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Structural Transitions at High Temperature in $Sr_2Fe_2O_5$

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The high-temperature behavior of $Sr_2Fe_2O_5$ has been well characterized by various techniques (DTA, X-ray diffraction, magnetic measurements) paying particular attention to keep the nominal composition constant. The transition from the low-temperature ordered form (with brownmillerite structure) to the high-temperature disordered form (of perovskite structure) has been explained in terms of microdomain formation. A structural model is proposed and discussed. © 1985 Academic Press, Inc.

In previous works dealing with nonstoichiometric perovskites AMO_{3-y} it had been shown that the anionic vacancy concentration y could reach or even exceed the value $y = 0.50$ without apparent modification of the structure. This is the case, for instance, for $SrTiO_{2.50}$, $SrVO_{2.50}$, or $BaFe_{1-x}Zn_xO_{2.50-x/2}$ (*1–4*) which exhibit by X-ray diffraction a cubic symmetry characteristic of the perovskite structure. Although the authors of these works did not appear to be fully convinced, they generally concluded that oxygen vacancies were "randomly distributed" within the network.

Recently, Shin *et al.* have given evidence of a crystallographic transition at high temperature ($T > 700°C$) in $Sr_2Fe_2O_5$ (*5*). They assumed a transition from a vacancy ordered state (of brownmillerite-type structure) to a statistically disordered state (oxygen deficient perovskite structure). On the other hand no transition could be observed in the case of $Ca_2Fe_2O_5$ which is brownmillerite-type up to 1200°C (*6*). $Sr_2Fe_2O_5$ seemed to be the first example of an ordering–disordering transition in AMO_{3-y} perovskite-type compounds at constant defect concentration ($y = 0.50$).

Moreover in recent investigations Grenier *et al.* have shown that in various ferrite systems a long-range vacancy ordering usually occurs when $y \gtrsim 0.25$ (*7*).

From this point of view, $Sr_2Fe_2O_5$ ($y = 0.50$) appears to be an anomaly in the structural model previously proposed (*8*).

This work is concerned with various characterizations of the $Sr_2Fe_2O_5$ transition; a structural model will be proposed in correlation with recent HRTEM observations of perovskite-related ferrites. Up to now, this kind of transition has only been studied in relation with a change of the defect concentration y involving an oxidation process (*9, 10*). Here particular attention is paid to keeping the composition of material constant.

Preparation and Characterization of $Sr_2Fe_2O_5$

Strontium ferrite $Sr_2Fe_2O_5$ has been prepared starting from a stoichiometric mix-

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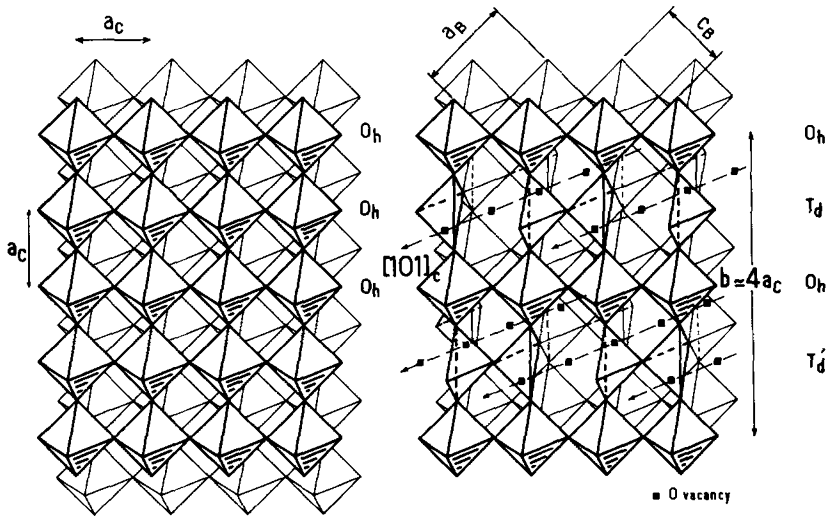

FIG. 1. Idealized structures of perovskite and brownmillerite. Left: AMO_3 ($SrTiO_3$), perovskite type. Right: $AMO_{2.50}$ ($Sr_2Fe_2O_5$), brownmillerite type.

ture of strontium carbonate $SrCO_3$ and iron nitrate $Fe(NO_3) \cdot 9H_2O$ dissolved in a nitric medium. Then the nitrates were decomposed at low temperature (≃400°C) and heated up to 900°C. After grinding the material was annealed at 1350°C for 24 hr in air, then quenched. At this stage, it was black, somewhat oxidized and containing about 16% Fe(+IV).

