

Antiferromagnetic 6L-Hexagonal Ferrites, $\text{Ba}_2\text{Sb}_2\text{M}_3^{\text{II}}\text{Fe}_8\text{O}_{22}$ ($M = \text{Zn}, \text{Mg}, \text{Ni}, \text{Co}$)

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Four oxides $\text{Ba}_2\text{Sb}_2\text{M}_3^{\text{II}}\text{Fe}_8\text{O}_{22}$ ($M = \text{Zn}, \text{Mg}, \text{Ni}, \text{Co}$) with a 6L-hexagonal structure have been synthesized. These compounds crystallize in the space group $P\bar{3}m1$ with $a \approx 5.9 \text{ \AA}$ and $c \approx 14.3 \text{ \AA}$. Their structure is built up from spinel S and Q blocks. The latter are formed by close packing of two cubic BaO_3 layers and two hexagonal O_4 layers, resulting in a total stacking $(\text{hcc})_2$. The study of magnetization versus temperature and magnetic field shows that the oxides are antiferromagnetic, with ordering temperatures ranging from 450 to 500 K for $M = \text{Mg}, \text{Ni}, \text{Co}$, and below 77 K for $M = \text{Zn}$. The Mössbauer study reveals that iron is only in the trivalent state and distributed over three sites: one tetrahedral site Te (25%) and two octahedral sites: Oc (50%) and Oc' (25%). This latter distribution of the Fe^{3+} ions is discussed by comparing the Mössbauer and crystallographic data. © 1986 Academic Press, Inc.

Introduction

The presence of metallic ions characterized by a nd^{10} electronic configuration in close-packed oxides, may change the nature of the oxygen close-packing. In addition to the well-known family of spinel oxides corresponding to the $M_3\text{O}_4$ general formula, a new series of oxides of tin or of antimony, such as LiFeSnO_4 (1, 2) and $\text{Li}_2\text{Cr}_{3-x}\text{Fe}_x\text{SbO}_8$ (3), has been isolated with a double hexagonal close-packing of the oxygen atoms (ABAC). In this regard, the large family of hexagonal ferrites whose structure is built up from spinel blocks S,

and of two other close-packed blocks called R and T (4-7) should also be influenced by the introduction of nd^{10} cations. The series of oxides $\text{Ba}_2\text{Sn}_2\text{M}^{\text{II}}\text{Fe}_{10}\text{O}_{22}$ characterized by a new close-packed block Q, recently discovered by Cadee and Ijdo (8), is in agreement with this point of view. Thus, it appeared that the introduction of Sb(V) in these oxides could lead to the formation of similar Q blocks. The present work deals with the synthesis and study of new isomorphous oxides $\text{Ba}_2\text{Sb}_2\text{M}_3^{\text{II}}\text{Fe}_8\text{O}_{22}$ ($M^{\text{II}} = \text{Ni}, \text{Co}, \text{Mg}, \text{Zn}$).

Experimental

Synthesis. The oxides $\text{Ba}_2\text{Sb}_2\text{M}_3^{\text{II}}\text{Fe}_8\text{O}_{22}$

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were prepared by heating the mixtures of chemically pure BaCO_3 , Sb_2O_3 , Fe_2O_3 , and divalent oxides MO ($M = \text{Ni}, \text{Zn}, \text{Mg}$) or CoCO_3 at temperatures ranging from 1000 to 1200°C. Several heatings were required to obtain homogeneous compounds, the last step being carried out in air at 1200°C to avoid any reduction of Fe^{3+} ions.

X-Ray and electron diffraction. The crystallographic data were obtained by two complementary methods: X-ray diffractometry by means of a Philips goniometer using $\text{CuK}\alpha$ radiation and electron diffraction carried out with an EM 200 Philips electron microscope. Scattering factors of ionic species (9) corrected for anomalous scattering were used for calculating intensities using a program previously described (10).

Magnetic study. ^{57}Fe transmission Mössbauer spectra have been recorded by standard techniques in the temperature range 4.2–823 K. The temperature dependence of the magnetization was measured with a vibrating sample magnetometer between 293 and 700 K and in an applied magnetic field of approximately $2.8 \times 10^5 \text{ A} \cdot \text{m}^{-1}$ (3.6 kOe).

