

The Formation of Nonequilibrium Microdomains during the Oxidation of $\text{Sr}_2\text{CoFeO}_5$

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The phase $\text{Sr}_2\text{CoFeO}_{5+y}$ has been studied by Mössbauer spectroscopy, X-ray powder diffraction, and magnetic susceptibility techniques. Quenching in air from 1200°C produces a partially oxidized material which contains small nonequilibrium microdomains of the brownmillerite $\text{Sr}_2\text{CoFeO}_5$ with excess oxygen accommodated in the domain walls. Quenching in liquid nitrogen from 1200°C produces stoichiometric $\text{Sr}_2\text{CoFeO}_5$ with a random distribution of cobalt and iron on the tetrahedral and octahedral sites. Annealing under argon at 800°C causes preferential occupation of the tetrahedral sites by cobalt. Both the nitrogen-quenched and the annealed sample are antiferromagnetic at room temperature. © 1988 Academic Press, Inc.

Introduction

There are a number of compounds with the general formula $A_2B_2O_5$ which are notionally derived from the perovskite structure ABO_3 by an ordering of oxygen vacancies such that there are alternate layers of distorted octahedrally and tetrahedrally coordinated B cations. They are frequently referred to as "brownmillerites" after the mineral brownmillerite, $\text{Ca}_2\text{FeAlO}_5$, which has been extensively studied as a constituent of Portland cement. The crystal structures of both this compound and of $\text{Ca}_2\text{Fe}_2\text{O}_5$, assumed to be isostructural, were refined (1) from X-ray data in the space group $Pcmn$ (orthorhombic with $c < a < b$ and the alternating cation layers normal to y). More accurate refinements for $\text{Ca}_2\text{Fe}_2\text{O}_5$ by Colville (2) (in $Pcmn$) and by Berggren

(3) (in the more conventional setting of $Pnma$) are also available. $\text{Ca}_2\text{FeAlO}_5$ has also been refined in the space group $Ibm2$ (4). Although aluminum shows a strong preference for the smaller tetrahedral site, cation ordering is only about 75% complete. A detailed analysis of the Mössbauer spectra of $\text{Ca}_2\text{Fe}_2\text{O}_5$ below the Néel temperature of $\sim 400^\circ\text{C}$ has shown (5) that the Fe^{3+} spins lie along the c -axis with antiferromagnetic coupling in both the octahedral and tetrahedral sublattices. This has been confirmed by neutron diffraction measurements (6, 7). In $\text{Ca}_2\text{FeAlO}_5$ a similar antiferromagnetic spin structure is found (8) but the spins now lie along the a -axis. This is a significant difference because the axis sequence $c < a < b$ is retained throughout the $\text{Ca}_2\text{Fe}_2\text{O}_5$ - $\text{Ca}_2\text{FeAlO}_5$ solid solution. Substitution of Fe^{3+} by Sc^{3+} takes place at octahedral sites, and by Ga^{3+} at tetrahedral sites, in parallel with similar observations in the garnet systems (9).

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The magnetic structure for $\text{Sr}_2\text{Co}_2\text{O}_5$ has been refined (10) from neutron diffraction data under the assumption that the space group is also *Pcmm*. The structure of $\text{Sr}_2\text{Fe}_2\text{O}_5$ derived from powder neutron data (11) features disordered $8i$ sites in the space group *Icmm*. A later single-crystal X-ray study (12) gave the space group as *Ibm2*, although no standard deviations are given, and the table of interatomic distances is clearly at variance with the table of atomic coordinates. However, despite the undoubted subtleties of the space groups, the Mössbauer spectra of $\text{Ca}_2\text{Fe}_2\text{O}_5$, $\text{Sr}_2\text{Fe}_2\text{O}_5$, and $\text{Sr}_2\text{Co}_2\text{O}_5$ show a close similarity in their magnetic structures (13). More recently, $\text{Sr}_2\text{Fe}_2\text{O}_5$ has been shown to undergo a transition to a high-temperature disordered form (apparently a cubic perovskite), and this has been explained (14) in terms of microdomain formation within a brownmillerite lattice.