Stoichiometric strontium ferrite (without oxygen excess) was obtained in a further step by reduction at 1000°C either in a stream of Ar + 2% H_2 ($p_{O_2} < 10^{-20}$ atm) for 12 hr or under dynamic vacuum (10^{-5} Torr). In any case the final material was brown and a chemical analysis confirmed the absence of Fe(+IV), i.e., the $Sr_2Fe_2O_5$ composition.

The X-ray pattern was indexed on the basis of the orthorhombic cell of the brownmillerite structure with the following parameters:

$$a = 5.530 \pm 0.002 \text{ Å}$$
$$b = 15.540 \pm 0.005 \text{ Å}$$
$$c = 5.666 \pm 0.002 \text{ Å}$$
$$V = 486{,}9 \pm 0.5 \text{ Å}^3$$

The indexation was in agreement with the space group $I_{2mb}(C_v^{22})$ previously determined on a crystal (*11*). The structure of $Sr_2Fe_2O_5$ is closely related to that of $Ca_2Fe_2O_5$ (space group *Pnma*, D_{2h}^{16}). As previously shown (*7*), these structures derive directly from the AMO_3 perovskite-type assuming that oxygen vacancies ($\frac{1}{6}$ of the oxygen atoms) are ordered along alternate rows $[101]_c = [100]_B$ (Fig. 1). In this way half-octahedral sites (O_h) are transformed into tetrahedral sites (T_d). The coordination number of the biggest cations (Sr or Ca) which was 12 in the perovskite decreases to 10 in the brownmillerite. The only significant difference between both structures lies in the orientation of (FeO_4) tetrahedra and more particularly in the positions of the tetrahedrally surrounded iron atoms (T_d) and of the O_3-oxygen atoms sharing corners of the tetrahedra. A neutron diffraction study has shown that the Debye–Waller factors of these atoms were anomalously large, especially those of the O_3 oxygens (*12*).

High-Temperature Investigations

Three kinds of investigations have been carried out at high temperature: DTA, X-

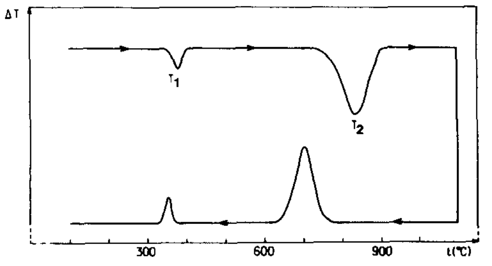

FIG. 2. DTA thermograph for $Sr_2Fe_2O_5$.

ray diffraction, and magnetic measurements.

To keep constant the initial composition during the measurements, the materials were set in a sealed golden tube (DTA, magnetic measurements), under high dynamic vacuum (10^{-4} Torr) (X-ray diffraction, Guinier-Lenné technique), or under controlled partial oxygen pressure (mixture of N_2–H_2 for X-ray diffraction with $p_{O_2} \simeq 10^{-20}$ atm).

A. DTA Study

The micro-DTA thermograph of $Sr_2Fe_2O_5$ is given in Fig. 2. Two transitions occur at increasing as well as at decreasing temperature:

—around 350°C (T_1) an endothermic transition without hysteresis involving a low energy;

—around 850°C (T_2) a second endothermic transition extending over about 150°C. The involved energy is more important.

B. High Temperature X-Ray Diffraction

Experiments have been carried out between 20 and 1000°C either by conventional X-ray diffractometer (CuK_α) radiation) or with a Guinier-Lenné camera. The crystallographic data obtained from both techniques were consistent. The thermal evolution of the main diffraction lines is shown in Fig. 3. Three temperature ranges appear:

—At $t \lesssim 350°C$ there is a brownmillerite-type domain (B).

—For $350°C \lesssim t \lesssim 850°C$ we observe a two-phase domain with coexistence of the spectra of the brownmillerite (B) and of a tetragonal perovskite-type phase (Q) whose concentration increases with the temperature.