Results and Discussion

Magnetic properties. Magnetization measurements versus magnetic fields show that these oxides are antiferromagnetic. An example of this antiferromagnetic behavior is shown in Fig. 1 for $\text{Ba}_2\text{Sb}_2\text{Ni}_3\text{Fe}_8\text{O}_{22}$. However, a weak ferromagnetic contribution ($\sim 0.3 \mu\text{B}$) is always observed. The

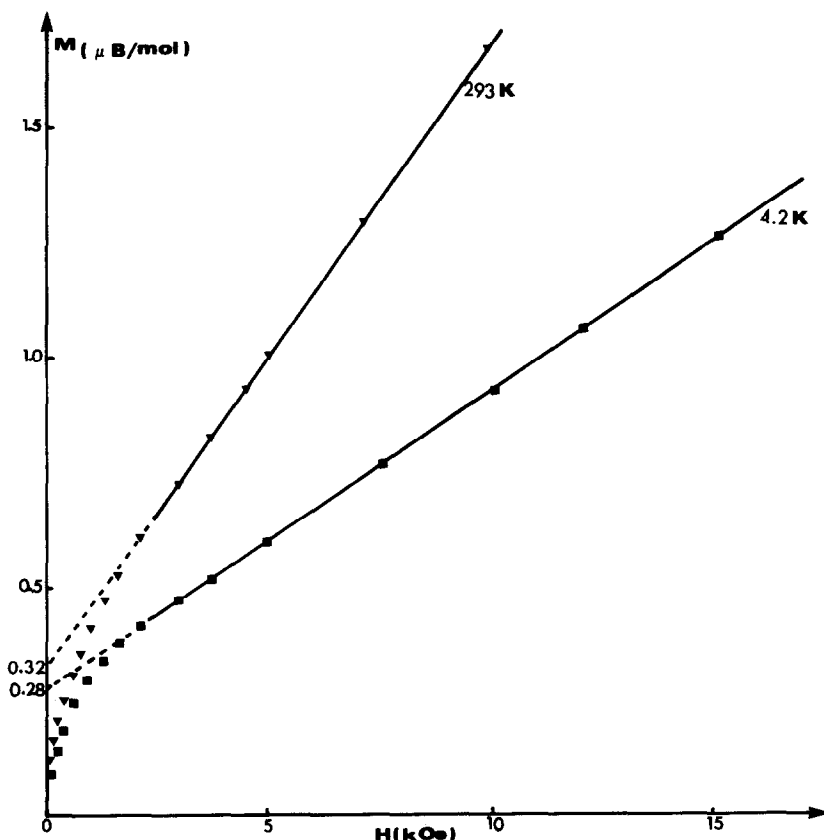


FIG. 1. Magnetization (M) of $\text{Ba}_2\text{Sb}_2\text{Ni}_3\text{Fe}_8\text{O}_{22}$ versus magnetic field (H).

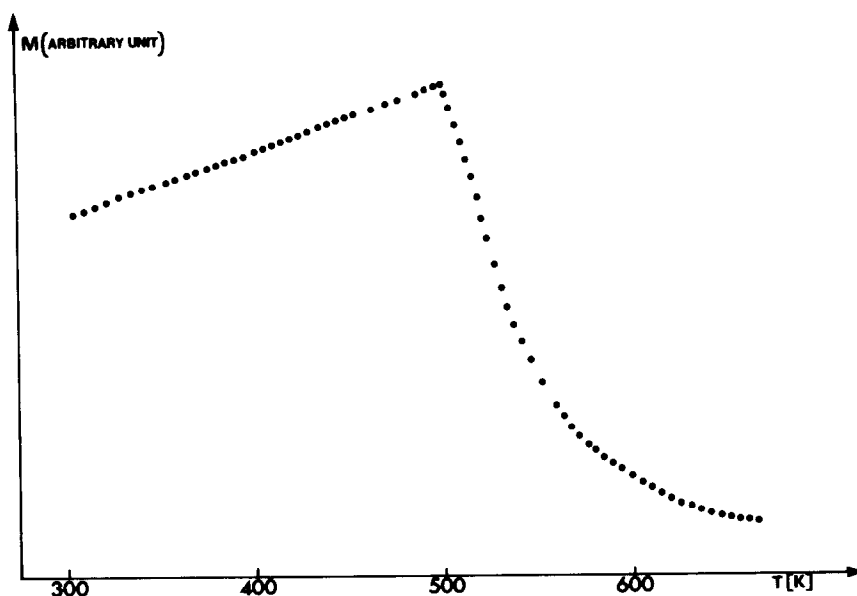


FIG. 2. Magnetization of $\text{Ba}_2\text{Sb}_2\text{Ni}_3\text{Fe}_8\text{O}_{22}$ versus temperature. The applied field is about 3600 Oe.