Although one might expect that phases could be prepared with mixed transition metal cations, little work has been done in this area. $\text{Ca}_2\text{Fe}_2\text{O}_5$ has been partially substituted by Cr^{3+} and Co^{3+} which show some preference for the octahedral and tetrahedral sites, respectively (15). In a previous investigation (13) of the system $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-y}$, we were unable to prepare a brownmillerite compound of composition $\text{Sr}_2\text{CoFeO}_5$. This seemed surprising in view of the similar structures of $\text{Sr}_2\text{Fe}_2\text{O}_5$ and $\text{Sr}_2\text{Co}_2\text{O}_5$. In this paper we describe the successful preparation of this phase by two different routes, and determine the site preferences of the iron and cobalt by Mössbauer spectroscopy. Unusual nonequilibrium microdomains produced by the rapid oxidation of this phase during quenching have been observed.

Experimental

Accurately weighed amounts of spectroscopic grade Co_3O_4 , Fe_2O_3 , and SrCO_3 in

the stoichiometric ratio appropriate for $\text{Sr}_2\text{CoFeO}_5$ were ground together in a ball mill, pressed into a pellet, and fired in a platinum crucible at 1200°C for 3 days with two intermediate grindings before quenching onto a metal plate in air. Aliquots of this material were then annealed under a variety of conditions as described under Results and Discussion. Initial characterization in each case was by X-ray powder diffraction recorded with a Philips diffractometer using nickel-filtered $\text{CuK}\alpha$ radiation. Chemical analyses for Fe/Co^{4+} were carried out by iodometric analysis as described previously (13). Mössbauer spectra were recorded in the range 78–300 K with a $^{57}\text{Co}/\text{Rh}$ source matrix at room temperature, isomer shift values are relative to the spectrum of metallic iron. The main spectrometer was an MS-102 Microprocessor by Cryophysics Ltd. Magnetic susceptibilities were measured in the temperature range 80–300 K by the Gouy method.

Results and Discussion

An earlier investigation of the phase SrFeO_{3-y} has shown that ordering of oxygen vacancies takes place to a degree which depends upon both the thermal history and the oxygen content of a given sample (16). Moreover the phase has very unusual magnetic properties. In an attempt to gain further information about this unique system, the $\text{SrCo}_x\text{Fe}_{1-x}\text{O}_{3-y}$ phase was studied by X-ray and Mössbauer spectroscopy using samples which had been slowly cooled in air to effect maximum oxidation (17). In view of the existence of $\text{Sr}_2\text{Fe}_2\text{O}_5$ and $\text{Sr}_2\text{Co}_2\text{O}_5$ it seemed likely that a composition $\text{Sr}_2\text{CoFeO}_5$ should also be a brownmillerite. In this event, preparation of this phase proves more difficult than expected.

$\text{Sr}_2\text{Co}_2\text{O}_5$ can be prepared by quenching from 1200°C in air. $\text{Sr}_2\text{Fe}_2\text{O}_5$ cannot be quenched in this way without oxidation, but can be heated at the same temper-

ature under argon to give the stoichiometric oxide. The initial preparation of "Sr₂CoFeO₅" which was quenched in air from 1200°C was a hard, black, well-sintered material (designated here as sample A). Chemical analysis gave the formulation to be Sr₂CoFeO_{5.27}, indicating a significant degree of oxidation to Co⁴⁺ or Fe⁴⁺. The X-ray powder pattern could be interpreted on the basis of a superposition of the pattern for a brownmillerite upon that for a cubic perovskite. It therefore seemed logical to conclude that the preparation was a two-phase mixture.