—At $t > 850°C$ a cubic perovskite-type domain (P) occurs. Figure 4 shows the variation vs temperature of the reduced parameter (a_r) of $Sr_2Fe_2O_5$ calculated from the above data. Clearly appear:

—a sharp transition of the cell parameters at 850°C which corresponds to a transition from the brownmillerite towards cubic perovskite symmetry. The observed temperature is in good agreement with the DTA observation (T_2).

—the presence of a tetragonal perovskite-type phase (Q) above 350°C,

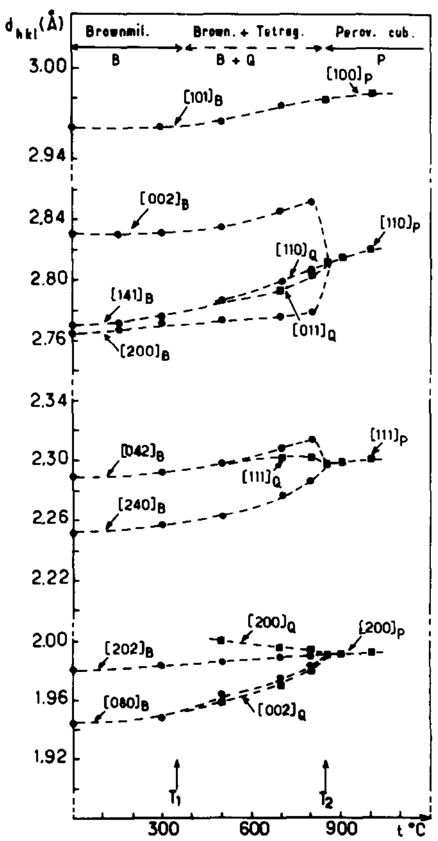

FIG. 3. Thermal evolution of the main X-ray diffraction lines of $Sr_2Fe_2O_5$.

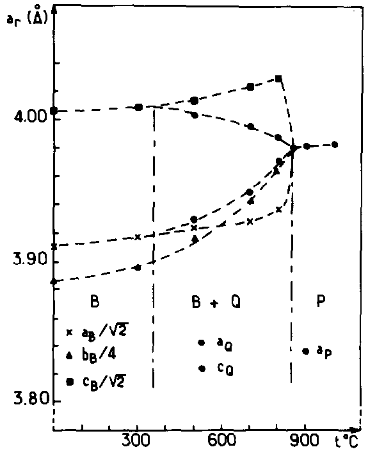

FIG. 4. Thermal variation of the reduced parameters (a_r) of $Sr_2Fe_2O_5$.

temperature at which DTA reveals a slight transition (T_1).

In the light of these results it might be concluded that the "disordered state" of the vacancies appears suddenly at 850°C following an "intermediate state" extending over 500°C which could correspond to a progressive growth of a tetragonal perovskite-type phase within an ordered brownmillerite-type phase.

This assumption is corroborated by the increase at rising temperature of the intensities of the diffraction lines corresponding to the Q phase and the decrease of those of the brownmillerite B in the same temperature range.

C. Magnetic Properties

The thermal evolution of the magnetic susceptibility of $Sr_2Fe_2O_5$ (Fig. 5) characterizes at low-temperature antiferromagnetic interactions whose Néel temperature is 715 K. We have plotted the susceptibility values of the homologous compound $Ca_2Fe_2O_5$ by comparison (*13*). Experimental data are reported in Table I.

The Néel temperatures for both ferrites are very close. This can be explained by the fact that in spite of increasing size of the alkaline-earth cation and consequently of the Fe–O–Fe distances (Table I), the covalency of π(Fe–O) bonds in competition with the σ(Sr–O) bonds also increases. This explanation is consistent with the values of the covalency parameters of the Fe–O bonds previously determined by neutron diffraction (*12*).

The magnetic structure is similar to the G-type arrangement of the orthoferrite series or of $Ca_2Fe_2O_5$ (*13*). This structure associated with the space group I_{2mb} is rela-

