigma_{423\text{ K}}$  for  $x \approx 0.01$ . The minimum of  $\sigma$  appears thus for a composition which should correspond to a maximum value of the number of interstitial fluoride ions trapped by the  $\text{Bi}^{3+}$  cations as isolated  $nn$  pairs, two equilibrium reactions being then in competition:

—at  $x < 0.01$ , nonassociated pair  $\rightleftharpoons$  associated  $nn$  pair

—at  $x > 0.01$ ,  $2[\text{associated } nn \text{ pair}] \rightleftharpoons 2:2:2 \text{ cluster}$ .

### B. Substitution Rates Higher than 0.05

Three samples have been selected, corresponding to  $x = 0.10$ , 0.20, and 0.30.

*a.  $\text{Cd}_{0.90}\text{Bi}_{0.10}\text{F}_{2.10}$  composition.* Thermal variation of the  $^{19}\text{F}$  spectrum in  $\text{Cd}_{0.90}\text{Bi}_{0.10}\text{F}_{2.10}$  is given in Fig. 5a. In addition of the  $p_1$  and  $p_m$  peaks, a new peak, called  $p_2$ , appears at low temperature and, in contrast to  $p_1$ , must be attributed to anions located outside the normal positions of the fluorite-type lattice.

When the temperature increases, the relative intensity of the  $p_2$  peak decreases on behalf of  $p_m$ . This result is clearly shown by deconvolution of the spectra recorded at different temperatures (Fig. 5b): between 293 and 413 K,  $p_1$  ( $\approx 80\%$ ) is temperature independent, and  $p_2$  represents about 15%

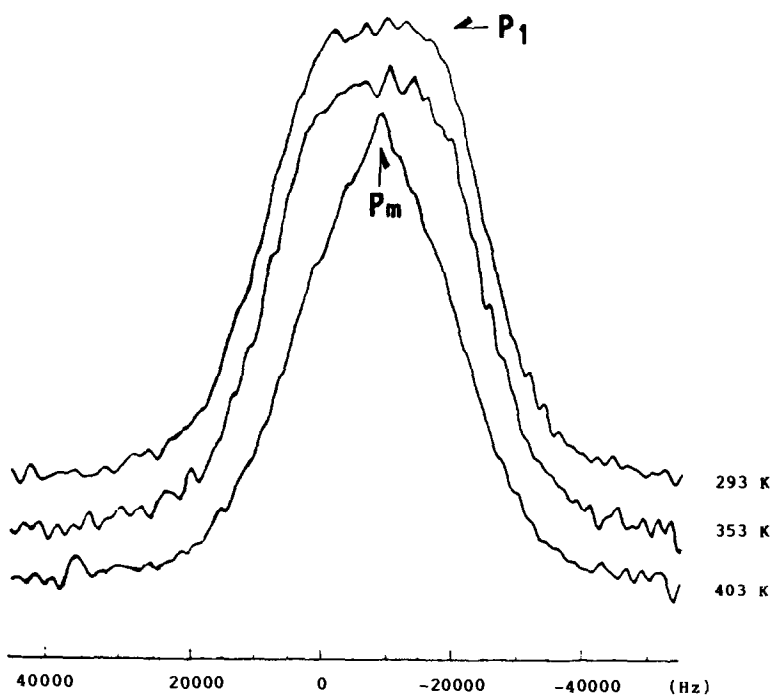


FIG. 4. Thermal variation of the  $^{19}\text{F}$  NMR spectrum for pure  $\text{CdF}_2$ .

of fluoride ions at 293 K and only 10% at 413 K.

*b.  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$  composition.* The  $^{19}\text{F}$  spectrum at various temperatures is given in Fig. 6a for  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$ . Three peaks are clearly identified: the  $p_1$  and  $p_2$  peaks analogous to those observed for  $\text{Cd}_{0.90}\text{Bi}_{0.10}\text{F}_{2.10}$  and a new peak, called  $p_3$ , located between the  $p_1$  and the  $p_2$  peaks. The relative intensity of  $p_3$  is too large to detect the eventual existence of a  $p_m$  peak. Nevertheless, the thermal variation of  $p_m$  for the ( $x = 0.10$ ) composition and  $p_3$  in the ( $x = 0.20$ ) composition are similar. One may assume that both peaks represent fluoride ions mobile above a certain temperature ( $\approx 290$  K).

Thermal variation of the three peaks observed,  $p_1$ ,  $p_2$ , and  $p_3$ , and the determination of their relative contribution by deconvolution of the whole spectrum as a

function of temperature shows the following results (Figs. 6a, 6b, and 6c):

—Below  $T \approx 270$  K, the contributions of  $p_1$ ,  $p_2$ , and  $p_3$  are independent of the temperature, which means that all fluoride ions are fixed in the NMR time scale below  $T \approx 270$  K.

—In the temperature range  $290 \leq T \leq 340$  K,  $p_2$  and  $p_3$  coalesce progressively at increasing temperature (Fig. 6a). This phenomenon results in an increase of  $p_3$  and simultaneously a decrease of  $p_2$  (Fig. 6c).