However, examination of the Mössbauer spectrum as a function of temperature (Fig. 1) revealed a far more subtle and interesting situation. At 290 K, the spectrum shows the characteristic 12-line hyperfine pattern

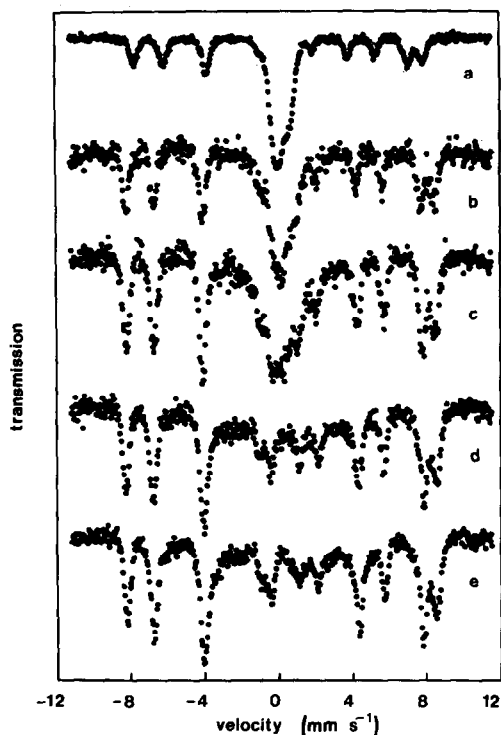


FIG. 1. The ⁵⁷Fe Mössbauer spectra of sample A (Sr₂CoFeO_{5.27}, quenched in air from 1200°C) at (a) 290 K, (b) 148 K, (c) 116 K, (d) 86 K, and (e) 78 K.

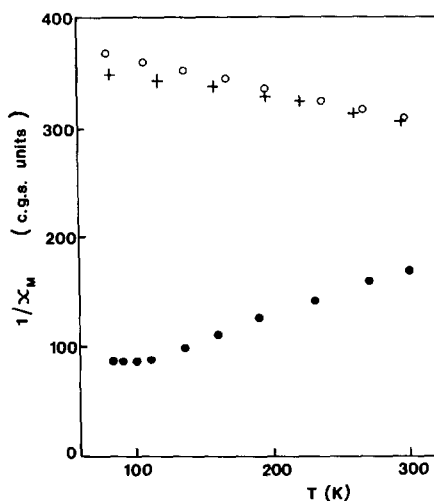


FIG. 2. The reciprocal magnetic susceptibility, $1/\chi_M$ in cgs units versus temperature for sample A, Sr₂CoFeO_{5.27} (filled circles), sample B, Sr₂CoFeO_{5.00} (crosses), and sample C, Sr₂CoFeO_{5.02} (open circles).

from an antiferromagnetic brownmillerite superimposed upon a central paramagnetic component which one could assign to a perovskite-like phase (17). However, below 150 K the brownmillerite pattern was seen to increase in intensity by a factor of two (i.e., by much more than can be simply explained in terms of an increase in recoilless fraction) at the expense of the paramagnetic component, until at 78 K it had become dominant. A degree of "baseline curvature" still remains at 78 K, the origin of which will be discussed later. The behavior is remarkably similar to the data (18) for ultra-fine particle α -Fe₂O₃ where superparamagnetism causes spectral collapse, although in the present case there can be no question of small particle sizes in the sintered pellet. However, this has led us to consider the possibility that our sample consists wholly of microdomains, of varying size, of brownmillerite, rather than being a two-phase mixture. We shall return to this aspect later. The magnetic susceptibility data are shown in Fig. 2. The reciprocal

susceptibility reaches a minimum at 120 K which is also consistent with the Mössbauer data, in that the central component has disappeared from the latter at this temperature.

Clearly a primary objective was to produce a material without oxidation, and it was found that this could be achieved in more than one way. A further sample was quenched from 1200°C into liquid nitrogen (sample B). The chemical analysis was $\text{Sr}_2\text{CoFeO}_{5.00}$ and the X-ray powder pattern could be indexed as a brownmillerite with $a = 5.49(1)$, $b = 15.67(2)$, $c = 5.63(1)$ Å. The Mössbauer spectrum at 290 K was now that of a "clean" antiferromagnetic brownmillerite pattern (Fig. 2, sample A). The hyperfine parameters are listed in Table 1. The magnetic flux density, B , the isomer shift, δ , and the quadrupole perturbation parameter, ϵ , are very similar to the values recorded previously (13) for $\text{Sr}_2\text{Fe}_2\text{O}_5$ and $\text{Sr}_2\text{Co}_2\text{O}_5$. The magnetic flux density at 290 K is comparable to the values for $\text{Sr}_2\text{Fe}_2\text{O}_5$ ($T_N = 700$ K) and $\text{Sr}_2\text{Co}_2\text{O}_5$ ($T_N = 570$ K) and suggests that the Néel temperature of this sample is similarly high. The area of the tetrahedral site pattern was 53% of the total, compared to 52% obtained from the equivalent spectrum for $\text{Sr}_2\text{Fe}_2\text{O}_5$. A small deviation from 50% can be explained in terms of a small difference in the recoilless fraction at the two sites. It can therefore be concluded that the equilibrium