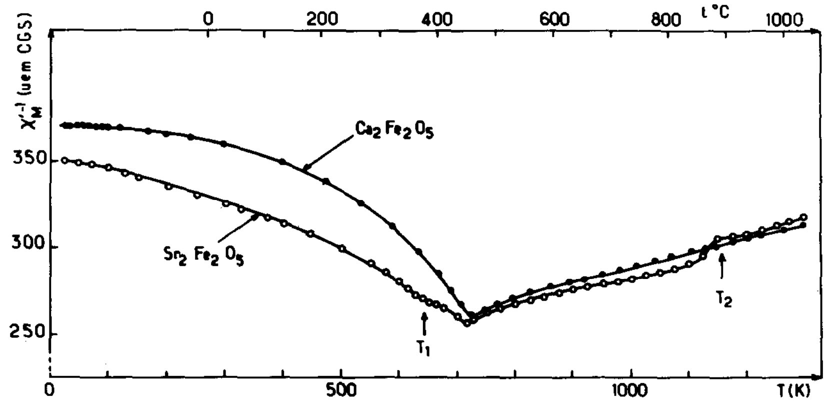

FIG. 5. Thermal variation of the inverse of the molar magnetic susceptibility for $Sr_2Fe_2O_5$ or $Ca_2Fe_2O_5$ (*13*).

TABLE I

MAGNETIC DATA FOR $Sr_2Fe_2O_5$ AND $Ca_2Fe_2O_5$

	T_N (K)	θ_p (K)	$C_{M_{exp}}$ (±0.10)	V_M (Å^3)	Fe$_0$–O–Fe$_0$ (Å)	Fe$_0$–O–Fe$_T$ (Å)	Fe$_T$–O–Fe$_T$ (Å)	θ_{p0} (K)	λ (K^{-1})
$Sr_2Fe_2O_5$	715	−3100	14.50	60.86	3.96	4.09	3.77	−1871	$-2.12.10^{-4}$
$Ca_2Fe_2O_5$	725	−2840	13.35	56.12	3.93	3.96	3.82	−1860	$-1.85.10^{-4}$

tively symmetric and cannot give rise to weak ferromagnetism as previously observed in $Ca_2Fe_2O_5$ (*14*). This has been confirmed by measuring the magnetization below the Néel temperature: $Sr_2Fe_2O_5$ does not show weak ferromagnetism but at very low temperature a very small component appears ($\sigma_0 \simeq 8.10^{-4}\ \mu_B$), probably due to a tiny distortion of the network.

The thermal evolution of the magnetic susceptibility (Fig. 5) shows two accidents which have not been observed for $Ca_2Fe_2O_5$:

—in the antiferromagnetic domain at 630 K ($\simeq$355°C);

—in the paramagnetic domain between 1125 and 1200 K ($\simeq$850–930°C).

These temperatures are in very good agreement with those observed by X-ray diffraction and DTA (T_1 and T_2).

The values of the Curie constant (C_M = 14.50 uem CGS for $720 < T < 1100$ K) and of the paramagnetic Curie temperature ($\theta_p \simeq 3100$ K) are very high. This phenomenon has been extensively explained by Grenier *et al.* in a previous work relative to $Ca_2Fe_2O_5$ (*13*). It results from the existence of strong magnetic interactions which lead to correcting the experimental data by a factor $(1 - \lambda\theta_{p_0})$ where θ_{p_0} is the true paramagnetic Curie temperature and λ the coefficient of the thermal variation of the molecular field. From the data of Table I it appears that the values of θ_{p_0} for both compounds are quite close, implying similar magnetic interactions; on the other hand, the value of $|\lambda|$ for $Sr_2Fe_2O_5$ is the highest, obviously involving a drastic evolution of the magnetic interactions at high temperature in relation to a large expansion of the lattice.

Discussion of the Results

The results unambiguously show a structural transition at high temperature ($T \simeq$ 850°C) which is characterized by:

—a change of crystallographic symmetry (orthorhombic and/or tetragonal to cubic) (apparently whatever the quenching rate may be the cubic phase cannot stand at room temperature):

—a first-order endothermic reaction showing a large temperature hysteresis;

—an anomaly of the magnetic susceptibility;

—no composition change.

This point must be emphasized. As a matter of fact the presence of strontium could induce a slight oxidation leading to either $Sr_2Fe_2O_{5+x}$ or $SrFeO_{3-y}$ ($y < 0.50$) and thus giving rise in an easier way to the cubic perovskite structure. In a previous work, Shin *et al.* have observed such a transition at 700°C, but their experiments were carried out under nitrogen atmosphere (i.e., with $p_{O_2} \simeq 10^{-4}$–10^{-5} atm) (*6*), which supposes partial oxidation. For sake of clarification, we have followed by DTA the evolution of the transition temperature as a function of oxygen partial pressure (Fig. 6). The temperature of the transition becomes constant when p_{O_2} is lowered down to 10^{-20} atm. Hence, under such conditions, i.e., those of our experimental work, the stoichiometry of $Sr_2Fe_2O_5$ re-