—Above  $T \approx 360$  K,  $p_1$  coalesces in turn with  $p_3$  when the temperature increases (Fig. 6a). Consequently, the rate of the mobile fluorine ions,  $p_3$ , increases quickly while  $p_1$  and  $p_2$  decrease.

Figures 6b and 6c give the deconvolution of the  $^{19}\text{F}$  spectrum of  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$  at 128

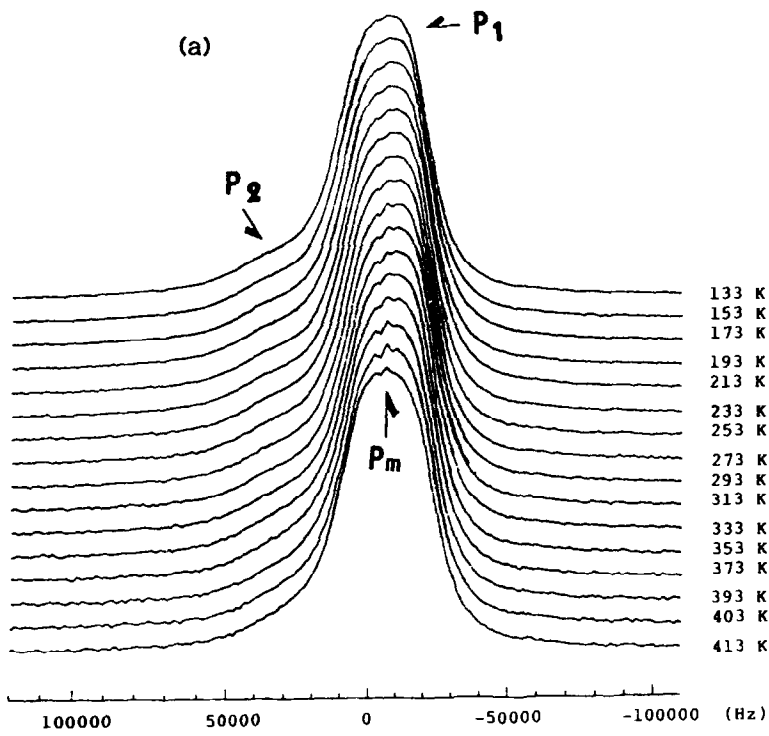


FIG. 5a. Thermal variation of the  $^{19}\text{F}$  NMR spectrum for the  $\text{Cd}_{0.90}\text{Bi}_{0.10}\text{F}_{2.10}$  composition.

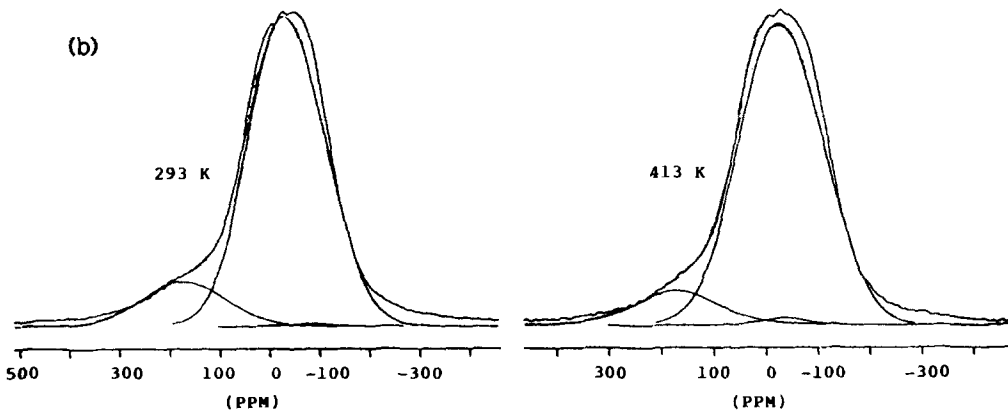


FIG. 5b. Deconvolution of the  $^{19}\text{F}$  NMR spectrum at 293 and 413 K for the  $\text{Cd}_{0.90}\text{Bi}_{0.10}\text{F}_{2.10}$  composition.



K and the temperature dependence of the fluoride ion rates considered as proportional to the areas of peaks  $p_1$ ,  $p_2$ , and  $p_3$ .

*c.  $\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$  composition.* Three peaks,  $p_1$ ,  $p_2$ , and  $p_3$ , can be so identified in the  $^{19}\text{F}$  spectrum of  $\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$  (Fig. 7a) and the thermal variation of this spectrum is very close to that observed for  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$ . Some differences can be detected:

—Whatever the temperature, the relative area of  $p_3$  is larger for  $\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$  than for  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$ ; in contrast, that of  $p_1$  is smaller for the ( $x = 0.30$ ) sample.

—The temperatures at which  $p_2$  and  $p_3$ , and then  $p_1$  and  $p_3$ , coalesce are lower for  $x = 0.30$ .