phase of $\text{Sr}_2\text{CoFeO}_5$ at 1200°C is a fully reduced brownmillerite phase with cobalt and iron distributed randomly over the octahedral and tetrahedral sites. This disorder will be a contributing factor to the broad linewidths (~ 0.46 mm sec⁻¹) which are observed in this sample. The magnetic susceptibility (Fig. 2) is low and nearly temperature independent, consistent with an antiferromagnetic material well below the Néel temperature. Quenching samples from 1000 and 1100°C into liquid nitrogen resulted in material which showed a small degree of oxidation, suggesting that the equilibrium phase in air at these temperatures contains an oxygen excess.

A third sample (C) was obtained by re-annealing sample A under argon at 800°C for 7 days to give a composition of $\text{Sr}_2\text{CoFeO}_{5.02}$ with substantial loss of oxygen. X-ray analysis gave a brownmillerite pattern with $a = 5.50(1)$, $b = 15.62(2)$, $c = 5.61(1)$ Å. The difference in lattice parameters between samples B and C is not significant. The magnetic susceptibility data (Fig. 2) were also basically similar. The Mössbauer spectrum at 290 K (Fig. 3b) was also that of an antiferromagnetic brownmillerite, but with a significant reduction in the area of the tetrahedral site sextet to 38%. This implies that, perhaps surprisingly, at lower temperatures the Co^{3+} orders selectively onto the tetrahedral sites. We were unable to quench samples under argon, and cannot therefore be certain that this represents the true equilibrium sample at exactly 800°C. A sample annealed at 800°C under argon for 2 days (to assist in oxygen loss) and then at 700°C under argon for 4 days was not significantly different, but the diffusion rates of cations will be significantly reduced at this temperature. It does not seem possible to prepare a fully ordered $\text{Sr}_2\text{CoFeO}_5$ phase by this method.

A preparation at 1200°C under argon (sample D) gave $\text{Sr}_2\text{CoFeO}_{4.84}$ which

TABLE I
⁵⁷Fe MÖSSBAUER PARAMETERS AT 290 K

Compound	Site	B (T)	δ (mm sec ⁻¹)	ϵ (mm sec ⁻¹)	% Area
$\text{Sr}_2\text{Fe}_2\text{O}_5$	O	50.1	0.37	-0.35	48
	T	42.2	0.17	0.30	52
$\text{Sr}_2\text{Co}_2\text{O}_5$	O	46.9	0.33	-0.29	51
	T	39.9	0.18	0.16	49
$\text{Sr}_2\text{CoFeO}_5$ (sample B)	O	48.0	0.36	-0.35	47
	T	40.6	0.16	0.24	53
$\text{Sr}_2\text{CoFeO}_5$ (sample C)	O	48.1	0.36	-0.36	62
	T	40.7	0.17	0.21	38

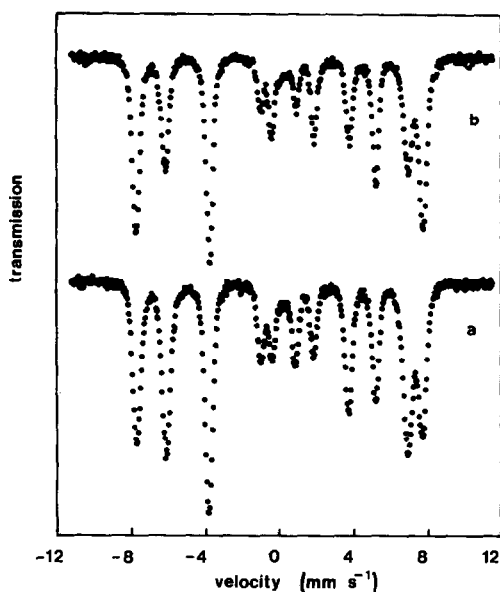


FIG. 3. The ^{57}Fe Mössbauer spectra at 290 K of (a) sample B, $\text{Sr}_2\text{CoFeO}_{5.00}$ quenched in liquid nitrogen from 1200°C , and (b) sample C, $\text{Sr}_2\text{CoFeO}_{5.02}$ annealed under argon at 800°C for 7 days.