temperature dependence of the magnetization (Fig. 2) allowed us to determine the ordering temperature of these phases. From Table I, it can be seen that three oxides ($M = \text{Ni}, \text{Mg}, \text{Co}$) exhibit a rather high ordering temperature, ranging from 450 to 500 K; these temperatures are to be compared to $T_c = 420$ K observed for the isostructural oxide $\text{BaSn}_{0.9}\text{Fe}_{5.47}\text{O}_{11}$ (8). On the other hand, a different behavior has been encountered for the zinc oxide, which exhibits a very low T_N (below 77 K). This

could be due to a decrease of the $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ superexchange interaction, resulting from a preferential occupation of the tetrahedral sites by the Zn^{2+} ions.

The Mössbauer spectra of these compounds (Fig. 3) show that iron is present only in the trivalent state. The ordering temperatures deduced from the Mössbauer results are in agreement with those determined from the magnetization (Table I). Table II specifies the fitted experimental parameters at 4.2 K and at room temperature, for the oxide $\text{Ba}_2\text{Sb}_2\text{Ni}_3\text{Fe}_8\text{O}_{22}$. The values of the isomer shift, of the quadrupole splitting and of the hyperfine magnetic field led us to place the Fe^{3+} ions on three sites: 25% Fe^{3+} in a tetrahedral site (Te) and 50% Fe^{3+} in a first octahedral site (Oc), and 25% Fe^{3+} in a second octahedral site (Oc'). This distribution pattern will be discussed further in conjunction with the crystallographic results.

Structural model. The X-ray and electron diffraction study leads to a hexagonal cell, with the unique space group $P3m1$. The unit cell parameters (Table III) are close to

TABLE I
ORDERING TEMPERATURES T_N DETERMINED
BY MÖSSBAUER SPECTROMETRY AND BY
MEASURING THE MAGNETIZATION OF THE
 $\text{Ba}_2\text{Sb}_2\text{M}_3\text{Fe}_8\text{O}_{22}$ COMPOUNDS

Compound	T_N (K)	
	Mössbauer	Magnetization
$\text{Ba}_2\text{Sb}_2\text{Ni}_3\text{Fe}_8\text{O}_{22}$	494 ± 2	500 ± 5
$\text{Ba}_2\text{Sb}_2\text{Co}_3\text{Fe}_8\text{O}_{22}$	450 ± 2	450 ± 10
$\text{Ba}_2\text{Sb}_2\text{Mg}_3\text{Fe}_8\text{O}_{22}$	368 ± 5	378 ± 10
$\text{Ba}_2\text{Sb}_2\text{Zn}_3\text{Fe}_8\text{O}_{22}$	<77	

