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# The Structural Consequences of Charge Disproportionation in Mixed-Valence Iron Oxides. II. The Crystal and Magnetic Structures of $BaLaFe_2O_{5.91}$ at 5 K

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The crystal structure of the low temperature antiferromagnetic phase of the cubic perovskite $BaLaFe_2O_{5.91}$ has been refined from neutron powder diffraction data collected at 5 K. Space group $Pm\bar{3}m$, $a = 3.9268(1)$ Å. The magnetic structure is consistent with a simple G-type antiferromagnetism but with an unusually low average magnetic moment of 1.87 $\mu_B$ per Fe atom. An interpretation of the structural and magnetic data is proposed in terms of a charge disproportionation and the simultaneous formation of a charge density wave and a spin density wave, but without any structural distortion. The spin system is envisaged as a random arrangement of cations, nominally $Fe^{3+}$ and $Fe^{5+}$ in a 3 : 1 ratio, with antiferromagnetic coupling between pairs of like atoms, and ferromagnetic coupling between unlike atoms. The compound can thus be described as a Mattis spin glass. © 1990 Academic Press, Inc.

## Introduction

The iron-bearing perovskites which contain oxidation states of iron greater than +3 are of considerable interest because of their unusual electronic properties. The cubic perovskite $SrFeO_3$ is a metallic oxide which orders antiferromagnetically at 134 K, and the $e_g^*$ orbitals of the nominally high-spin $Fe^{4+}$ ion are broadened into an itinerant electron band (*1*). Mössbauer spectroscopy confirms (*2*) that all iron sites are electronically equivalent above 4.2 K. In contrast the structurally related material $CaFeO_3$ which is a paramagnetic $Fe^{4+}$ oxide at 290 K shows a charge disproportionation at lower temperatures, finally becoming antiferromagnetic below 116 K (*3, 4*) with two electronically inequivalent iron sites present in equal proportions. Subsequent work on related solid solutions (*5*) has shown that in general the charge states of the low temperature species are nonintegral, and that the charge disporportionation can be represented as

$$2Fe^{4+} \rightleftharpoons Fe^{(4-\lambda)+} + Fe^{(4+\lambda)+}, \quad 0 \leq \lambda \leq 1.$$

In a recent paper (*6*) we described a study of $Sr_2LaFe_3O_{8.94}$, and obtained for the first time the crystal and magnetic structures in both the paramagnetic averaged valence and antiferromagnetic mixed-valence phases of a material showing charge disproportionation. The crystal structure of the distorted perovskite was refined from powder neutron diffraction data in the rhombohedral space group $R\bar{3}c$ in both cases; the magnetic structure was refined in $P\bar{3}m1$ using a model derived from considerations of the exchange interactions between ideal lo-

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calized $Fe^{3+}$ and $Fe^{5+}$ electron configurations. The results were interpreted in terms of a charge density wave (CDW) and spin density wave (SDW), both commensurate with the crystal lattice and both propagating along the [111] axis of the rhombohedral crystal so as to produce two distinct iron sites. Surprisingly, there was no evidence for any periodic structural distortion (PSD) accompanying the CDW, the structure in the antiferromagnetic mixed-valence phase retaining the same symmetry as the paramagnetic averaged-valence phase. It was suggested that the strain field produced by the CDW is perturbed by local variations brought about by the disordered arrangement of Sr and La and the oxygen vacancies, thereby preventing the cooperative PSD which would otherwise occur.

As part of a continuing investigation into charge disproportionation phenomena, we have carried out a structural characterization by neutron powder diffraction of the low temperature antiferromagnetic mixed-valence phase of $BaLaFe_2O_{5.91}$ which has been characterized earlier by Mössbauer spectroscopy in our laboratory (*7*). Samples made in the $Ba_{1-x}La_xFeO_{3-y}$ system remain cubic for $0.1 \leq x \leq 0.8$, and for large $y$ there is no evidence of the ordered-vacancy structures which exist for the Ca/La and Sr/La systems. The $x = 0.50$ composition was chosen for the present study because the low oxygen vacancy concentration and the comparatively narrow Mössbauer linewidths suggested that structural ordering might occur in the low temperature phase.