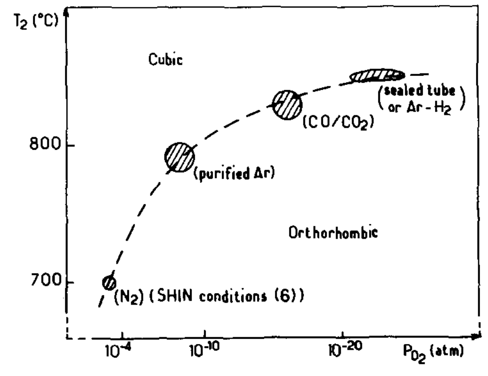

FIG. 6. Evolution of the transition temperature T_2 for $Sr_2Fe_2O_5$ vs oxygen partial pressure.

mains perfectly constant as confirmed moreover by chemical analysis.

Shin *et al.* concluded in their work that the transition corresponded to "a complete phase transition from a brownmillerite-type structure to a cubic perovskite structure accompanying random displacement of the oxygen atoms or the oxygen vacancies throughout the oxygen lattice sites of the latter structure."

But in a recent investigation, Komornicki *et al.* have shown that a statistical vacancy disordering is quite impossible as it could give rise to a too important local decrease in the coordination of the largest cation (*15*). In addition, vacancy distribution calculations correlated to Mössbauer data have shown that the oxygen vacancies can only be arranged along rows of variable lengths.

Moreover, Grenier *et al.*, studying nonstoichiometric perovskite-related ferrites AMO_{3-y} have generally found a long-range vacancy ordering for $y \gtrsim 0.25$ (*7*). If this is so, how can such an important defect concentration ($y = 0.50$) exist, supposing that one-sixth of the oxygen atoms are missing and implying that drastic local perturbations arise without apparent structural modifications?

An answer can be found on the base of HRTEM observations of Alario-Franco *et al.* of nonstoichiometric ferrites such as $Sr_{0.80}Nd_{0.20}FeO_{2.60}$ ($y = 0.40$) (*16*) or $La_{1-x}Ca_xFeO_{3-y}$ ($2/3 \leq x < 1$; $0.25 \lesssim y \lesssim 0.40$) (*9, 17*). Those phases were prepared at high-temperature ($t \gtrsim 1350°C$) and then quenched. In each case the X-ray diffraction spectrum was similar to that of the cubic perovskite but the microscopic diffraction patterns exhibited additional spots beside the cubic symmetry reflections. The corresponding images revealed a texture formed by the intergrowth of three sets of microdomains whose size was of 10^5 to 10^6 Å^3. Their structure was analogous either to that of brownmillerite or to that of the so-called G-type structure ($A_3M_3O_8$, $n = 3$ term, $y = 0.33$). In a previous work we have shown that the vacancy ordering in the microdomains can occur along rows in six different directions characterizing three types of microdomains [the nomenclature is given in Ref. (*18*)].

In this connection a similar phenomenon can be considered for the high-temperature form of $Sr_2Fe_2O_5$ and Fig. 7 shows a schematic representation of this microdomain texture as it can be imagined for this phase.

Nevertheless, as previously discussed (*18*), it should be noticed that for the previous ferrites the formation of such micro-

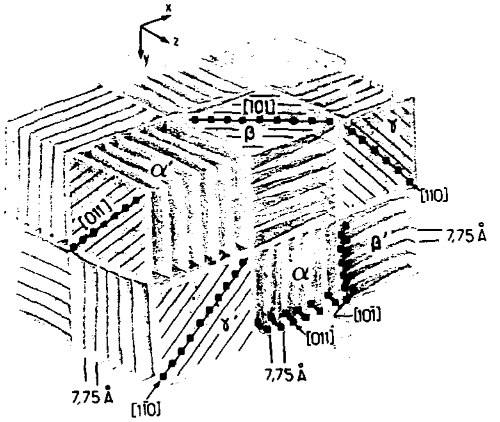

FIG. 7. Supposed microdomain structure of the high-temperature form of $Sr_2Fe_2O_5$.