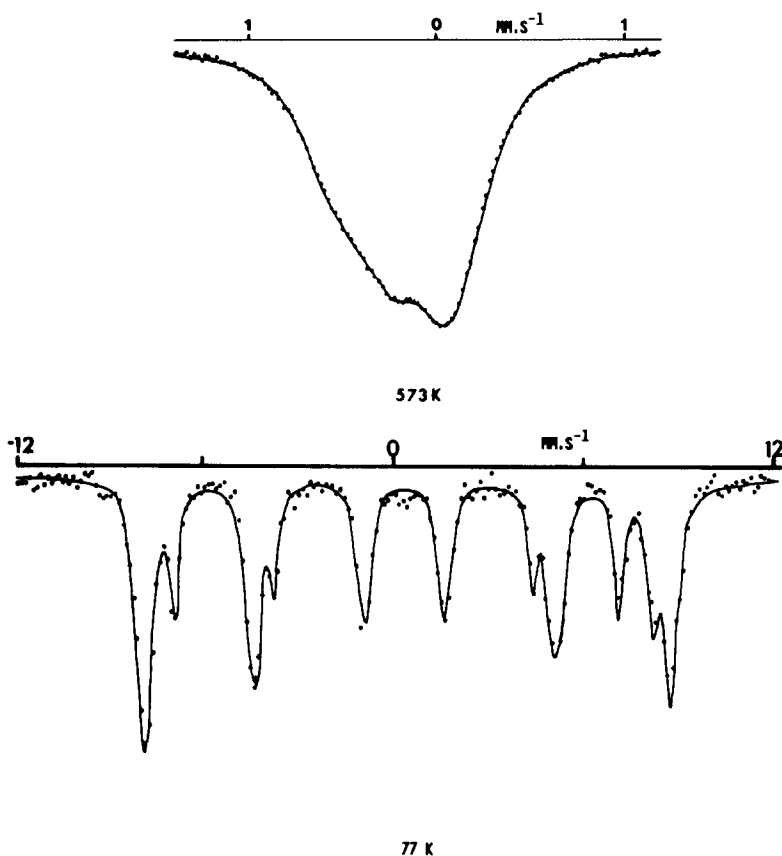


FIG. 3. Mössbauer resonance pattern of $\text{Ba}_2\text{Sb}_2\text{Ni}_3\text{Fe}_8\text{O}_{22}$ at 573 and 77 K.

those obtained for $\text{BaSn}_{0.9}\text{Fe}_{5.47}\text{O}_{11}$, and the cell volume increases with the size of the divalent ion. The value of the "c" parameter is in agreement with a six-layer close-

packed structure (6L). The close relationships to $\text{BaSn}_{0.9}\text{Fe}_{5.47}\text{O}_{11}$ suggest a very similar structure (Fig. 4) built up from spinel blocks S and from Q blocks. The lat-

TABLE II
MÖSSBAUER DATA OF $\text{Ba}_2\text{Sb}_2\text{Ni}_3\text{Fe}_8\text{O}_{22}$

Temperature (K)	Site	IS (mm · sec ⁻¹)	Γ (mm · sec ⁻¹)	2ϵ (mm · sec ⁻¹)	H (kOe)	%
4.2	Oc	0.48(1)	0.45(2)	0.01(2)	530(2)	51(2)
	Oc'	0.39(1)	0.49(2)	-0.06(2)	504(2)	27(2)
	Te	0.31(1)	0.31(2)	-0.25(3)	455(2)	22(2)
295	Oc	0.29(1)	0.70(2)	-0.08(2)	420(2)	49(2)
	Oc'	0.35(1)	0.44(2)	-0.04(2)	392(2)	27(2)
	Te	0.19(1)	0.46(2)	-0.24(2)	266(2)	24(2)

Note. IS, isomer shift relative to metallic iron; Γ , half height width; 2ϵ , quadrupole shift; H , hyperfine field.

TABLE III
CRYSTALLOGRAPHIC DATA, EXPERIMENTAL DENSITY
 d_{exp} , AND THEORETICAL DENSITY d_{th} OF THE
 $\text{Ba}_2\text{Sb}_2\text{M}_3\text{Fe}_8\text{O}_{22}$ COMPOUNDS

M	a (Å)	c (Å)	V (Å ³)	d_{exp} (g/cm ³)	d_{th} (g/cm ³)
Ni	5.882(2)	14.237(8)	426.6	5.90(5)	5.81
Mg	5.901(6)	14.220(2)	428.8	5.52(5)	5.38
Co	5.906(2)	14.285(3)	431.5	5.81(5)	5.75
Zn	5.916(2)	14.327(6)	434.2	6.05(5)	5.79

ter blocks are formed of two close-packed cubic BaO_3 layers, stacked with two hexagonal oxygen layers. Starting from this model, we have studied the structure of

