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A High-Resolution Electron Microscopic Study of Some Members of the Vernier Structural Series $Ba_p(Fe_2S_4)_q$

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$BaFe_2S_4$ and $Ba_{13}(Fe_2S_4)_{12}$ have been imaged at high resolution in an electron microscope. Agreement between observed and calculated images for $BaFe_2S_4$ is good. Marked heterogeneity exists in all the specimens observed and sharp unit cell boundaries are not observed. Rather, there are broad, wavy fringes suggesting that these structures should be thought of as a solid solution of moderately ordered structures. © 1986 Academic Press, Inc.

Introduction

The infinitely adaptive series $Ba_{1+x}Fe_2S_4$ or $Ba_p(Fe_2S_4)_q$ was initially investigated by Grey (*1, 2*) in 1974. More recently, this nonstoichiometric series has been studied by X-ray diffraction (*3, 4*) and electron diffraction and electron microscopy (*5, 6*). Based on X-ray powder diffraction results, an ordered "vernier" structure was postulated for members of the series within the composition range $0.072 \leq x \leq 0.142$ (*1–4*). One subcell of the "vernier" structure is composed of columns of Ba ions while the other consists of chains of edge-sharing tetrahedra. A superstructure is formed at the point of registration of the two tetragonal subcells. This type of structural problem has been investigated as in the case of $MnSi_{1+x}$ (*7–9*) or $Rh_{17}Ge_{22}$ (*10*). $Ba_{1+x}Fe_2S_4$ is particularly intriguing with respect to structure due to the results of various measurements of physical properties. Magnetic susceptibility and electronic properties indicate semiconductor-type behavior in the parent compound β-$BaFe_2S_4$ ($x = 0$) while the $x \neq 0$ members exhibit metallic behavior (*11*). In addition, Mössbauer spectra show only a single averaged Fe valence state over the entire crystal which varies slightly depending on the value of x (*11*). A clear picture of the structures should provide insight into designing compounds with desired electronic properties. Sample preparation variables were examined including annealing temperature and time (*12, 13*). Two weeks at temperatures of 700–900°C were judged appropriate for the production of a single phase as determined by powder X-ray diffraction (*12*).

Electron diffraction patterns exhibit distinct periodicity corresponding to the supercell although disorder can be seen on close examination of the patterns (*5, 6*). Electron microscope images by contrast show a large amount of disorder in the supercell lattice fringes which are moiré-like in appearance (*5*). Structural details remain sketchy as no quantitative comparison of electron microscope images with images

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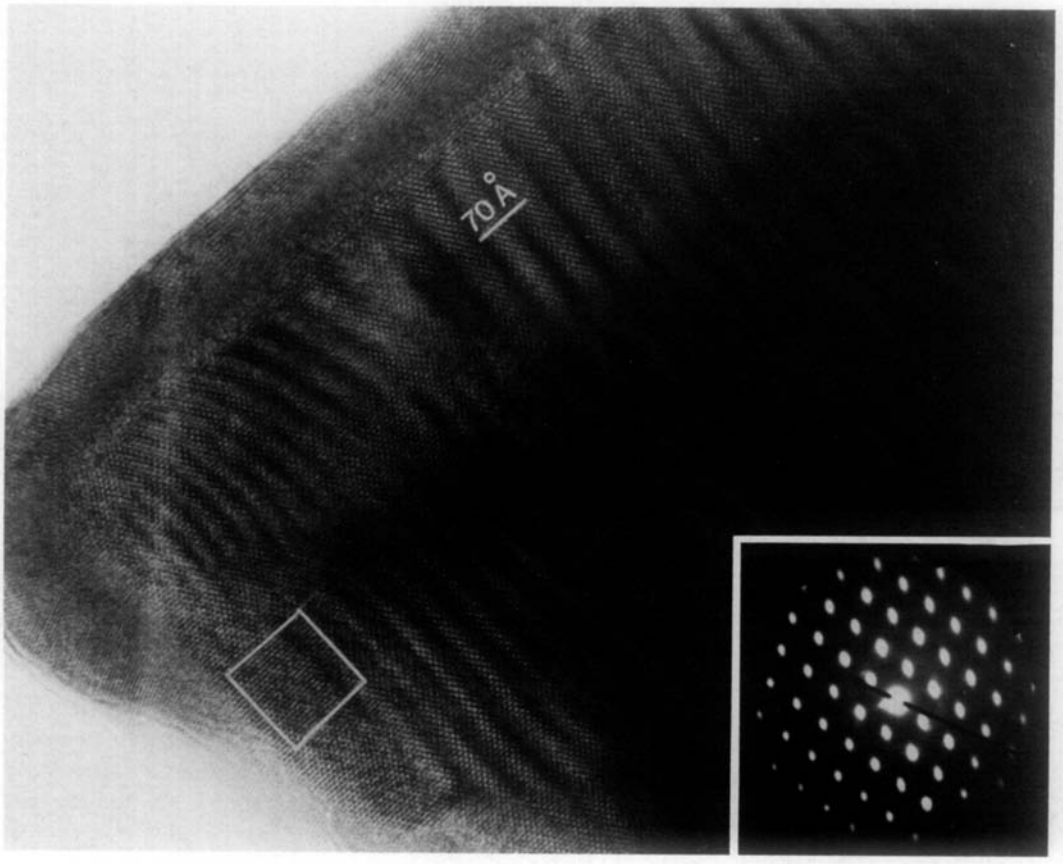