## Experimental

The methods of preparation, chemical analysis, and X-ray characterization of our sample of $BaLaFe_2O_{5.91}$ have been described previously (*7*), except that the 10-g sample for the neutron measurement was slow-cooled in oxygen rather than in air. Powder X-ray diffraction measurements indicated a single cubic perovskite unit-cell having $a_0 = 3.929$ Å. Neutron powder diffraction data were collected on the diffractometer D1a at ILL Grenoble, using a wavelength of 1.909 Å and a $2\theta$ step size of 0.05°. Data were collected over the angular range $0 < 2\theta < 156°$ at a temperature of 5 K using a 10-g sample contained in a vanadium can. The experiment lasted for ~11 hr. The low-angle section of the diffraction pattern was also recorded at room temperature for comparison purposes.

## Results

The limited neutron diffraction data collected at room temperature could be indexed in a primitive cubic unit cell with a unit cell parameter $a_0 \sim 3.93$ Å, in good agreement with the value determined in the preliminary X-ray characterization of the sample. However, extra peaks, which could be indexed in a face-centered cubic unit cell with $a_0 = 7.8535(1)$ Å, were apparent in the data collected at 5 K. All data analysis was carried out by the Rietveld method (*8*) using the following neutron scattering lengths: $b_{Ba} = 0.52$, $b_{La} = 0.83$, $b_{Fe} = 0.95$, $b_O = 0.58 \times 10^{-12}$ cm. The background level was interpolated between regions where there were no Bragg peaks, and the statistical variations in the background were taken into account in assigning a weight to each profile point. The Bragg peaks were assumed to have a Gaussian profile. In our preliminary refinements of the low temperature structure, we used various space groups in order to allow for the possibility that the additional Bragg scattering stems, at least in part, from a cooperative displacement of the anions. Such displacements would lead to the creation of crystallographically distinct six-coordinate sites for the transition metal, in some cases in the ratio 3 : 1 as suggested by the Mössbauer results reported previously (*7*). We also allowed for the possibility that the ad-

TABLE I

STRUCTURAL PARAMETERS FOR $BaLaFe_2O_{5.91}$ AT 5 K (SPACE GROUP $Pm\bar{3}m$)

| Atom | Site | $x$ | $y$ | $z$ | $B_{iso}$(Å$^2$) |
|---|---|---|---|---|---|
| Ba/La | 1b | ½ | ½ | ½ | 0.17(3) |
| Fe | 1a | 0 | 0 | 0 | 0.12(3) |
| O | 3d | ½ | 0 | 0 | 1.14(3) |

*Note.* $a_0$ = 3.9268(1) Å. $\mu_{Fe}$ = 1.87(2) $\mu_B$.

ditional peaks were due to magnetic scattering; again consistent with the Mössbauer data. It became clear from our refinements that there are no cooperative anion displacements in this compound at low temperatures and that the additional scattering is solely magnetic in origin. We therefore proceeded to refine the crystal structure in space group $Pm\bar{3}m$ with only one variable structural parameter, the isotropic temperature factor, for each atom. The anion site occupancy was fixed at unity, the actual vacancy concentration (1.5%) being too small to be refined using our data. The La and Ba atoms were assumed to be completely disordered over the A sites of the perovskite structure.

The observed magnetic scattering was consistent with the adoption of a G-type magnetic structure in which each iron atom on the simple cubic transition metal sublattice is coupled antiferromagnetically to its six nearest neighbors. This was modeled by including the magnetic moment of the iron atom as a variable parameter in the structure refinement. Initially the angular dependence of the magnetic scattering length was approximated by the $Fe^{3+}$ form factor calculated by Watson and Freeman (*9*), but during the final stages of the refinement this curve was expanded empirically to give a better fit to the data at high $Q$. This structural model refined to give an agreement index $R_{wpr}$ = 10.2% ($R_{exp}$ = 2.9%, $R_{nuc}$ = 3.2%, $R_{mag}$ = 21.5%). The final parameters are listed in Table I and the corresponding bond lengths are given in Table II. The observed and calculated diffraction profiles, and their difference, are plotted in Fig. 1.

## Discussion

The crystal structure of $BaLaFe_2O_{5.91}$ at 5 K is that of a simple cubic perovskite with a small concentration of vacancies on the anion sublattice. All the iron cations occupy crystallographically equivalent sites, and bond length–bond strength calculations (*10*) suggest that an Fe–O distance of 1.963 Å represents an average cation valency of 3.42, in excellent agreement with the value of 3.41 predicted from the stoichiometry of our sample. The O–O distance of 2.777 Å is within the range of values expected for a cubic perovskite. The crystal structure is thus apparently consistent with the existence of an averaged-valence state, $Fe^{3.41+}$, over the B sublattice of the perovskite structure. The adoption of a G-type magnetic structure in such a compound is in itself unremarkable. However, the magnitude of the ordered magnetic moment of the iron cations is unusually low, and suggests that the simple model described above may be too naive. In order to achieve a satisfactory description of this compound it is necessary to consider the diffraction data and the Mössbauer data together.

