

NOTES

Orientation Anomaly in the Electron Diffraction Patterns of $\text{Ba}_{1+x}\text{Fe}_2\text{S}_4$

$\text{Ba}_{1+x}\text{Fe}_2\text{S}_4$ is well known as an infinitely adaptive phase (1-3). Another notation for this compound is $\text{Ba}_p(\text{Fe}_2\text{S}_4)_q$, where p and q are integers, and the ratio of p/q is equal to $1+x$ in the notation $\text{Ba}_{1+x}\text{Fe}_2\text{S}_4$. The structure analyses of two members of the series, $\text{Ba}_5\text{Fe}_9\text{S}_{18}$ (2) and $\text{Ba}_9\text{Fe}_{16}\text{S}_{32}$ (3), have revealed that these have the "vernier" structure (4), i.e., there are two arrays, a Ba chain with c_1 unit length and an $(\text{FeS}_2)_x$ edge-shared tetrahedron chain with c_2 unit length along the c -axis. In the stoichiometric β - BaFe_2S_4 (5), c_1 is equal to c_2 , while in the nonstoichiometric members, for example, in $\text{Ba}_9\text{Fe}_{16}\text{S}_{32}$ ($x = 0.125$), $9c_1$ is equal to $8c_2$. For further understanding of the complex structure of this phase, we tried to observe the details of local structure by electron microscopy. In this note, we report briefly a new finding of orientation anomaly observed by electron diffraction.

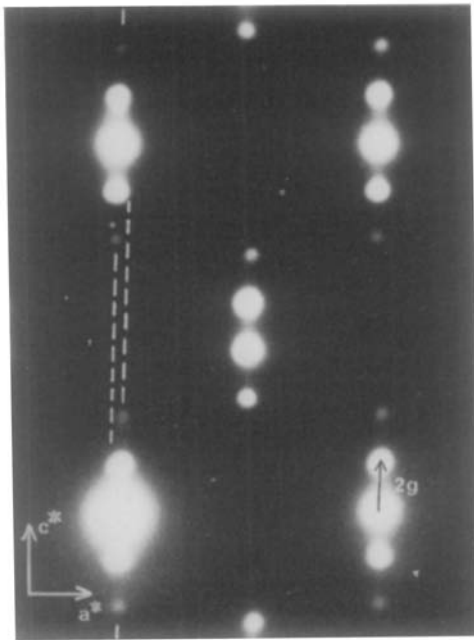
Many samples with different nominal compositions ($0 \leq x \leq 0.20$) were prepared at several annealing temperatures between 600 and 900°C. The details of the phase diagram on this phase will be published elsewhere in the near future (6). Obtained products were identified by X-ray powder diffraction and then the crushed crystallites were examined using a JEM-7A electron microscope.

In Fig. 1, a typical example of electron diffraction patterns with [010] zone is shown together with the schematic drawing of that of β - BaFe_2S_4 . Each of the elemental

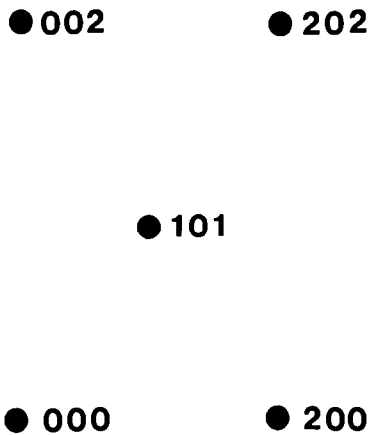
spots splits into a group of spots, and the rows of superlattice spots are not parallel to the c^* -axis of β - BaFe_2S_4 . According to Grey's analysis (1, 2), the vector $2g [= 2(c_1^* - c_2^*)]$ corresponds to the spacing between superlattice spots, shown in Fig. 1a. The observed angle between c^* and g , projected on the (100)* reciprocal plane, ranges from 5 to nearly 0°. This orientation anomaly clearly indicates that the real supercell is not tetragonal, though the crystal symmetry of $\text{Ba}_5\text{Fe}_9\text{S}_{18}$ (2) and $\text{Ba}_9\text{Fe}_{16}\text{S}_{32}$ (3) was reported to be tetragonal. Even in the case of small inclination, two cases were observed; in one superlattice spacing g is commensurate with c_1^* and c_2^* , i.e., $|c_1^*| = p|g|$ and $|c_2^*| = q|g|$, and in the other it is incommensurate (spacing anomaly). In this note we do not refer to the details of the relation between these anomalies and composition or heat treatment of samples.

Obtained lattice images from thin fragments showed wavy lattice fringe patterns and also the existence of many defects even in the case of long annealing time (3 months at 700°C). One example is shown in Fig. 2. The wavy interfringe spacings correspond to $|g|$ spacings. It is interesting to note that two other regular fringe patterns almost perpendicular to the c -axis (≈ 5.5 and 5.0 \AA) are also resolved without defects.

