PHYSICAL REVIEW B VOLUME 48, NUMBER 5 1 AUGUST 1993-I

Mössbauer study of $(Fe_{1-x}Ni_x)_7Se_8$

Hang Nam Ok, Kyung Seon Baek, and Eng Chan Kim
Department of Physics, Yonsei University, Seoul 120-749, Korea

Chul Sung Kim
Department of Physics, Kookmin University, Seoul 136-702, Korea

(Received 19 January 1993; revised manuscript received 5 April 1993)

$(Fe_{1-x}Ni_x)_7Se_8$ (x=0.02,0.05,0.08) has been studied with Mössbauer spectroscopy and x-ray diffraction. The crystal structure is found to be a triclinic superstructure of the NiAs structure while Fe_7Se_8 has a hexagonal structure. Abrupt change of quadrupole shifts near 122 K suggests that the spin-rotation transition proceeds abruptly, in contrast with the gradual transition reported for Fe_7Se_8 with a triclinic superstructure. The iron ions at all four sites are found to be in a highly covalent ferrous state. Both Néel and Debye temperatures are found to decrease with increasing nickel concentration.

I. INTRODUCTION

The fundamental crystal structure of Fe_7Se_8 is known to be of the NiAs type.[1] Since one-eighth of the iron sites are vacant, the composition can be represented as Fe_7VSe_8, where V stands for an iron vacancy. Two types of superstructure due to ordering of the vacancies are known.[1] One is the hexagonal superstructure (3c structure) that has the following unit-cell constants:[1] $A=2a=7.234$ Å, and $C=3c=17.65$ Å, where a and c designate the unit-cell lengths of the fundamental NiAs structure; more recent measurement[2] shows that $A=7.2613$ Å and $C=17.675$ Å. The other is a triclinic superstructure (4c structure) that has the following unit-cell lengths: $A=\sqrt{3}B$, $B=2a$, and $C=4c$. Quenching from about 400 °C produces the 3c structure whereas slow cooling yields the 4c structure.[3]

Ferrimagnetic ordering in Fe_7Se_8 was studied with the neutron-diffraction method.[4] According to this measurement, the magnetic moments of iron atoms are parallel to those of the atoms on the same layer parallel to the (001) plane, while they are antiparallel to those of the atoms on the next layer. When the temperature of the crystal is lowered from the Néel temperature, the direction of the moment, which is at first on the (001) plane, changes toward the [001] direction. The behavior of this spin-rotation process depends on the type of crystallographic superstructure in the specimen. For the 3c structure the spin-rotation process takes place abruptly at 130 K. However, in the case of the 4c structure the process starts at about 220 K and shows a gradual shift with decreasing temperature. The spin-rotation shift toward the c axis is never completed, and even at 4.2 K, a tilt of about 20° has been observed.

There are three main types[5] of iron sites, A, B, and C. An A site is in the c plane with Fe vacancies, whereas the B and C sites are in the c plane with no Fe vacancies. An A site ion has two adjacent ferromagnetic cation sites vacant, while B and C sites have four and three adjacent antiferromagnetic cations, respectively, absent. The A sites can be further subdivided into A_1 and A_2 sites, taking into account the next-nearest-neighbor ferromagnetic c planes. The relative ratio of the numbers of A_1, A_2 and B, and C sites in the superstructure are 1:2:2:2.

In the present study, the effects of the cationic substitution of Ni for Fe on the crystallographic and magnetic properties have been investigated by preparing the mixed system $(Fe_{1-x}Ni_x)_7Se_8$ and by using Mössbauer and x-ray techniques.

II. EXPERIMENT

Synthesis of the $(Fe_{1-x}Ni_x)_7Se_8$ (x=0.02, 0.05, 0.08) samples was accomplished by the following direct-reaction method. The starting materials were Fe, Ni, and Se powders of 99.995%, 99.99%, 99.999% purity, respectively. Mixtures of proper proportions of the elements sealed in evacuated quartz ampoules were heated to 600 °C for 24 h, at 900 °C for 24 h, at 1100 °C for 1 h, at 950 °C for 7 days, and then cooled down to room temperature. Extra precautions have been exercised to prevent oxygen from diffusing into the quartz ampoule and selenium vapors from escaping from the initial mix during the sealing process, as described elsewhere.[5,6] The samples were ground and pressed into pellets before being sealed into evacuated quartz ampoules for another firing. The second firing proceeded at 950 °C for 7 days, and then the samples were cooled down to 400 °C. After being kept at 400 °C for 24 h, they were quenched to room temperature. The samples were ^{57}Fe enriched to 6.7 at. % of the metal atoms in the samples for Mössbauer measurements.