FIG. 1. Diffraction pattern and image of a sample of β-$BaFe_2S_4$. Notice the diffuse streaking along c^* in the diffraction spots that is reflected in the wavy moiré-like fringes with a spacing of 35 Å.

calculated from X-ray diffraction models have been made and the fit of the model to the X-ray diffraction data is only highly accurate in the case of β-$BaFe_2S_4$ (R = 3% versus R = 8–15% for $x \neq 0$ members studied) (*1–4*).

In this examination of the $Ba_{1+x}Fe_2S_4$ series, we have used electron diffraction and microscopy combined with lattice image simulations based on the X-ray diffraction structural models.

Experimental

Samples were prepared (*14*) and the value of x carefully determined from peak measurements on X-ray powder diffraction patterns (*2*). Sample compositions examined were $BaFe_2S_4$, $Ba_{1.083}Fe_2S_4$, $Ba_{1.086}Fe_2S_4$, and $Ba_{1.132}Fe_2S_4$. High-resolution lattice-structure images were obtained from a JEOL 200 CX electron microscope with a top entry tilting stage. Samples were ground with mortar and pestle, then dispersed in acetone. Holey carbon supported by a 3-mm copper grid was used for the sample support.

Calculations were performed on a "Comparitor" system described in detail by Rae Smith and Eyring (*15*). Electron diffraction patterns (EDP) and lattice images were generated using structural parameters deter-

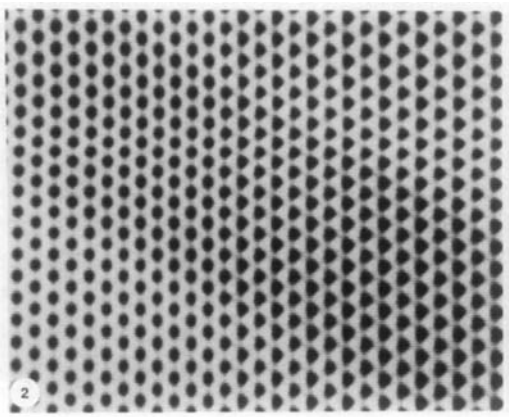

FIG. 2. The region in Fig. 1 marked by a rectangle has been digitized and compared with an image generated from the model obtained from X-ray diffraction. The match is considered quite satisfactory although it represents only a small region of the crystal.