showed a broadened X-ray pattern basically similar to a brownmillerite. The Mössbauer spectrum at 290 K was still a magnetic pattern but with drastically broadened lines. This is presumably an oxygen-deficient brownmillerite due to reduction to Co^{2+} ($\text{Sr}_2\text{Fe}_2\text{O}_5$ does not reduce significantly under these conditions), but cannot be profitably examined further by these techniques. It was also noticed that sample D was not stable over long periods at room temperature, there being major changes in the Mössbauer spectrum of the absorber after a lapse of some weeks.

A sample annealed at 900°C under argon (sample E) was also substoichiometric, $\text{Sr}_2\text{CoFeO}_{4.93}$, but the X-ray and Mössbauer data were more representative of a brownmillerite. The area of the tetrahedral site pattern was 48%, indicating a more random distribution than that found after annealing at 800°C under argon. However, the added complication of nonstoichiome-

try makes it difficult to carry out any thermodynamic investigation of the cation redistribution process.

We shall now discuss the evidence for the existence of microdomains in sample A quenched in air from 1200°C . In magnetically ordered solids, the strong spin-exchange interactions result in an average value of the spin $\langle S_z \rangle$ along the direction of magnetisation z which has a long relaxation time ($\gg 10^{-7}$ sec) because the cooperative interactions are long-range. In the Mössbauer spectrum the result is a static hyperfine splitting at all temperatures below the ordering temperature. However $\langle S_z \rangle$ is not strictly a static quantity and within each magnetic domain fluctuates with a relaxation time $\tau = \tau_0 \exp(KV/kT)$ where kT is the thermal energy, V is the volume of the domain, and K is the energy per unit volume (19). Thus the relaxation time can be decreased by decreasing the volume of the domain or by raising the temperature. If $\tau = 10^{-7}$ sec then a partial collapse of the Mössbauer hyperfine splitting occurs, and there is total collapse if $\tau \ll 10^{-7}$ sec. The classic demonstration of this is in fine-particle oxides where particle sizes of $< 200 \text{ \AA}$ can cause such a collapse (18), although the finer details of the relaxation are often obscured by a distribution in particle size and a consequent distribution in the relaxation time. The presence of microdomains in the brownmillerite lattice with a size of $< 200 \text{ \AA}$ may be expected to result in relaxation effects in an exactly analogous way. Furthermore, the X-ray diffraction pattern of such a material will show an apparent cubic symmetry because the scattering experiment takes a spatial average over $\sim 200 \text{ \AA}$.

There is much good evidence for the existence of microdomains in this type of oxide, although Mössbauer spectroscopy has not often been used in their characterization. Alario-Franco *et al.* (20) observed a microdomain texture in the solid solution