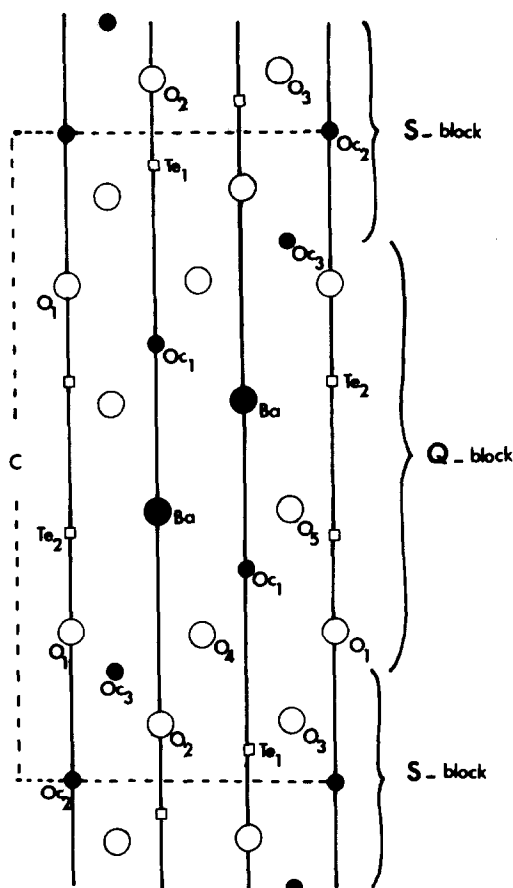


FIG. 4. The (110) plane of $\text{Ba}_2\text{M}_{13}\text{O}_{22}$ compounds.

$\text{Ba}_2\text{Sb}_2\text{Ni}_3\text{Fe}_8\text{O}_{22}$. The intensity calculations have been performed on the first 30 observed reflections, i.e., 95 hkl .

Taking into account the Mössbauer results, 25% Fe^{3+} in tetrahedral coordination and 75% Fe^{3+} in octahedral sites, ($2\text{Ni}^{2+} + 2\text{Fe}^{3+}$) ions were placed on tetrahedral sites and ($6\text{Fe}^{3+} + 1\text{Ni}^{2+}$ and 2Sb^{5+}) were distributed statistically in the octahedral sites. A first calculation led to a discrepancy R factor ($R = \sum|I_0 - I_c|/\sum I_0 = 0.25$). It was lowered to $R = 0.085$ by a preferential distribution of the antimony ions on only two octahedral sites Oc_1 and Oc_2 and by refining the atomic parameters.

At this stage, it was apparent that the proportion of Fe^{3+} ions in tetrahedral and in octahedral sites was in agreement with the Mössbauer results; it is not possible, of course, to distinguish between Fe^{3+} and Ni^{2+} ions in tetrahedral sites of the structure, owing to the small difference between the scattering factors of Fe^{3+} and Ni^{2+} ions.

Finally, the lowest R factors ($R = 0.067$) was reached for the atomic parameters given in Table IV. If one takes into account the great number of parameters compared to the number of reflections, it is obvious that the accuracy of the atomic positions cannot be considered as significant. Never-

TABLE IV
ATOMIC POSITIONS, OCCUPATION RATES
IN THE STRUCTURE OF $\text{Ba}_2\text{Sb}_2\text{Ni}_3\text{Fe}_8\text{O}_{22}$,
SPACE GROUP: $P\bar{3}m1$

Site	Position	x	y	z	Occupation rate (%)	B (Å ²)
Ba	2(d)	$\frac{1}{2}$	$\frac{1}{2}$	0.417(1)	100	1.0
Te ₁	2(d)	$\frac{1}{2}$	$\frac{1}{2}$	0.955(3)	100Fe	1.0
Te ₂	2(c)	0.0	0.0	0.384(3)	100Ni	1.0
Oc ₁	2(d)	$\frac{1}{2}$	$\frac{1}{2}$	0.680(2)	66Sb; 34Ni	1.0
Oc ₂	1(a)	0.0	0.0	0.0	67Sb; 33Ni	1.0
Oc ₃	6(i)	0.174(2)	0.348(2)	0.172(1)	100Fe	1.0
O ₁	2(c)	0.0	0.0	0.236(5)	100	1.0
O ₂	2(d)	$\frac{1}{2}$	$\frac{1}{2}$	0.084(4)	100	1.0
O ₃	6(i)	0.163(5)	0.325(5)	0.909(4)	100	1.0
O ₄	6(i)	0.496(5)	0.992(5)	0.228(4)	100	1.0
O ₅	6(i)	0.183(5)	0.366(5)	0.585(3)	100	1.0

theless, the low R value confirms the validity of the structural model.

Accordingly, the probable distribution of the metallic ions can be summarized as $\text{Ba}_2(\text{Fe}_2)_{\text{Te}_1}(\text{Ni}_2)_{\text{Te}_2}(\text{Fe}_6)_{\text{Oc}_3}(\text{Sb}_{1.33}\text{Ni}_{0.66})_{\text{Oc}_1}(\text{Sb}_{0.66}\text{Ni}_{0.33})_{\text{Oc}_2}\text{O}_{22}$.