The temperature dependence of the fluoride ion rates supposed to be proportional to the  $p_1$ ,  $p_2$ , and  $p_3$  peak areas is given in Fig. 7b.

The  $^{19}\text{F}$  NMR study of the samples relative to high values of  $x$  has allowed us to show two exchange mechanisms between fluoride sublattices in the  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  solid solution:

—A first exchange, called  $\text{F}_3\text{—F}_2$ , between the fluoride ions corresponding to the  $p_3$  and  $p_2$  peaks occurs at a temperature that lowers as  $x$  is raised.

—A second exchange, called  $\text{F}_3\text{—F}_1$ , between anions belonging to the  $p_3$  and  $p_1$  peaks, starts, for a given  $x$  value, at a temperature which is higher than that of the  $\text{F}_3\text{—F}_2$  exchange.

An investigation by  $^{19}\text{F}$  NMR of the disordered fluorite related solid solution  $\text{Pb}_{1-x}\text{In}_x\text{F}_{2+x}$  ( $0 \leq x \leq 0.25$ ) and of the ordered phase  $\text{Pb}_2\text{InF}_7$  ( $x = 0.33$ ) had already allowed us to prove in these materials the existence of two types of motions (21):

—the local motions, weakly activated and affecting only the interstitial fluoride anions ( $\text{F}_i$ );

—the long range motions, more activated, concerning anions belonging to both sublattices  $\text{F}_N$  (fluoride ions located in normal positions of the fluorite-type lattice) and  $\text{F}_i$ , involving an exchange between these sublattices.

This investigation allowed us on the other hand to determine, for various compositions of  $\text{Pb}_{1-x}\text{In}_x\text{F}_{2+x}$  and for  $\text{Pb}_2\text{InF}_7$ , the thermal variation of the fraction ( $f_m$ ) of mobile fluoride ions and to show that the ions mobile at low temperature are the  $\text{F}_i$  anions located in the interstitial sites. The variation of  $f_m$  for the ordered phase  $\text{Pb}_2\text{InF}_7$  is quite significant (Fig. 8): it is composed of two quasilinear parts, separated by a wide quasihorizontal plateau and the fraction  $f_i$  of interstitial anions can be identified with the value of  $f_m$  at the temperature of the first slope change, in agreement with the structural properties of  $\text{Pb}_2\text{InF}_7$  (22).

The curve representative of the thermal variation of the percentage  $p_3$  of mobile ions in  $\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$  (Fig. 7b) can be divided thus into three parts, two quasilinear parts separated by a small horizontal plateau between 330 and 350 K. Consequently, below 330 K,  $p_3$  represents only interstitial fluoride ions and the fraction  $f_i(x = 0.30)$  calculated at 330 K is equal to  $\sim 0.57$  ( $2.30 \times 25\% = 0.575$ ).

The thermal variation of  $p_3$  in  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$  can also be divided into three parts. The plateau shown between 340 and 360 K is slightly shifted toward high temperatures and the fraction  $f_i$  calculated at 340 K is lower for the  $x = 0.20$  composition than for  $x = 0.30$ :  $f_i(x = 0.20) \approx 0.44$  ( $2.20 \times 20\% = 0.44$ ).

Unlike  $p_3$ , the  $p_1$  and  $p_2$  peaks represent fluoride ions that are not mobile under our experimental conditions;  $p_1$  and  $p_2$  can be identified respectively as fluoride ions located in the normal positions of the fluorite structure and as fluoride ions slightly relaxed from those normal positions:

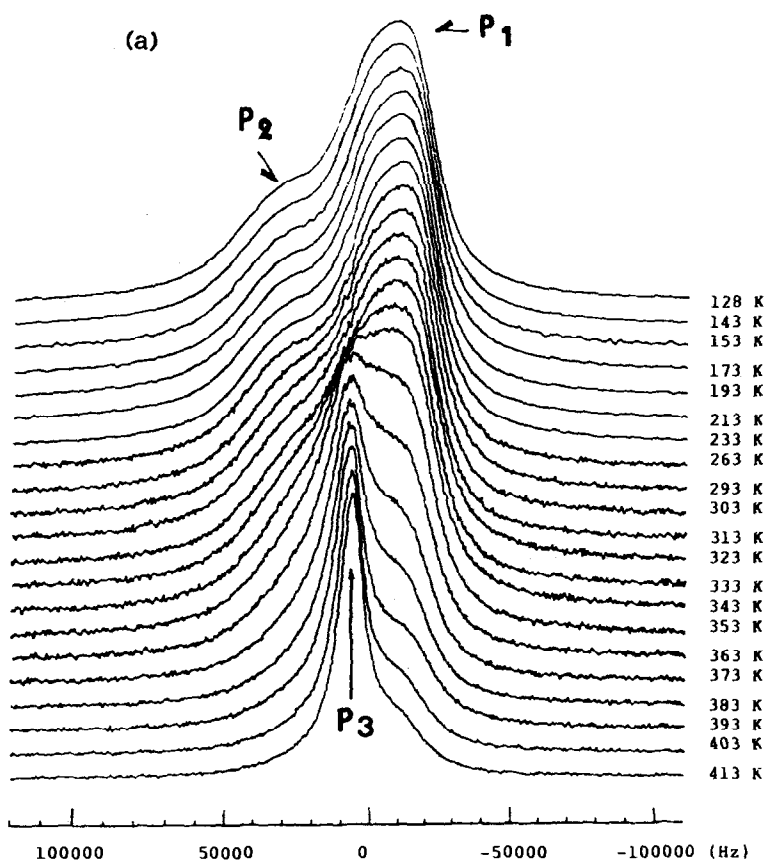


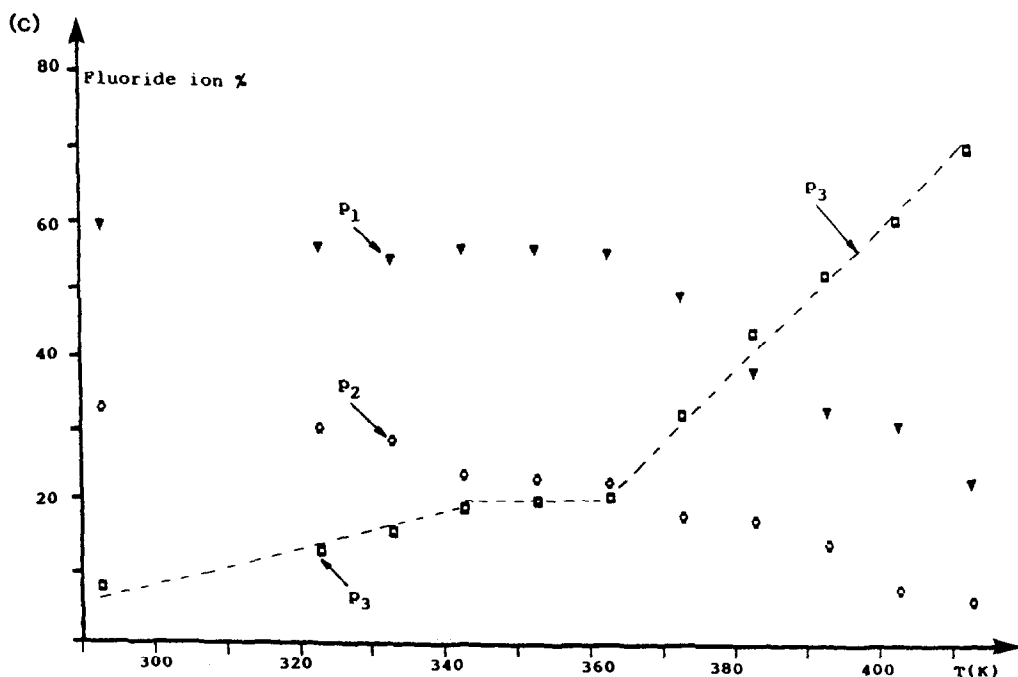
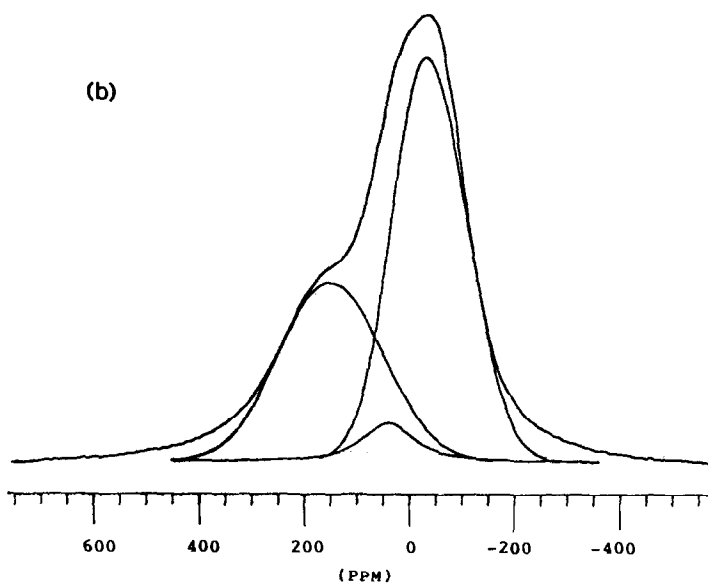
FIG. 6. (a) Thermal variation of the  $^{19}\text{F}$  NMR spectrum for the  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$  composition. (b) Deconvolution of the  $^{19}\text{F}$  NMR spectrum at 128 K for the  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$  composition. (c) Temperature dependence of fluoride ion rates proportional to areas of peaks  $p_1$ ,  $p_2$ , and  $p_3$  for  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$ .