$\text{Sr}_x\text{Nd}_{1-x}\text{FeO}_{3-y}$ reduced in argon. The X-ray diffraction pattern appeared cubic, but the electron diffraction data showed the existence of tetragonal microdomains intergrown in three dimensions with an average size of about $(50 \text{ \AA})^3$. The compound $\text{Ca}_2\text{LaFe}_3\text{O}_8$ has a structure which is ideally an intergrowth of the perovskite and brownmillerite structures such that layers of cations in tetrahedral coordination alternate with two layers of cations in octahedral coordination. Annealing at 1400°C in air and then quenching produced an oxidized material which was cubic to X-rays, but electron diffraction data including electron micrographs revealed the existence of a three-dimensional intergrowth of microdomains of the parent phase (21). It was also suggested that the oxygen excess in this material is accommodated within the domain walls, i.e., the smaller the domains the greater will be the oxygen excess. In the calcium-rich solid solution, $\text{Ca}_{1-x}\text{La}_x\text{FeO}_{3-y}$, the reduced samples show a disordered intergrowth of the $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Ca}_2\text{LaFe}_3\text{O}_8$ compositions such that local compositions are very heterogeneous, and a variable amount of oxygen deficiency can be accommodated as the Ca/La ratio changes. In the oxidized samples quenched from high temperature, brownmillerite-type microdomains were observed with a size of $\sim(100 \text{ \AA})^3$. The micrographs show a regular fringe separation within each microdomain, and oxygen excess is believed to be in the domain walls (22). The $\text{CaFe}_x\text{Mn}_{1-x}\text{O}_{3-y}$ solid solution shows even more complex behavior with six or nine sets of microdomains observed by intergrowth of $\text{Ca}_2\text{Fe}_2\text{O}_5$ -like domains and CaMnO_3 -like domains (23, 24). The temperature dependences of the Mössbauer spectrum and the magnetic susceptibility of the composition $\text{Ca}_3\text{Mn}_{1.35}\text{Fe}_{1.65}\text{O}_{8.02}$ (25) are very similar to those of $\text{Sr}_2\text{CoFeO}_5$, although Nguyen *et al.* chose to explain their results by invoking the phenomenon of magnetic frustration,

rather than microdomain formation. Finally, the brownmillerite $\text{Sr}_2\text{Fe}_2\text{O}_5$ has been observed to show a cubic X-ray pattern above 850°C , and a structural model has been proposed in terms of microdomain formation, but without oxygen excess in the domain walls (14).

There is very clear evidence for microdomains in the electron micrographs of several of these materials which are all structurally related to $\text{Sr}_2\text{CoFeO}_5$. We are confident that the Mössbauer spectroscopic data for the partially oxidized sample A also show the existence of microdomains in this system. The apparent mixed cubic/brownmillerite X-ray pattern, together with the Mössbauer data, suggest a domain size of $\sim(150\text{--}250 \text{ \AA})^3$. However, the spectra of the fully reduced samples quenched in liquid nitrogen (B) and annealed at 800°C in argon (C) show no evidence for relaxation effects even at 290 K, and the X-ray patterns are those of a highly crystalline brownmillerite; it may thus be presumed that the effective domain size in these samples is $\gg(200 \text{ \AA})^3$. This would suggest that the microdomains in sample A are produced by the accommodation of excess oxygen in the domain walls, i.e., the microdomains are produced during the diffusion of oxygen into the lattice during quenching, and are therefore not in thermodynamic equilibrium with the phase. In view of this conclusion, it is necessary to question whether the microdomains produced in some of the other systems are in true thermodynamic equilibrium at high temperatures, or whether they are an artifact of oxidation during quenching.

A second pellet of " $\text{Sr}_2\text{CoFeO}_5$ " quenched in air from 1200°C was examined. About 20 mg was carefully scraped off from the surface of a 2-g pellet to give a Mössbauer sample representative of the surface layer (sample F). The pellet was then abraded to about half its original size, and then powdered to give a sample representa-

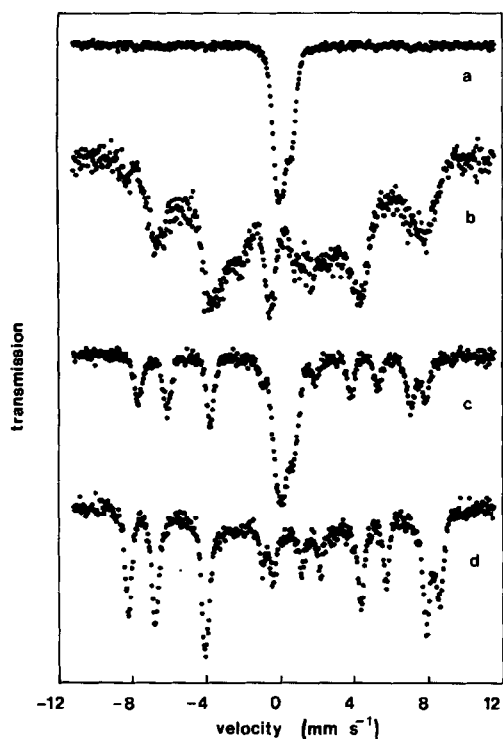


FIG. 4. The ^{57}Fe Mössbauer spectra of a pellet quenched in air from 1200°C : a surface sample F at (a) 290 K and (b) 78 K and the inside sample G at (c) 290 K and (d) 78 K.