The location of the Ni^{2+} ions in a tetrahedral environment may appear as rather unusual although it has been encountered in several oxides of the spinel type (11). It has been retained with respect to the Mössbauer assignments which lead to isomer shifts and hyperfine magnetic fields of Fe^{3+} ions in tetrahedra lower than those observed for octahedrally coordinated Fe^{3+} ions.

If one assumes that the location of the Ni^{2+} ions is more likely in octahedral sites in association with Fe^{3+} ions, another possible distribution can be considered: $\text{Ba}_2(\text{Fe}_2)_{\text{Te}_1}(\text{Fe}_2)_{\text{Te}_2}(\text{Fe}_4\text{Ni}_2)_{\text{Oc}_3}(\text{Sb}_{1.33}\text{Ni}_{0.67})_{\text{Oc}_1}(\text{Sb}_{1.33}\text{Ni}_{0.67})_{\text{Oc}_2}\text{O}_{22}$.

However, such a distribution appears as less probable since it leads to tetrahedral isomer shift for $(\text{Fe}^{3+})_{\text{Te}_2}$ ($0.35 \text{ mm} \cdot \text{sec}^{-1}$ at 295 K (Table II) greater than the octahedral shift ($0.29 \text{ mm} \cdot \text{sec}^{-1}$).

As previously explained, the question whether Fe^{3+} and Ni^{2+} ions are located on the Te_1 and Te_2 sites respectively, cannot be resolved by X-ray diffraction. However, the interatomic distances (Table V) are quite in agreement with this distribution: the Te_2 tetrahedra are indeed much more distorted than the Te_1 tetrahedra in accordance with the Jahn–Teller effect observed for tetrahedrally coordinated Ni^{2+} ions (12, 13). The mean $\langle \text{Ni}-\text{O} \rangle_{\text{Te}_2}$ distance (1.92 \AA) greater than the $\langle \text{Fe}-\text{O} \rangle_{\text{Te}_1}$ one (1.86 \AA) is also in agreement with the value calculated from the ionic radii (14): 1.93 \AA for $\text{Ni}-\text{O}$ and 1.89 \AA for $\text{Fe}-\text{O}$.

The distribution of Fe^{3+} ions in octahedral sites Oc_3 does not agree, at first sight, with the Mössbauer results which indicate that Fe^{3+} ions should be located on two octahedral sites with the distribution ratios $\frac{2}{3}$

TABLE V
INTERATOMIC DISTANCES FOR $\text{Ba}_2\text{Sb}_2\text{Ni}_3\text{Fe}_8\text{O}_{22}$
IN ÅNGSTRÖMS^a

Ba–O ₄	3.16	3 ×	O ₁ –O ₃	2.64	3 ×
Ba–O ₅	2.83	3 ×	O ₁ –O ₄	2.94	6 ×
Ba–O ₅	2.94	6 ×	O ₂ –O ₃	2.94	6 ×
Te ₁ –O ₂	1.84	1 ×	O ₂ –O ₄	2.63	3 ×
Te ₁ –O ₃	1.86	3 ×	O ₃ –O ₃	2.87	2 ×
Te ₂ –O ₁	2.12	1 ×	O ₃ –O ₄	2.61	2 ×
Te ₂ –O ₅	1.92	3 ×	O ₄ –O ₄	2.87	2 ×
Oc ₁ –O ₄	2.17	3 ×	O ₃ –O ₅	2.65	2 ×
Oc ₁ –O ₅	2.05	3 ×			
Oc ₂ –O ₃	2.10	6 ×			
Oc ₃ –O ₁	1.99	1 ×			
Oc ₃ –O ₂	2.04	1 ×			
Oc ₃ –O ₃	2.06	2 ×			
Oc ₃ –O ₄	1.83	2 ×			

^a Standard deviations may be estimated to 0.01–0.03 Å.