In our earlier work (*7*) it was clearly shown that the cubic $Ba_{1-x}La_xFeO_{3-y}$ system shows a charge disproportionation at low temperatures. The particular results for a sample of composition $BaLaFe_2O_{5.94}$ are

TABLE II

BOND LENGTHS (IN Å) IN $BaLa_2O_{5.91}$ AT 5 K

| | |
|---|---|
| Fe–O | 1.963 |
| Ba/La–O | 2.777 |
| O–O | 2.777 |

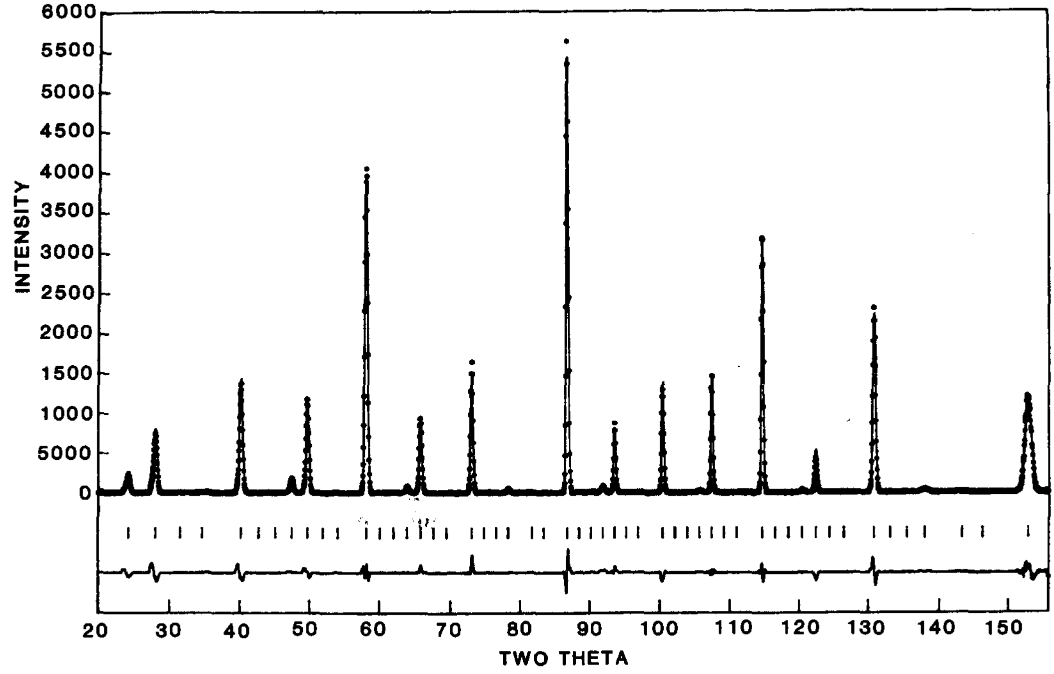

FIG. 1. The observed (. . .), calculated (—), and difference neutron diffraction profiles for BaLa $Fe_2O_{5.91}$ at 5 K.

most relevant to the present work. At 4.2 K the Mössbauer spectrum comprises two magnetic hyperfine sextets with flux densities of 51.0 and 27.1 T with areas in the ratio 78 : 22, i.e., in excellent agreement with the predicted $Fe^{3+}/Fe^{5+}$ ratio for this composition. With increase in temperature the spectrum shows progressive relaxational collapse above 150 K until the magnetic hyperfine splitting disappears at ca. 250 K. Above this temperature the spectrum still shows unresolved structure, and it was established that the $Fe^{3+}/Fe^{5+}$ species (ratio 78 : 22) have been replaced by a new arrangement of charges best described as $Fe^{3+}/Fe^{4+}$ (ideal ratio 56 : 44); i.e., there is an effective change in the oxidation states. It seems possible that the onset of magnetic order and the charge disproportionation are interconnected, but this has not been verified.