—The  $p_2$  peak appears only for the high substitution rates ( $x \geq 0.10$ ), in other words when the numbers of substitutional cations and charge-compensating fluoride ions are high enough to involve a slight distortion of the fluorite-type cell. That hypothesis could be justified by the composition dependence of the unit cell volume of  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  (19): though the size of the  $\text{Bi}^{3+}$  cation is slightly larger than that of the  $\text{La}^{3+}$  ion, the dilatation of the elementary cell is weaker for  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  than for  $\text{Cd}_{1-x}\text{La}_x\text{F}_{2+x}$  and is very close to that observed for

$\text{Cd}_{1-x}\text{Nd}_x\text{F}_{2+x}$  which contains a substitutional cation of smaller size (19).

—When  $x$  increases, the number of relaxed anions fixed at low temperature increases to the detriment of that of normal fluoride ions which decreases simultaneously (Fig. 6c and 7b). Nevertheless, the  $p_1 > p_2$  relation is always verified under our experimental conditions, for any  $x$  and temperature.

—The temperature at which the  $p_2$  and  $p_3$  fluoride sublattices coalesce is lower than that at which the  $p_1$  and  $p_3$  later merge. This



result, valid whatever the value of  $x$ , shows that the relaxed anions belonging to the  $p_2$  sublattice become mobile prior to the fluoride ions of the  $p_1$  sublattice.

### V. Diffusion and Clusterization in the $Cd_{1-x}Bi_xF_{2+x}$ Solid Solution

The  $^{19}F$  NMR study of the  $Cd_{0.80}Bi_{0.20}F_{2.20}$  and  $Cd_{0.70}Bi_{0.30}F_{2.30}$  compositions has al-

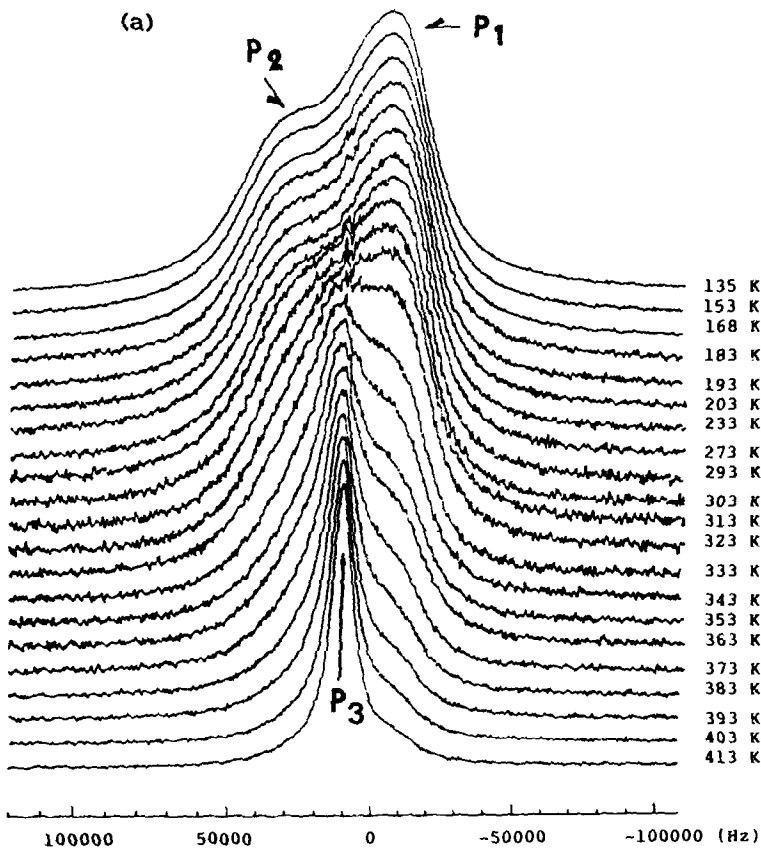


FIG. 7a. Thermal variation of the  $^{19}\text{F}$  NMR spectrum for the  $\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$  composition.

lowed us to show the existence of three fluoride sublattices and to determine the nature of these different sublattices. The thermal variation of the fraction  $f_m$  of mobile fluoride ions has been established and an estimation of the sum of true interstitial fluoride ions has been proposed:

$$f_i = 0.44 \text{ for } (x = 0.20)$$

$$f_i \approx 0.57 \text{ for } (x = 0.30).$$

The composition dependence of electrical properties for the  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  solid solution (19) allowed us to show for  $x \geq 0.05$  a

linear variation of  $\log \sigma_{423 \text{ K}}$  and  $\Delta E_\sigma$  when  $x$  increases:  $\log \sigma_{423 \text{ K}} \approx k_1 x$  and  $\Delta E_\sigma \approx k_2 x$ . By analogy with the  $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$  solid solution (15), the existence in  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  of 2:2:2 clusters has been proposed (19). These clusters constituted by the association of two vacancies ( $\square$ ) in the normal positions of the fluorite-type structure, two interstitial fluoride ions of type  $\text{F}' (\frac{1}{2}, u, u)$  and two interstitial fluoride ions of type  $\text{F}'' (v, v, v)$ , should be located close to 2  $\text{Bi}^{3+}$  ions to ensure their electrical neutrality.