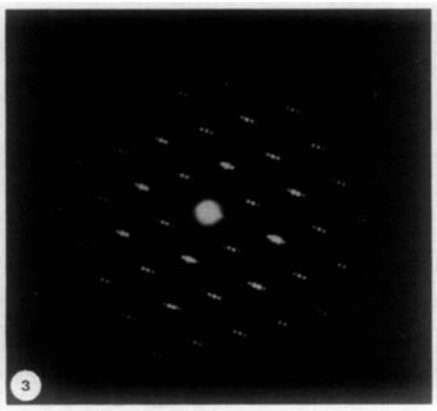

FIG. 3. An electron diffraction pattern of $Ba_{13}(Fe_2S_4)_{12}$ that shows both orientation and spacing anomalies. The loss of intensity in the superstructure spots away from the subcell spots results from the imperfect vernier structure.

mined by X-ray diffraction. These were compared with high-resolution images by digitizing portions of the electron micrograph (EM) negative with an autodensitometer (*15*). Image size was 256 × 256 pixels with a resolution of 0.003 cm in each direction.

Results

All samples exhibited inhomogeneity in the electron microscope images, including the $x = 0$ phase, β-$BaFe_2S_4$ (Fig. 1). [100] EDPs of β-$BaFe_2S_4$ clearly showed disorder along the c^* axis as diffuse diffraction

FIG. 4. A high-resolution image of $Ba_{13}(Fe_2S_4)_{12}$ showing the characteristic wavy form of the superstructure. β-$BaFe_2S_4$ is shown to be coherently intergrown.