The Mössbauer evidence described above shows that all sites are not in fact magnetically equivalent, and that our analysis of the neutron data using only one average moment is indeed an oversimplification. After allowing for the effects of covalency in the Fe–O bonds, the ordered moment for the $Fe^{3+}$ cation (with localized electrons) might be expected to lie between 3.9 and 4.5 $\mu_B$; that at an $Fe^{5+}$ cation might be expected to lie between 2.0 and 2.3 $\mu_B$. These values do not lead to an average of 1.87 $\mu_B$ per cation when used in the appropriate 3 : 1 ratio in a G-type ordering scheme. However, the value can be rationalized by invoking ferromagnetic coupling along 180° superexchange pathways between cations having the nominal electronic configurations $Fe^{3+} : 3d^5$ and $Fe^{5+} : 3d^3$ (*11*). Similar ferromagnetic coupling was seen in $Sr_2LaFe_3O_{8.94}$, where the observed moments of 3.61 and 2.72 $\mu_B$ are consistent with the existence of nonintegral charge states. Thus we envisage the transition-metal arrangement in $BaLaFe_2O_{5.91}$ as a random distribution of cations, nominally $Fe^{3+}$ and $Fe^{5+}$ in a 3 : 1 ratio, over the sites of a primitive cubic sublattice. This nonfrustrated spin system will have antiferromagnetic coupling between neighboring pairs of like atoms and ferromagnetic coupling between "$Fe^{3+}$" and "$Fe^{5}$" neighbors; thus $BaLaFe_2O_{5.91}$ can be described as a Mattis spin glass (*12*). The magnitude of the average magnetic moment at any site would be expected to be approximately $[(3 \times 4\mu_B) - (1 \times 2.5\ \mu_B)]/4$, that is ca. 2.4 $\mu_B$, and to have the direction that the moment of the majority species ($Fe^{3+}$) would take at that site. Thus in a diffraction experiment we would expect to see a G-type ordering with an anomalously low magnetic moment per cation. The observed moment of 1.87 $\mu_B$ is presumably reduced below the predicted value by local spin misalignments or some other form of departure from idealized behavior.

This model, based on a disordered distribution of $Fe^{3+}$ and $Fe^{5+}$, is consistent with the Mössbauer data in that the spectra recorded for $Ba_{1-x}La_xFeO_{3-y}$ at 4.2 K are in general broader than the spectrum of $Sr_2LaFe_3O_{8.94}$, which has an ordered charge distribution. The somewhat high temperature factor found for the oxide ions may be indicative of local anion displacements, in turn brought about by local ordering of the different charge states of iron. It may, however, also reflect the presence of vacancies on the anion sublattice. These vacancies may also be responsible for the electron trapping in the room temperature paramagnetic Ba phase, a feature which was not found in the averaged valence phase of $Sr_2LaFe_3O_{8.94}$ itself, but was clearly observed at higher vacancy concentrations.

The barium system shows some significant differences compared to $Sr_2LaFe_3O_{8.94}$ which was the subject of Part I of this series (*6*). At room temperature, where neither material is magnetically ordered, all the iron sites in the rhombohedrally distorted Sr phase are electronically equivalent in the Mössbauer spectrum, whereas in the cubic Ba phase this is clearly not the case. In the low temperature Sr phase showing charge disproportionation, the hyperfine parameters for the $Fe^{3+}$ site are clearly anomalous (*6*) for a localized-electron configuration in six-coordination: this together with the observed ordered spin structure leads easily to an interpretation embodying a charge density wave and spin density wave propagating through the crystal and so effectively producing nonintegral oxidation states. However, at 4.2 K the hyperfine parameters for the Ba phase, and in particular the flux density of 51 T at the $Fe^{3+}$ site, are much closer to expectation (54–56 T) for a fully localized electronic system. Nevertheless, if a linear correlation of electron charge and flux density is assumed between $Sr_2Fe_2O_5$ ($Fe^{3+}$) and $SrFeO_3$ ($Fe^{4+}$) then the "$Fe^{3+}$" site in $BaLaFe_2O_{5.940}$ has an actual charge of ca. +3.14, and hence the actual charge on the "$Fe^{5+}$" site is only ca. +4.5. A similar calculation for the two flux densities (41.6 and 27.9 T) in $CaFeO_3$ (*3, 4*) gives actual charges of ca. +3.4 and +4.6, respectively. Note that the Mössbauer parameters for "$Fe^{5+}$" in $CaFeO_3$ and $BaLaFe_2O_{5.940}$ are very similar as are the calculated charges; it is the charge density at the "$Fe^{3+}$" site which changes significantly between the two compounds. These observations give us grounds to believe that all these charge disproportionation systems should be treated in CDW/SDW terms. Neither the Ba nor Sr charge disproportionation phases show any evidence for a periodic structural distortion. In both cases the disorder at the A sites may well introduce local lattice strains which prevent the development of a cooperative PSD.

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