X-ray-diffraction patterns of the samples were obtained with Cu $K\alpha$ radiation. A slow scanning speed of 0.25° advance in 2θ/min, was used in order to optimize resolution of the closely spaced reflections. A Mössbauer spectrometer of the electrochemical type was used in the constant-acceleration mode. A ^{57}Co single-line source in a rhodium matrix was used at room temperature.

III. RESULTS

Figure 1 shows x-ray-diffraction patterns for $(Fe_{0.98}Ni_{0.02})_7Se_8$ and Fe_7Se_8 at room temperature. Every peak in the patterns for $(Fe_{1-x}Ni_x)_7Se_8$ can be indexed

0163-1829/93/48(5)/3212(4)/$06.00

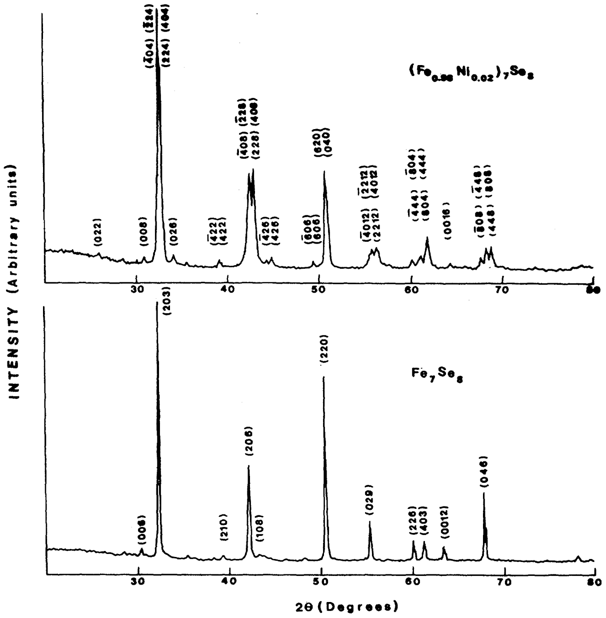

FIG. 1. X-ray-diffraction patterns for $(Fe_{0.98}Ni_{0.02})_7Se_8$ and Fe_7Se_8 at room temperature.

on a triclinic unit cell while those in the patterns for Fe_7Se_8 can be indexed on a hexagonal unit cell. Close examination and analysis of the observed peak positions and intensities show that the $(Fe_{1-x}Ni_x)_7Se_8$ ($x=0.02$, 0.05, 0.08) samples have the triclinic 4*c* structure. The lattice constants are listed in Table I. The unit-cell constant *A*, *B*, and *C* decrease with increasing nickel concentration. This can be expected in view of the fact that the ionic radius of 0.72 Å for Ni^{2+} ions is smaller than 0.76 Å for Fe^{2+} ions.[7] On the other hand, analysis of the patterns for Fe_7Se_8 shows that the specimen has the hexagonal 3*c* structure with the following unit-cell constants: $A=7.233\pm0.005$ Å and $C=17.55\pm0.01$ Å, which are close to those of Okazaki and Hirakawa[1] but somewhat smaller than those of Parise *et al.*[2]

Figure 2 shows some of the Mössbauer spectra of $(Fe_{1-x}Ni_x)_7Se_8$ measured at various absorber temperatures. Using a least-squares computer program, four sets of six Lorentzian lines corresponding to the A_1, A_2, *B*, and *C* sites were fitted to the Mössbauer spectra below Néel temperature under the well-known restraints,[8] which are valid when the quadrupole interaction is much weaker than the magnetic hyperfine interaction.