tive of the inner region (sample G). Both samples were examined by Mössbauer spectroscopy (Fig. 4). Sample G proved to be very similar to sample A, confirming that the earlier data were closely representative of the bulk, and that microdomains permeated the whole pellet. The main difference seems to be a greater brownmillerite component in the spectrum of sample G at 290 K, which is consistent with larger microdomains in the center of the pellet. The surface sample (F) proved to contain much less brownmillerite and showed that oxidation at the immediate surface produced a new phase, presumably a perovskite. The Mössbauer spectrum at 290 K still shows faint traces of brownmillerite. The spectrum at 78 K is a diffuse magnetic pattern,

but with distinct features which are not apparent in the equivalent spectrum from samples A and G. The diffuse background to the 78 K spectra of both these samples can be attributed to the iron cations in the domain walls. As the domain size decreases below $(200 \text{ \AA})^3$ the proportion of cations in the walls increases rapidly. Estimates based on a simple model show that cubes of volume $(50, 100, 200 \text{ \AA})^3$ have 39, 21, 11% of the cations at the surface of the cube, respectively. The spins of these cations will not be strongly coupled to any particular domain and can be predicted to contribute a broad relatively featureless background to the spectrum at 78 K as indeed is observed in Figs. 1 and 4. Furthermore, if the electron deficit is also accommodated on these cations, the maximum value of the mag-

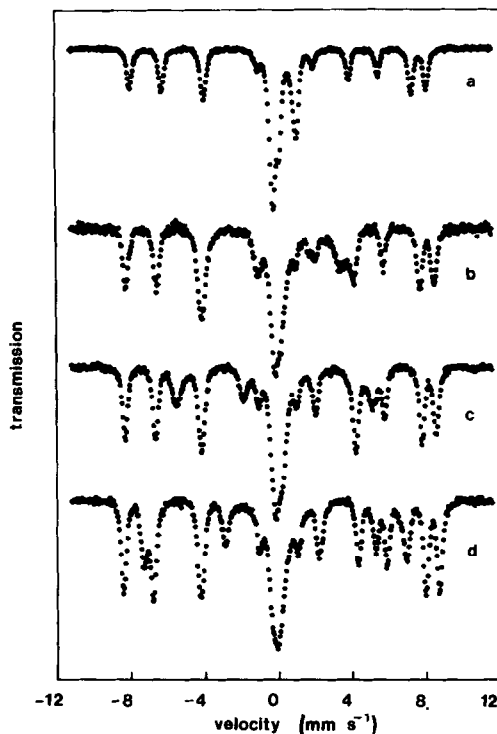


FIG. 5. The ^{57}Fe Mössbauer spectra of a preparation of $\text{Sr}_2\text{Fe}_2\text{O}_5$ quenched in air from 1200°C at (a) 290 K, (b) 210 K, (c) 180 K, and (d) 78 K.

netic hyperfine field which they can produce will be significantly less than in the brownmillerite bulk.

The compound $\text{Sr}_2\text{Fe}_2\text{O}_5$ also shows substantial oxidation when quenched in air from 1200°C with an X-ray pattern very similar to that of sample A. However, an examination by Mössbauer spectroscopy has found no evidence for microdomain behavior. Typical spectra are shown in Fig. 5, and by comparison with earlier work on this phase (16) it can be seen that the data are consistent with a two-phase perovskite + brownmillerite reaction product. In particular, the increase in intensity of the brownmillerite component with decreasing temperature is small enough to be compatible with an increase in the recoilless fraction; the perovskite phase becomes magnetic below ~210 K and produces new hyperfine lines which are clearly visible, and there is no evidence for any diffuse components in the background.

Acknowledgments

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