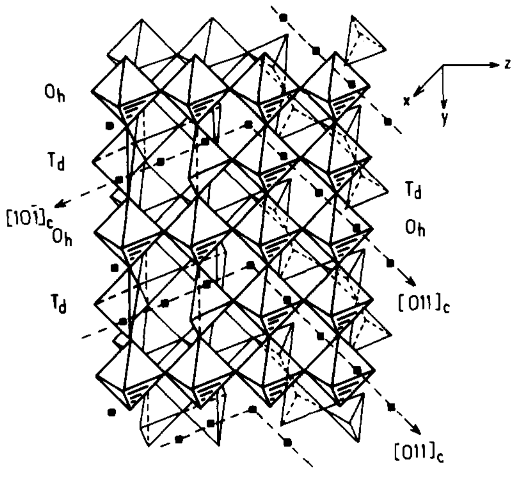

FIG. 8. Microdomain boundary in hypothesis 1 (infinite rows).

domains results from an oxygen excess located in the domain walls, hence this excess is related to their size. For instance, for $Sr_{0.80}Nd_{0.20}FeO_{2.60}$ ($y = 0.40$) the stoichiometry of the microdomains is that of the brownmillerite ($y = 0.50$). For $Ca_{2/3}La_{1/3}FeO_{2.745}$ too, y is 0.255 instead of $y = 0.33$ which corresponds to the stoichiometry of the microdomains which are of the G type.

On the contrary, as just mentioned, the transformation of $Sr_2Fe_2O_5$ at high temperature does not imply any composition change. Two ways of structural changing can then be assumed:

(1) the ratio between octahedra and tetrahedra (equal to 1 in $Sr_2Fe_2O_5$) remains constant but their arrangement becomes different.

(2) Octahedra and tetrahedra disappear in the same proportion leading simultaneously to the formation of fivefold coordinated sites to keep the stoichiometry constant.

This implicitly supposes that strontium and iron atoms remain practically located in the perovskite (or brownmillerite) positions; only the oxygen arrangement (and consequently the vacancy arrangement) is concerned.

According to a previous work (*15*), the first assumption implies that the length of the vacancy rows is infinite, as any finite-length row yields the formation of fivefold coordinated sites. In fact the existence of a microdomain texture implicates that these infinite rows are broken in various directions. It appears (*18*) that, from the point of view of electrostatic energy and in order to obtain perpendicular tetrahedral sheets, the most suitable angle is 120°C. Figure 8 shows the boundary between two microdomains. Such a hypothesis necessarily leads to a sequence ($O_h\ T_d\ O_h\ T_d$ . . .) instead of the brownmillerite sequence ($O_h\ T_d\ O_h\ T'_d$ . . . , Fig. 1). This must reasonably be ruled out as the structural rearrangement would be too important.

In the second assumption we shall consider the internal structure of the microdomains to be of brownmillerite-type structure. Figure 9 shows the boundary between two microdomains in this hypothesis, in which it appears that only half of the vacancy files are infinite and half are finite within each domain, ended by fivefold coordinated sites. These sites can be clearly viewed in Fig. 10 which represents a

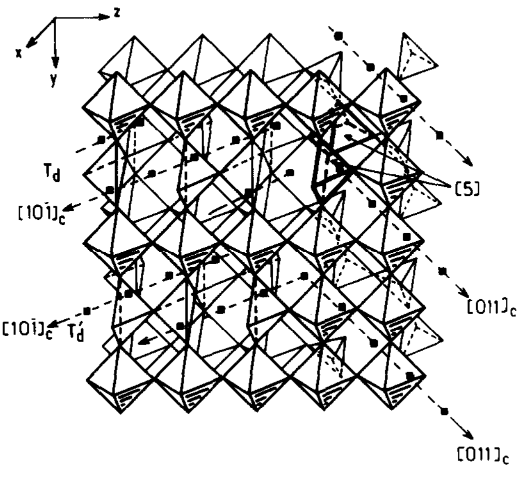

FIG. 9. Microdomain boundary according to hypothesis 2 (discontinuity of vacancy rows, creation of fivefold coordinated sites).