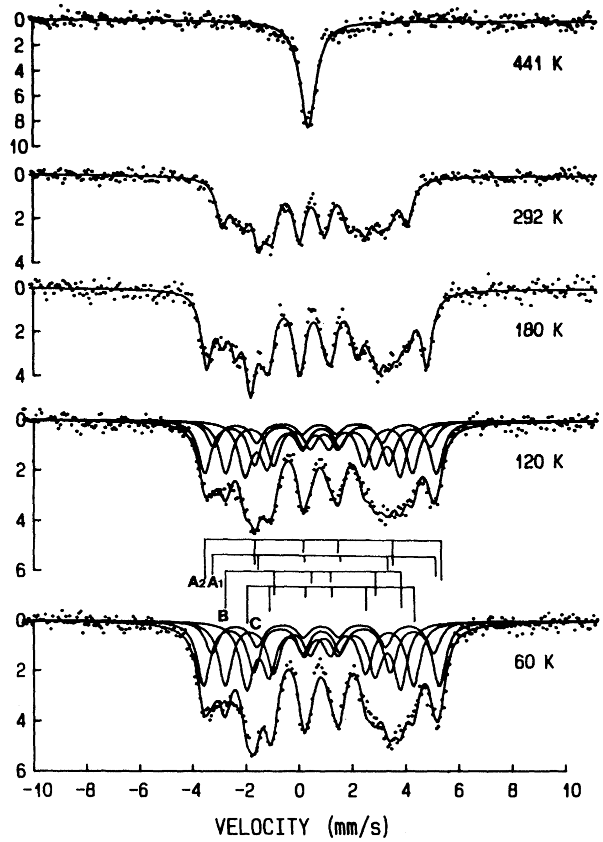

FIG. 2. Mössbauer spectra of $(Fe_{0.098}Ni_{0.02})_7Se_8$ at various temperatures.

Figure 3 shows the temperature dependence of the quadrupole shift defined by $\Delta E_Q=(V_6-V_5+V_1-V_2)/4$, where V_i represents the position of the *i*th absorption line. The quadrupole shift value for $(Fe_{0.98}Ni_{0.02})_7Se_8$ jumps abruptly at 123±1 K corresponding to the spin rotation from lying in the (001) plane above the transition to pointing along the [001] direction below, which was observed for Fe_7Se_8.[3,4] However, it is noteworthy that the spin rotation for $(Fe_{1-x}Ni_x)_7Se_8$ proceeds abruptly while that for Fe_7Se_8 with the same triclinic 4*c* structure proceeds gradually over a wide range of temperatures exceeding 200 K. It is also found that the spin-rotation temperature for $(Fe_{1-x}Ni_x)_7Se_8$ decreases slowly with increasing nickel concentration to become 121±1 K for $(Fe_{0.92}Ni_{0.08})_7Se_8$.

Figure 4 shows the temperature dependence of magnetic hyperfine fields for $(Fe_{0.98}Ni_{0.02})_7Se_8$. There seem to be some bumps near 123 K related to the spin rotation, which are similar to those[3] observed for Fe_7Se_8 with 3*c* structure. *A*, *B*, and *C* sites have 18, 14, and 13 interplanar superexchange links,[5] and may be expected to have magnetic hyperfine field magnitudes in the proportion of 18:14:13, neglecting all intraplanar and all cation-cation

TABLE I. Lattice constants of triclinic unit cell for $(Fe_{1-x}Ni_x)_7Se_8$.

x	A (Å)	B (Å)	C (Å)	α(deg)	β(deg)	γ(deg)
0.02	12.62_1[a]	7.213_5	22.98_2	89.52_5	89.54_5	89.55_5
0.05	12.61_1	7.211_5	22.93_2	89.53_5	89.54_5	89.55_5
0.08	12.51_1	7.182_5	22.91_2	89.53_5	89.54_5	89.54_5

[a] Subscript below each number indicates estimated error in the last digit.