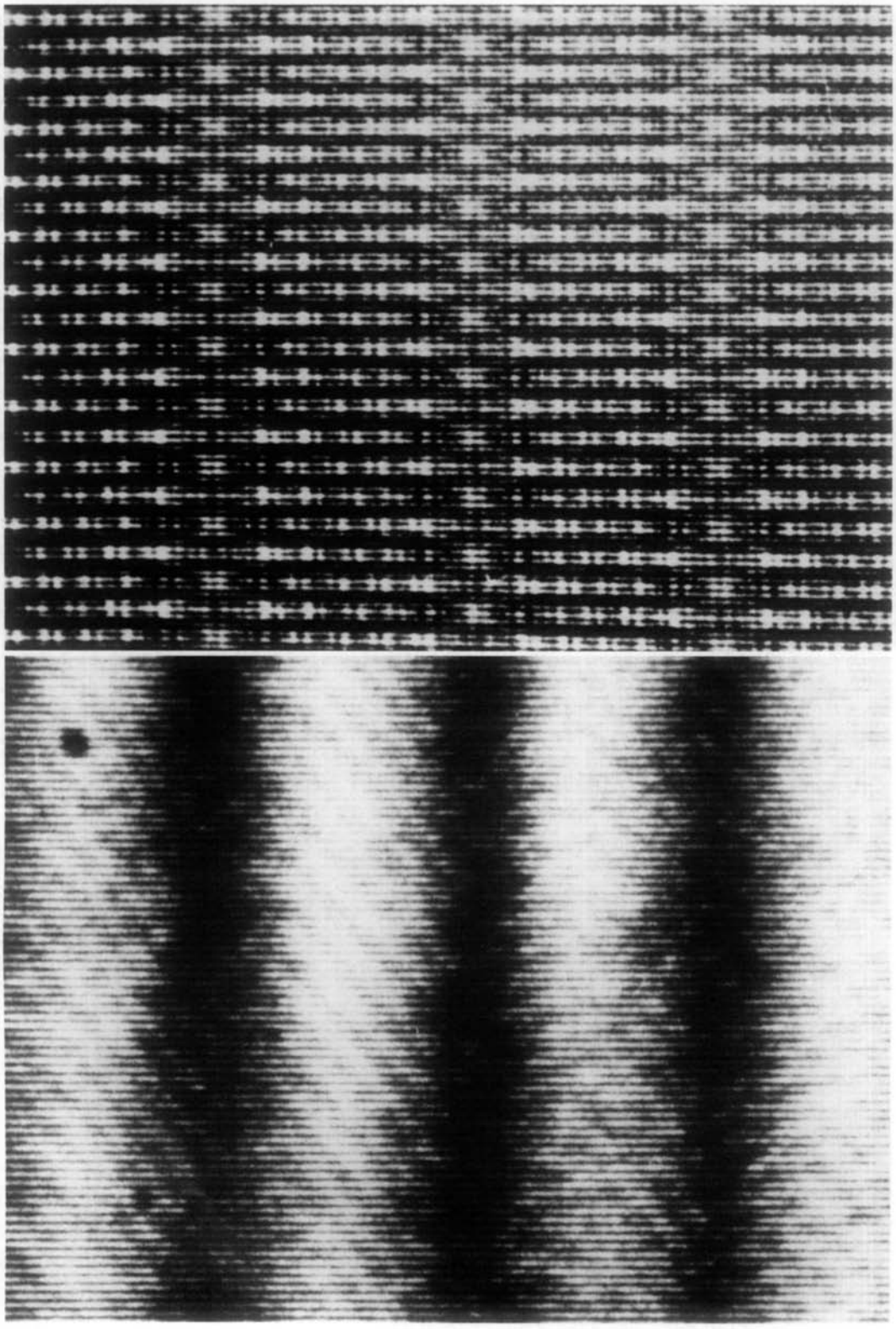

FIG. 5. A photographic match between the observed and calculated images of $Ba_{13}(Fe_2S_4)_{12}$. Numerical evaluation of the fit was not possible. Notice the difference in regularity between the two images suggesting the lack of uniformity of the vernier match.

spots (Fig. 1). The image exhibited disorder as well in the form of wavy, moiré-like fringes with a spacing of about 35 Å. The small square outlined on Fig. 1 was digitized and compared with an image generated from the X-ray diffraction model and appropriate imaging conditions. Figure 2 shows the good match found between the experimental and calculated images. Clearly this model is correct for only exceedingly small portions of the crystal, however.

Samples of $x \neq 0$ members exhibited two types of disorder in their EDPs. Figure 3 shows a [100] zone of $Ba_{13}(Fe_2S_4)_{12}$. Careful examination of the typical patterns of these materials revealed orientation anomalies where the c^* rows are tilted slightly from the vertical direction (e.g., groups of spots do not all lie on the same straight line) and spacing anomalies where mismatch or irregular spacings of the diffraction spots were observed. The loss of intensity of the superstructure spots between bright subcell spots indicated variations from a perfect vernier structure. As in the case of β-$BaFe_2S_4$ large fringes corresponding to the c axis of the supercell of $Ba_{13}(Fe_2S_4)_{12}$ are wavy in nature, Fig. 4. Coherent intergrowth of β-$BaFe_2S_4$ was observed in all samples. Attempts to compare model images with the experimental images were unsuccessful, even in the case of low-resolution images where a sufficient number of unit cells in the c axis direction were available to provide a diffractogram for indexing. The scale was adjusted photographically and thus a reasonable approximation of the structure was found using the X-ray diffraction model, Fig. 5. Numerical evaluation of the fit was not possible due to the manner in which the fit was made. The small fringes tilted a small angle from the c axis fringes represent the angular discrepancy of the (001) rows in the EDP. Attempts to do dark field imaging of the superstructure were unsuccessful due to the very low intensity of the supercell diffraction spots. Construction of a supercell of monoclinic symmetry did not make any significant change in the calculated images.

Discussion

The disorder in the images indicates local fluctuations in the composition and/or misalignment of the subcell units. The largest discrepancy is along the c axis. In all cases, EDPs have diffuse spots rather than distinct well ordered reciprocal lattice points. These observations are in agreement with previous electron microscopic studies (*5*, *6*). The good fit between experimental and calculated images for β-$BaFe_2S_4$ indicates the presence of small regions of order within the crystal. A proper description of the structure of these phases should refer to any crystal having a range of compositions. The accommodation of extra Ba ions in the supercell does seem to follow the general model as determined from X-ray diffraction but not in as ordered a fashion as the model suggests. It is perhaps more appropriate to describe this system as a solid solution of moderately ordered phases, where the overall or average composition determines the electrical and magnetic behavior of the sample.

Acknowledgments

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