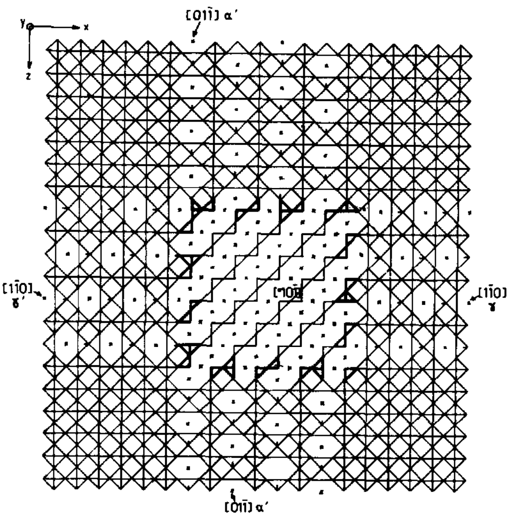

FIG. 10. (0*k*0) plane of the high-temperature form of $Sr_2Fe_2O_5$ (hypothesis 2).

(0*k*0) plane. Although it is difficult to calculate their proportion, it may be supposed that they equally affect octahedra and tetrahedra to keep the oxygen stoichiometry constant.

Conclusions

The previous investigations unambiguously show the possibility of a structural transformation of $Sr_2Fe_2O_5$ at high temperature related to a vacancy "ordering–disordering" transition without composition change. Nevertheless, in view of recent HRTEM observations, the apparent disorder is likely to be only partial, due to the high vacancy concentration. As previously observed, in other ferrites the formation of microdomains is probable at high temperature. The hypothesis that octahedra and tetrahedra disappear simultaneously leading to fivefold coordinated sites seems to be the most credible.

First, this hypothesis supposes the brownmillerite-type structure (i.e., the low-temperature form) within the microdomains; such a phenomenon has also been observed in the oxidized ferrites $Ca_xLa_{1-x}FeO_{3-y}$ (*9, 17*). Second, the instability of the HT phase even after very fast quenching may be explained by the fact that trivalent iron, whose electronic configuration is $3d^5$ is located in a fivefold coordinated site, i.e., in a normally unstable situation.

The formation of the microdomains would involve a migration of the vacancies correlated to the high mobility of the O_3 oxygen (*12*). The mechanism could be the following: around 350°C, some vacancy files are broken and tetragonal domains progressively appear within the brownmillerite lattice. Their number becomes greater and greater as the thermal agitation increases up to a point where a sharp transition occurs leading to a macroscopicly "disordered phase," i.e., at 850°C.

Measurements of the oxygen-ion conductivity have been carried out on $Sr_2Fe_2O_5$ at high temperature. The data are plotted in Fig. 11. They actually show a conductivity as low as that of stoichiometric perovskite compounds such as $LaAlO_3$ or $CaTiO_3$ and much lower than that of the nonstoichiometric $CaTi_{0.7}Al_{0.3}O_{2.85}$ compound (*19*). Moreover no transition has been observed around 850°C. This result is confirmed by the rather low oxygen-diffusion factor previously determined ($D_{25°C} \simeq 10^{-43}$ cm²/sec: $D_{1000°C} \simeq 2.10^{-11}$ cm²/sec (*20*).

In this way we can conclude that the migration of oxygen atoms in the lattice is very small and that the vacancies are strongly interacting. In fact, there is no fundamental difference between the so-called "low-temperature ordered phase" and the "high-temperature disordered phase." In other words the "perovskite phase" is not really disordered, as its ionic conductivity would have been much larger than that of a stoichiometric phase.

Further studies such as Mössbauer spectroscopy or HRTEM observations at high temperature are in progress to confirm the proposed hypothesis.