and $\frac{1}{3}$. This would lead to 4 Fe^{3+} ions in the Oc_3 sites and two Fe^{3+} ions in the Oc_1 sites, involving a drastic increase of R resulting from a different distribution of the antimony ions which are the heavy atoms of the structure. Whatever the distribution may be in the octahedral sites, the occupation ratios deduced from the Mössbauer results cannot be verified by an X-ray diffraction study. Nevertheless, these latter results are significant, if one takes into account the high scattering power of antimony compared to iron and nickel. Moreover, the preferential occupation of the octahedral sites Oc_1 and Oc_2 by antimony ions is quite in agreement with the results observed by neutron diffraction for $\text{BaSn}_{0.9}\text{Fe}_{5.47}\text{O}_{11}$ (8); it was indeed observed that the Oc_3 sites were only occupied by Fe^{3+} ions, whereas the $\text{Sn}(\text{IV})$ ions, which exhibit, similar to $\text{Sb}(\text{V})$, a nd^{10} configuration, were located in Oc_1 and Oc_2 sites. The observation of two types of octahedral Fe^{3+} sites in Mössbauer studies can be explained by the fact that the Oc_3 sites are surrounded by two sites, Oc_1 and Oc_2 , which are statistically occupied by antimony and nickel ions. It appears that, from a local point of view, the Fe^{3+} ions on the Oc_3 sites experience several types of environment via the Ni^{2+} ions. The fact that the octahedral lines are rather broad is in

agreement with this point of view. Such an effect of random distribution of magnetic ions has already been observed in previous Mössbauer studies especially in spinels and in hexagonal ferrites (15, 16).

The structure of $\text{Ba}_2\text{Sb}_2\text{Ni}_3\text{Fe}_8\text{O}_{22}$ is characterized by only a weak displacement of the metallic ions from their ideal positions, especially in the Q blocks. This behavior is different from that observed in other hexagonal ferrites for which displacements of 0.25 Å have been reported for the barium ions of the T blocks in the Y-structure (4, 5). By contrast, displacements of about 0.20 and 0.30 Å are observed for some oxygen ions (O_1 and O_4). As a result the distance between a BaO_3 layer and the adjacent oxygen layer increases by about 0.30 Å, whereas the distance between the oxygen layers, at the junction of the Q and S blocks, decreases drastically. The latter distance is 2.05 Å, compared to 2.32 and 2.21 Å in M_2Y compounds and $\text{BaFe}_{12}\text{O}_{19}$, respectively. This distance is also smaller than that observed in the isostructural oxide $\text{BaSn}_{0.9}\text{Fe}_{5.47}\text{O}_{11}$. This particular behavior can be explained by the presence of Ni^{2+} in the tetrahedral Te_2 sites, owing to their Jahn-Teller effect which involves a repulsion of the O_1 atoms.

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References

1. J. CHOISNET, M. HERVIEU, AND B. RAVEAU, *J. Solid State Chem.* **40**, 344 (1981).
2. PH. LACORRE, M. HERVIEU, J. PANNETIER, J. CHOISNET, AND B. RAVEAU, *J. Solid State Chem.* **50**, 196 (1983).
3. P. TARTE, R. CAHAY, J. PREUDHOMME, M. HERVIEU, J. CHOISNET, AND B. RAVEAU, *J. Solid State Chem.* **44**, 282 (1982).
4. J. SMIT AND H. P. J. WIJN, "Ferrites," Eindhoven (1959).
5. P. B. BRAUN, *Philips Res. Rep.* **12**, 491 (1957).
6. J. S. ANDERSON AND J. L. HUTCHINSON, *Contemp. Phys.* **16**, 443 (1975).
7. D. M. EVANS AND L. KATZ, *Acta Crystallogr. Sect. B* **28**, 1219 (1972).
8. M. C. CADÉE AND D. J. W. IJDO, *J. Solid State Chem.* **40**, 290 (1981).
9. D. T. CROMER AND J. T. WABER, *Acta Crystallogr.* **18**, 104 (1965).
10. C. C. PHAM, J. CHOISNET, AND B. RAVEAU, *Bull. Acad. R. Belg. Sci.* **61**, 473 (1975).
11. F. S. GALASSO, in "Solid State Physics," Vol. 7, Pergamon, Oxford (1970).
12. J. D. DUNITZ AND L. E. ORGEL, *J. Phys. Chem. Solids* **3**, 20 (1957).
13. E. PRINCE, *J. Appl. Phys.* **32**, 68 (1961).
14. R. D. SHANNON AND C. T. PREWITT, *Acta Crystallogr.* **25**, 925 (1969).
15. J. L. DORMANN, *Rev. Phys. Appl.* **15**, 1113 (1980).
16. X. OBRADORS, A. ISALGNÉ, A. COLLOMB, M. PERNET, J. TEJADA, AND J. C. JOUBERT, in "Proceedings, 4th Int. Conf. Ferrite, San Francisco, 1984."