We propose here a structure model to explain the orientation and spacing anomalies. The structure of this compound may be described by the displacive modulation on the "vernier" structure. The modulation



(a)



(b)

FIG. 1. Electron diffraction pattern showing orientation anomaly. (a) [010] zone diffraction pattern. The angle between c^* and g is about 2° . (b) Schematic [010] zone diffraction pattern of β -BaFe₂S₄ with the basic structure.

may exist in both the Ba chain and the (FeS₂)_x tetrahedron chain. In Fig. 3, we drew the structure model, which has the modulation only in the Ba chain along the [110] direction of the tetragonal cell for simplicity. This model can explain the orientation anomaly. Adding to this modulation, if the displacive modulation of the Ba chain and/or the (FeS₂)_x tetrahedron chain along the c -axis is taken into consideration, the spacing anomaly can be easily explained. The situation is very similar to that of MnSi_{2-x} ($x \approx 0.25$) (7). As for the wavy lattice fringes, we have no adequate expla-

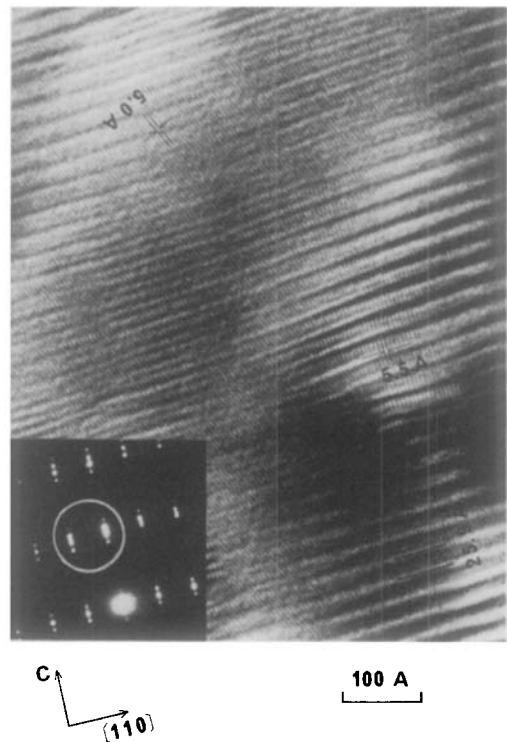


FIG. 2. Two-dimensional lattice fringe image (dark field image). [110] incidence. The inset is the corresponding diffraction pattern (also showing small orientation anomaly) and the diffraction spots used for imaging are shown in the circle. The wide lattice fringes with the spacing 25.9 Å correspond to $2g$. The narrow lattice fringes with the spacing 5.5 and 5.0 Å correspond to the $d(110)$ and $d(114)$ of the average tetragonal cell, respectively. The lateral displacement of the lattice fringes can be seen at several positions.

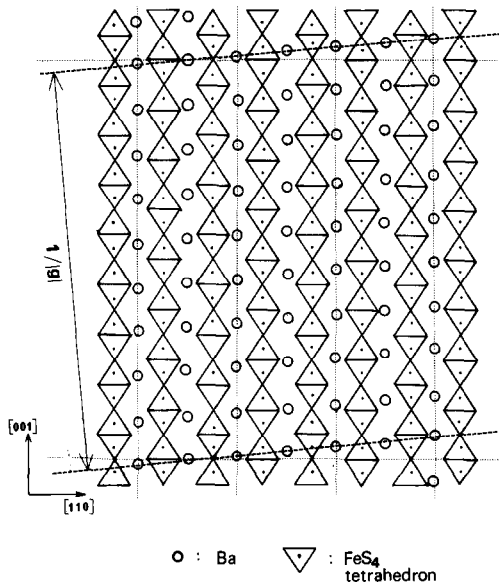


FIG. 3. A structure model explaining the orientation anomaly. Note the "phase" change of Ba-chain periodicity in successive chains. The thin dotted lines show the supercell of $\text{Ba}_9\text{Fe}_{16}\text{S}_{32}$ based on the "vernier" model. The thick broken lines show the periodic "phase shift" in Ba chains.

nations. It seems likely that these anomalies in electron diffraction and lattice image have a close relation to the high concentration of Ba and Fe vacancies (6) of these

microphases. High-resolution electron microscopic observation will give the details of the modulated structure, and we are now investigating this.

References

1. I. E. GREY, *J. Solid State Chem.* **11**, 128 (1974).
2. I. E. GREY, *Acta Crystallogr. Sect. B* **31**, 45 (1975).
3. J. T. HOGGINS AND H. STEINFINK, *Acta Crystallogr. Sect. B* **33**, 673 (1977).
4. J. S. ANDERSON, *J. Phys. (Paris)* **38**, C7-17 (1977).
5. J. S. SWINNEA AND H. STEINFINK, *J. Solid State Chem.* **32**, 329 (1980).
6. N. NAKAYAMA, K. KOSUGE, AND S. KACHI, submitted for publication.
7. R. DE RIDDER, G. VAN TENDELOO, AND S. AMELINCKX, *Phys. Status Solidi A* **33**, 383 (1976).

N. NAKAYAMA
K. KOSUGE
S. KACHI

Department of Chemistry
Faculty of Science
Kyoto University
Kyoto 606, Japan

Received November 14, 1979