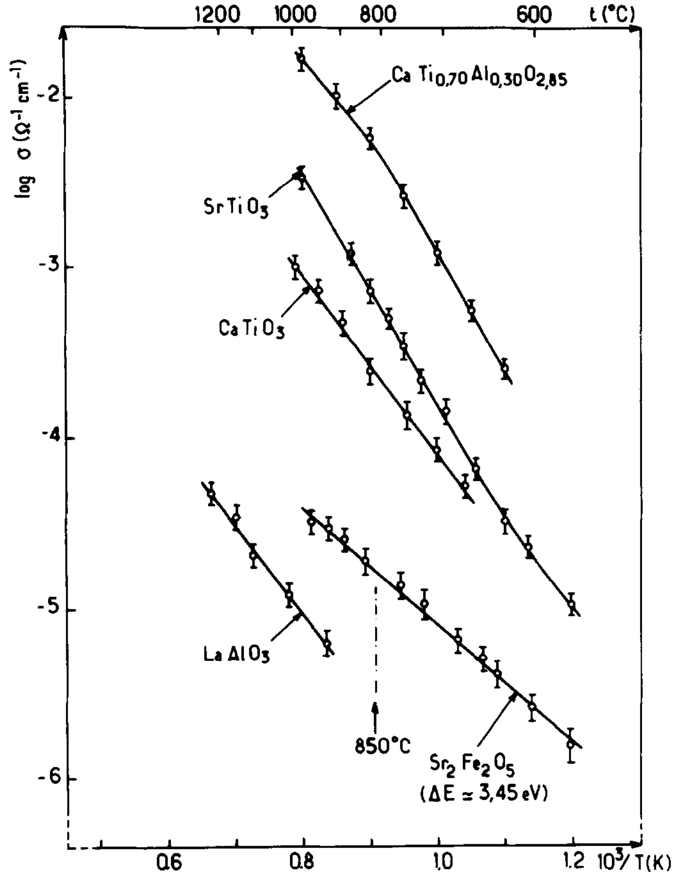

FIG. 11. Thermal variation of the ionic conductivity for $Sr_2Fe_2O_5$ and various perovskite-type phases.

Acknowledgments

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References

1. M. A. ALARIO-FRANCO AND M. VALLET-REGI, *Nature* (*London*), **270**, 706 (1977).
2. B. C. TOFIELD, *Nature* (*London*), 713 (1978).
3. M. KESTIGIAN, J. G. DICKINSON, AND R. WARD, *J. Amer. Chem. Soc.* **52**, 463 (1963).
4. P. NEU, M. ZANNE, AND C. GLEITZER, *J. Solid State Chem.* **36**, 205 (1981).
5. S. SHIN, M. YONEMURA, AND H. IKAWA, *Mater. Res. Bull.* **13**, 1017 (1978).
6. S. SHIN, M. YONEMURA, AND H. IKAWA, *Bull. Chem. Soc. Japan*, **52**, 947 (1979).
7. J. C. GRENIER, M. POUCHARD, AND P. HAGENMULLER, *Struct. Bonding* (*Berlin*) **47**, 1 (1981).
8. M. POUCHARD AND J. C. GRENIER, *C. R. Acad. Sci. Paris Ser. C* **284**, 311 (1977).
9. M. A. ALARIO-FRANCO, M. J. HENCHE, M. VALLET, J. M. G. CALBET, J. C. GRENIER, A. WATTIAUX, AND P. HAGENMULLER, *J. Solid State Chem.* **46**, 23 (1983).
10. M. A. ALARIO-FRANCO, J. M. G. CALBET, M. VALLET, AND J. C. GRENIER, *J. Solid State Chem.* **49**, 219 (1983).
11. M. VON-HARDER AND H. K. MÜLLER-BUSCHBAUM, *Z. Anorg. Allg. Chem.* **464**, 169 (1980).
12. C. GREAVES, A. J. JACOBSON, B. C. TOFIELD, AND B. E. F. FENDER, *Acta Crystallogr. B* **31**, 641 (1975).
13. J. C. GRENIER, M. POUCHARD, AND R. GEORGES, *Mater. Res. Bull.* **8**, 1413 (1973).
14. T. TAKEDA, Y. YAMAGUCHI, AND S. TOMIYOSHI, *J. Phys. Soc. Japan.* **24** 446 (1968).
15. S. KOMORNICKI, J. C. GRENIER, M. POUCHARD,

AND P. HAGENMULLER, *Nouv. J. Chim.* **5,** 161 (1981).

16. M. A. ALARIO-FRANCO, J. C. JOUBERT, AND J. P. LEVY, *Mater. Res. Bull.* **17,** 733 (1982).

17. M. A. ALARIO-FRANCO, J. M. GONZALES-CALBET, M. VALLET-REGI, AND J. C. GRENIER, *J. Solid State Chem.* **49,** 219 (1983).

18. J. C. GRENIER, M. POUCHARD, P. HAGENMULLER, M. J. R. HENCHE, M. VALLET, J. M. G. CALBET, AND M. A. ALARIO-FRANCO, *Rev. Chim. Miner.* **20,** 726 (1983).

19. T. TAKAHASHI, *in* "Superionic Conductors" (G. B. Mahan and N. L. Doth Eds.) Plenum, New York (1976).

20. YAMAMOTO AND KIRIYAMA, *in* "Proceedings of the Ninth Symposium on Ceramics (Japan)," p. 41 (1971).