The existence of 2:2:2 clusters in  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  supposes a linear increase of  $n_\square$ ,  $n_{\text{F}'}$ , and  $n_{\text{F}''}$  when  $x$  increases, such as  $n_\square =$

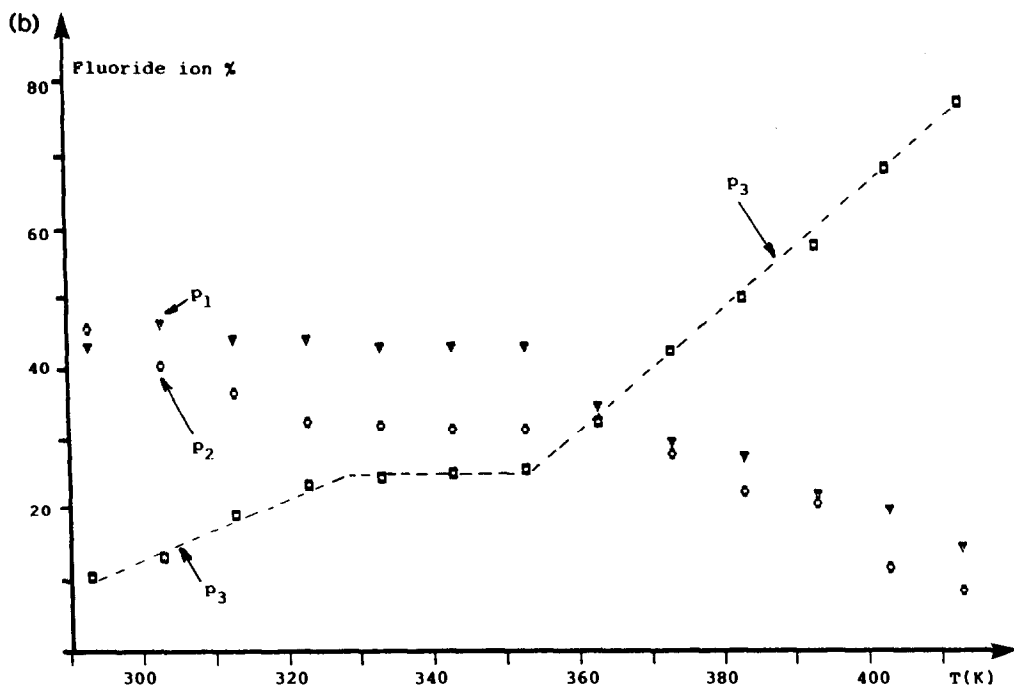


FIG. 7b. Temperature dependence of fluoride ion rates proportional to areas of peaks  $p_1$ ,  $p_2$ , and  $p_3$  for  $\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$ .

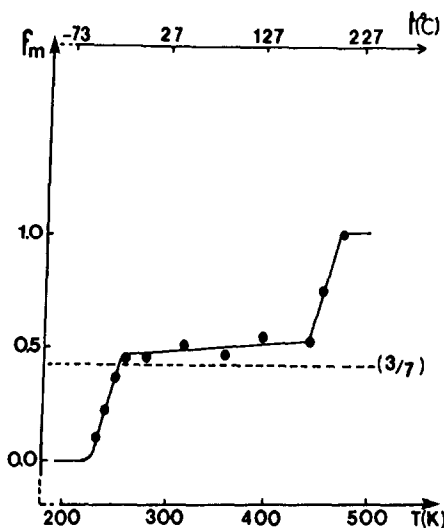


FIG. 8. Thermal variation of the fraction  $f_m$  of mobile fluoride ions for  $\text{Pb}_2\text{InF}_7$  (21).

$n_{F'} = n_{F''} = x$ . It results for the sum of interstitial ions ( $n_{F'} + n_{F''}$ ) in the theoretical values 0.40 and 0.60 for  $x = 0.20$  and  $x = 0.30$ , respectively. The good agreement between these values and the experimental values calculated from the  $^{19}\text{F}$  NMR spectra ( $f_i \approx 0.44$  and  $0.57$ , respectively, for  $x = 0.20$  and  $0.30$ ) shows that the formation of 2:2:2 clusters in  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  is a quite reasonable hypothesis.

The NMR study has allowed us to evaluate only the sum of the true interstitial fluoride ions in  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$ . It was not possible to show whether several types of interstitial ions are present or not; it is not surprising, in so far as the  $F'$  and  $F''$  anions of the 2:2:2 cluster play similar roles in the transport properties.

## VI. Comparison of Activation Energies Deduced from NMR and Conductivity Measurements

The activation energy of the mobile fluorine relaxation in  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$  and  $\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$  has been determined from the thermal variation of the jump frequency in these materials.