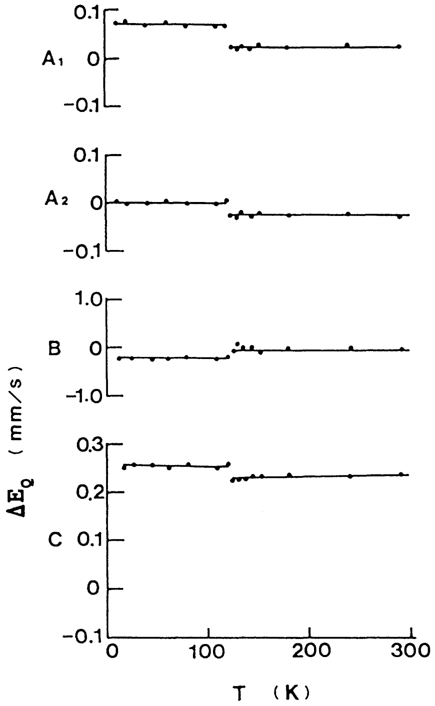

FIG. 3. Temperature dependence of the quadrupole shifts ΔE_Q for $(Fe_{0.98}Ni_{0.02})_7Se_8$.

interactions which are supposed to be much weaker than interplanar interactions.[9,10] The three experimental magnetic hyperfine fields of A, B, and C sites at 12 K are found to be 273 (the weighted average value of the hyperfine fields at A_1 and A_2 sites), 210, and 195 kOe, respectively. These values are in the ratio of 18.0:13.8:12.9, which is in agreement with the above-mentioned ratio 18:14:13.

The isomer shifts at room temperature for $(Fe_{1-x}Ni_x)_7Se_8$ are listed in Table II. The isomer-shift values of 0.50 to 0.69 mm/s relative to iron metal are consistent with irons in either a high-spin Fe^{3+} or a highly covalent ferrous state.[11] The magnitudes of the magnetic hyperfine fields, as shown in Fig. 4, exclude the first alternative. Selenium is known to form strongly covalent bonds and since the iron ions are bound only to selenium, a large covalency is not unexpected.

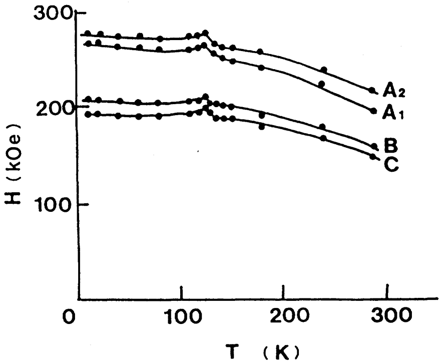

FIG. 4. Temperature dependence of the magnetic hyperfine fields H for $(Fe_{0.98}Ni_{0.02})_7Se_8$.

TABLE II. Isomer shifts at room temperature relative to iron metal for $(Fe_{1-x}Ni_x)_7Se_8$.

x	Subspectrum	Isomer shift (mm/s)
0.02	A_1	0.61
	A_2	0.58
	B	0.51
	C	0.67
0.05	A_1	0.61
	A_2	0.59
	B	0.50
	C	0.69
0.08	A_1	0.62
	A_2	0.58
	B	0.51
	C	0.68
		(±0.01)

Figure 5 shows the Néel temperature as a function of nickel concentration x. It is noted that the Néel temperature decreases linearly with increasing nickel concentration. This implies that Fe^{2+}-Se-Ni^{2+} superexchange interaction in $(Fe_{1-x}Ni_x)_7Se_8$ is weaker than Fe^{2+}-Se-Fe^{2+} superexchange interaction.

Figure 6 shows ln$F$ versus T^2 for $(Fe_{0.98}Ni_{0.02})_7Se_8$, where F stands for the total resonance absorption area of a Mössbauer spectrum at T. F is proportional to the recoil-free fraction f. The Debye model gives the following expression[12] for the natural logarithm of f:

$$\ln f = -\frac{3E_R}{2k_B\Theta}\left[1+\frac{4T^2}{\Theta^2}\int_0^{\Theta/T}\frac{x\,dx}{e^x-1}\right], \qquad (1)$$

where E_R is the recoil energy of ^{57}Fe for the 14.4 keV

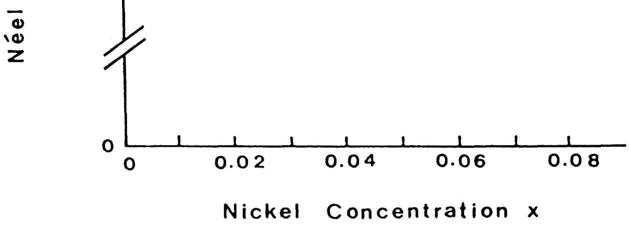

FIG. 5. Néel temperature as a function of nickel concentration x for $(Fe_{1-x}Ni_x)_7Se_8$.