Line narrowing occurs when the fluorine jump frequency  $\nu_s$  is of the same order as the rigid lattice linewidth value. The thermal variation of  $\nu_s$  can be deduced from that of  $\Delta\nu_{1/2}$  using the expression (23):

$$\nu_s = \frac{\alpha [\Delta\nu_{1/2} - \Delta\nu_r]}{\tan\left|\frac{\pi}{2}\left|\frac{\Delta\nu_{1/2} - \Delta\nu_r}{\Delta\nu_R - \Delta\nu_r}\right|^2\right|},$$

where

$-\Delta\nu_{1/2}$  is the half-width measured at the  $T$  temperature,

$-\Delta\nu_R$  is the half-width of the rigid lattice determined at low temperature,

$-\Delta\nu_r$  is a residual half-width due to the field inhomogeneity at high temperature,

$-\alpha$  is a constant function of the line shape. The value of  $\alpha$  has been chosen equal to 1 because of the nearly gaussian shape of the line at low temperature.

The determination of  $\Delta\nu_{1/2}$  is difficult in our temperature domain due to partial overlapping of the  $p_3$  line with  $p_2$ , then with those of  $p_2$  and  $p_1$ . Consequently, the jump frequency  $\nu_s$  has been determined in the high temperature domain, above 350 K.

Figure 9 gives the variation of  $\log \nu_s$  vs  $10^3 T^{-1}$  for  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$  and  $\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$ :  $\nu_s$  increases with temperature according to a  $\nu_s = \nu_0 \exp(-\Delta E_F/kT)$  law. An activation energy  $\Delta E_F \approx 0.26$  eV can be deduced for both materials.

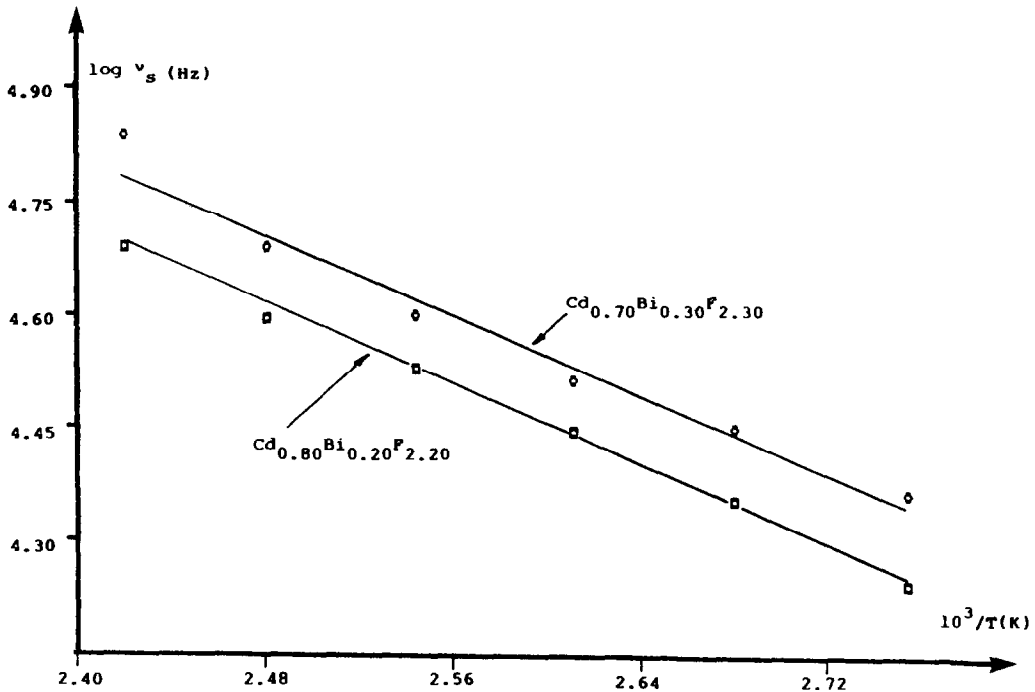


FIG. 9. Variation of  $\log \nu_s$  vs  $10^3 T^{-1}$  for  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$  and  $\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$ .

In the temperature domain considered where the anionic motions become quicker with increasing temperature, they contribute to a relaxation which is thermally activated. In the temperature range where relaxation results simultaneously from the atomic and spin diffusion, the measured activation energy represents 3/4 of the activation energy of the atomic motions (24, 25). Consequently, the activation energy of mobile fluoride ions ( $p_3$  sublattice) calculated for the  $x = 0.20$  and  $x = 0.30$  compositions is  $\Delta E_1 = 0.26 \times 4/3$ , i.e., 0.35 eV.

On the other hand, at a given temperature, the jump frequency  $\nu_j$  in the temperature range 350–410 K is higher for  $\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$ , which has better electrical performance than  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$  (Fig. 9).

We have also determined, in the same temperature range, the variation of the fraction  $f_m$  of mobile fluoride ions vs  $10^3 T^{-1}$  for

$\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$  and  $\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$  (Fig. 10). Like the jumping frequency,  $f_m$  is thermally activated according to a  $f_m = f_0 \exp(-\Delta E_2/kT)$  law. A similar value of  $\Delta E_2$  ( $\Delta E_2 \approx 0.19$  eV) can be deduced for both  $x = 0.20$  and  $0.30$  compositions which are consequently characterized by quasi-identical values of the sum  $\Delta E_1 + \Delta E_2 = \Delta E_t$ . Furthermore, in the considered temperature domain,  $f_m$  is larger for  $x = 0.30$ , which has the best electrical performance.

The activation energies  $\Delta E_t$  deduced from the NMR studies are in good agreement with those determined by conductivity measurements; this result indicates that the motions of  $\text{F}^-$  ions in these materials are diffusive.

As both materials are characterized by very close values of  $\Delta E_t$  and thus of  $\Delta E_{\sigma}$ , the best transport properties observed for  $x = 0.30$  seem to be related only to the num-

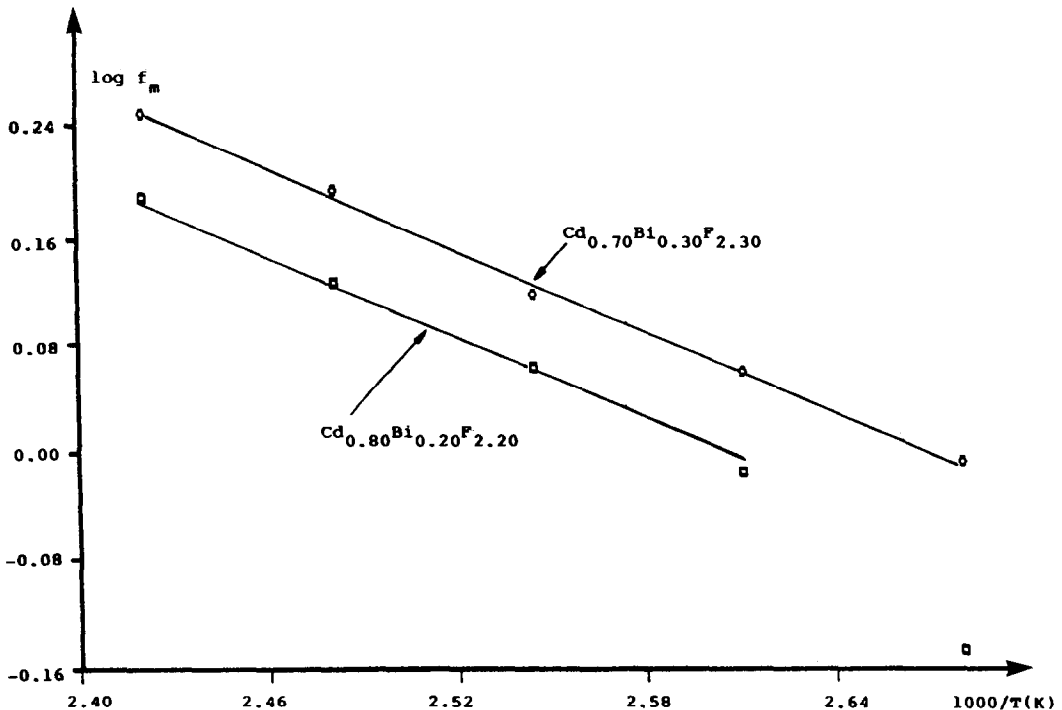


FIG. 10. Variation of  $\log f_m$  vs  $10^3 T^{-1}$  for  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$  and  $\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$ .

ber of mobile ions, which is higher in  $\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$  than in  $\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$ . This result is in quite good agreement with the existence of the 2:2:2 clusters proposed for  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$ : as a matter of fact, the numbers of vacancies and interstitial fluoride ions are proportional to the substitution rate in the 2:2:2 cluster.

	$\Delta E_1(\text{eV})$	$\Delta E_2(\text{eV})$	$\Delta E_3(\text{eV})$	$\Delta E_r(\text{eV})$
$\text{Cd}_{0.80}\text{Bi}_{0.20}\text{F}_{2.20}$	$\approx 0.35$	$\approx 0.19$	$\approx 0.54$	0.58
$\text{Cd}_{0.70}\text{Bi}_{0.30}\text{F}_{2.30}$	$\approx 0.35$	$\approx 0.19$	$\approx 0.54$	0.57

## VII. Conclusions

The investigation by  $^{19}\text{F}$  NMR of the  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  solid solution has allowed us to show the existence of three fluoride sublattices  $F_1$ ,  $F_2$ , and  $F_3$ , which represent, respectively, anions located in the normal positions of the fluorite structure, relaxed anions from those positions, and anions located in interstitial sites.

$F_3$ - $F_2$  and  $F_3$ - $F_1$  exchanges appearing successively at increasing temperature have been detected for the high substitution rates. The motions of the mobile  $\text{F}^-$  ions above  $T \approx 350$  K are of diffusive nature.

The NMR results are in good agreement with the formation in  $\text{Cd}_{1-x}\text{Bi}_x\text{F}_{2+x}$  of 2:2:2 clusters, the number of which increases linearly with  $x$ . A higher conductivity results from a larger number of mobile fluorine ions.

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