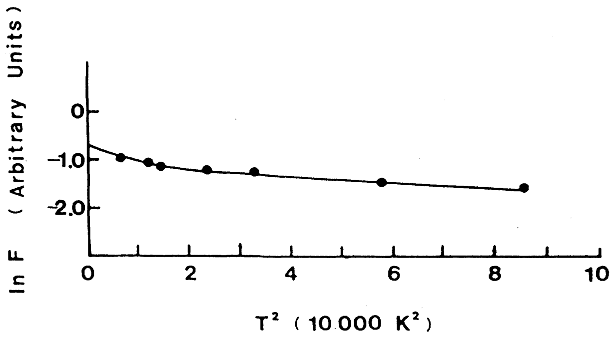

FIG. 6. Natural logarithm of the resonance absorption area F vs T^2 for $(Fe_{0.98}Ni_{0.02})_7Se_8$.

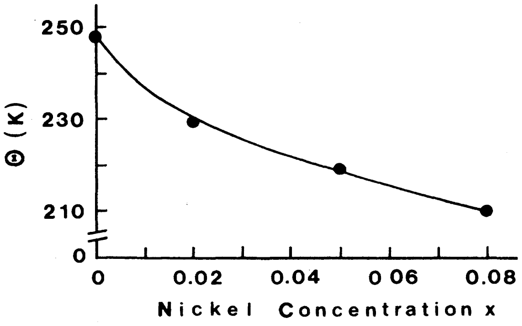

FIG. 7. Debye temperature Θ as a function of nickel concentration x for $(Fe_{1-x}Ni_x)_7Se_8$.

gamma ray. Θ and k_B represent the Debye temperature and Boltzmann constant, respectively. Equation (1) with a proper additive constant was fitted to the data in Fig. 6, using a least-squares computer program to get the Debye temperature Θ. Figure 7 shows the Debye temperature as a function of the nickel concentration x, for $(Fe_{1-x}Ni_x)_7Se_8$. It can be seen in Fig. 7 that the Debye temperature decreases with increasing nickel concentration x. Ni ions replacing Fe ions seem to weaken the interatomic binding force between Fe and Se ions.

ACKNOWLEDGMENTS

This work was supported by the Basic Science Research Institute Program of the Ministry of Education, the Republic of Korea, 1993, and by the Maeji Institute of Academic Research, Yonsei University.

---

[1] A. Okazaki and K. Hirakawa, J. Phys. Soc. Jpn. **11**, 930 (1956); A. Okazaki, *ibid.* **16**, 1162 (1961).

[2] J. B. Parise, A. Nakano, M. Tokonami, and N. Morimoto, Acta Crystallog. Sect. B **35**, 1210 (1979).

[3] C. Boumford and A. H. Morrish, Phys. Status Solidi A **22**, 435 (1974).

[4] M. Kawaminami and A. Okazaki, J. Phys. Soc. Jpn. **29**, 649 (1970).

[5] H. N. Ok and S. W. Lee, Phys. Rev. B **8**, 4267 (1973).

[6] K. S. Baek, K. Y. Park, H. J. Kim, and H. N. Ok, Phys. Rev. B **41**, 9024 (1990).

[7] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1960), p. 518.

[8] K. S. Baek, E. J. Hahn, and H. N. Ok, Phys. Rev. B **36**, 763 (1987).

[9] L. M. Levinson and D. Treves, J. Phys. Chem. Solids **29**, 2227 (1968).

[10] J. B. Goodenough, *Magnetism and Chemical Bond* (Interscience, New York, 1963).

[11] R. Ingalls, F. van der Woude, and G. A. Sawatzky, in *Mössbauer Isomer Shifts,* edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978).

[12] R. L. Mössbauer and W. H. Wiedermann, Z. Phys. **159**, 33 (1960); B. Kaufmann and H. J. Lipkin, Ann. Phys. (N.Y.) **18**, 294 (1962).