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Mössbauer Study of Ferrimagnetic Fe_7Se_8†

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Mössbauer spectra of ferrimagnetic Fe_7Se_8 have been taken at various temperatures ranging from liquid-nitrogen temperature to the specimen's Néel point. Three sets of six-line hyperfine patterns were obtained and assigned to three magnetically nonequivalent sites of a superstructure of the crystal. Isomer shifts indicate nearly Fe^{2+} for all three sites. Change of sign of quadrupole splittings above and below 130 °K were observed and may be interpreted to be due to the spin-rotation from *c* axis to *c* plane with increasing temperature. The Néel temperature was determined to be (447 ± 1) °K.

I. INTRODUCTION

Fe_7Se_8 has been extensively studied because of its interesting crystallographic transformation and ferrimagnetic properties.[1-6] Two types of crystallographic superstructures[1,3] of ferrimagnetic Fe_7Se_8 have been proposed. One is the triclinic superstructure (4*c* structure) that has a unit-cell length along the *c* axis four times as long as that of the unit cell of the fundamental NiAs structure. The other is the orthorhombic superstructure (3*c* structure) that has the following unit-cell constants: $A=\sqrt{3}B=12.53$ Å, $B=2a=7.234$ Å, and $C=3c=17.65$ Å, where a and c designate the unit-cell lengths of the fundamental NiAs structure. The 3*c* structure can be obtained by quenching a sample from 320 °C, and it is stable down to at least liquid-nitrogen temperature.

The magnetic properties have been studied by magnetic torque and magnetization measurements[2,5] and by the neutron-diffraction method.[4] According to these measurements, the magnetic moments of iron atoms at high temperatures are parallel to the *c* plane and parallel to each other on the same atomic layer, while they are antiparallel to those 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 in the *c* plane, changes towards the *c* axis. The behavior of this spin-rotation process depends on the type of crystallographic superstructure in the specimen. For the 4*c* structure the spin-rotation process begins at about 220 °K and shows a gradual shift with decreasing temperature, while the process occurs abruptly at 130 °K in the case of the 3*c* structure. 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. Fatseas[6] took Mössbauer spectra for $Fe_{0.875}Se$ and found two kinds of magnetic hyperfine fields at room temperature: 310 and 225 kOe.

The purpose of this paper was to prepare ^{57}Fe-enriched Fe_7Se_8 samples and determine whether the Mössbauer data are consistent with the existing models of the magnetic structure.

II. EXPERIMENTAL

Fe_7Se_8 samples were prepared by the following method: Iron powder of 99.995% purity was reduced by hydrogen gas at 950 °C. A mixture of the proper proportions of this powder (157 mg) and selenium of 99.999% purity was sealed into an evac-

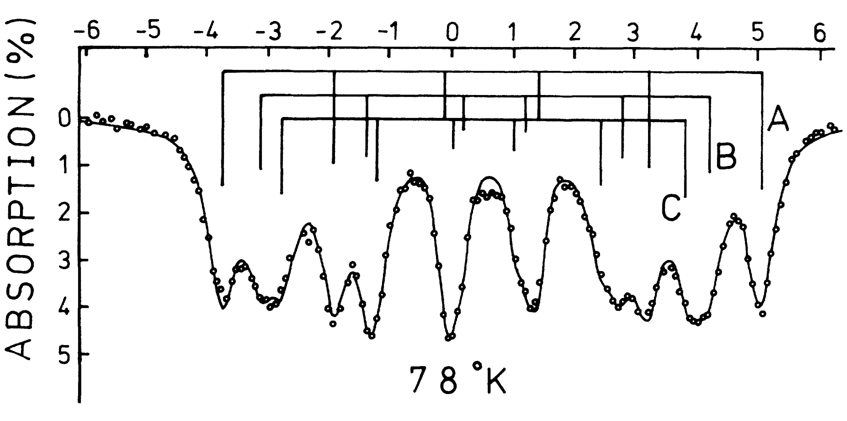

FIG. 1. Mössbauer spectrum of Fe_7Se_8 at 78 °K. The solid curve on the data points indicates the least-squares fit of 18 Lorentzians by a computer. The line positions and relative intensity ratios are shown by the lines.

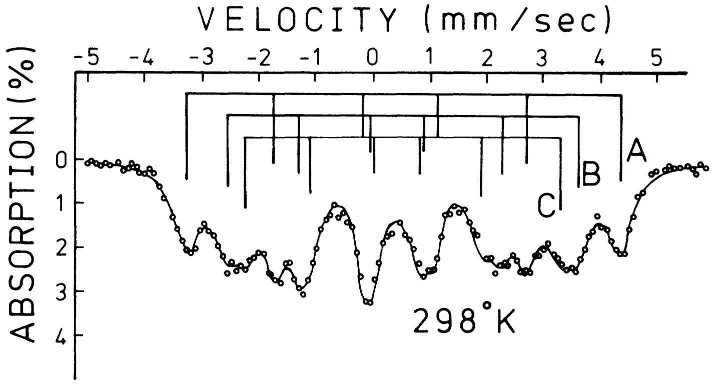

FIG. 2. Mössbauer spectrum of Fe_7Se_8 at 298 °K.

uated quartz tube which had previously been heated to 800 °C in an hydrogen atmosphere to eliminate oxygen adsorbed into the quartz wall. The sealed mixture was heated at 600 °C for 1 day, at 900 °C for 1 day, and at 1100 °C for 1 hour. Then after being kept at 950 °C for seven days, it was cooled down to 400 °C at the rate of 10 °C/min. To prevent oxygen from diffusing into the quartz ampoule, the ampoule was surrounded by a flow of high-purity nitrogen gas during the whole period of heating. To obtain the 3*c* structure the sample was quenched to room temperature from about 400 °C. Because of the small volume of the sample it was easy to carry out the quenching very quickly.

The sample was ^{57}Fe enriched to 6.7 at.% and x-ray diffraction studies showed that the sample had the 3*c* structure. Mössbauer spectra were taken using an electromechanical transducer[7] driven in the constant-acceleration mode in conjunction with a 512-channel multichannel analyzer. ^{57}Co in palladium at 300 °K was used as the source.

III. RESULTS

The Mössbauer spectra were taken at various temperatures ranging from liquid-nitrogen temperature to 460 °K. Figures 1 and 2 show the spectra at 78 and 298 °K, respectively, which consist of three-component subspectra arising from three magnetically nonequivalent sites very similar to that of pyrrhotite[8] (Fe_7S_8). These Mössbauer spectra have been fitted with three sets of six Lorentzians using a least-squares computer program and the results at 78 and 298 °K are shown in Table I.

Isomer shifts of 0.65 to 0.70 mm/sec at room temperature suggest the ferrous character of iron ions at all three sites because the isomer shift of ferrous sulfide,[9] FeS, is 0.82 mm/sec relative to Fe, and those of ferric sulfides[10] such as Fe_3S_4 (greigite) and $CuFeS_4$ are 0.26 and 0.21 mm/sec, respectively, relative to Fe. These results can not be explained by ferrous- and ferric-ion models[11] such as $Fe_2^{3+}Fe_5^{2+}Se_8$, but it seems that ionic

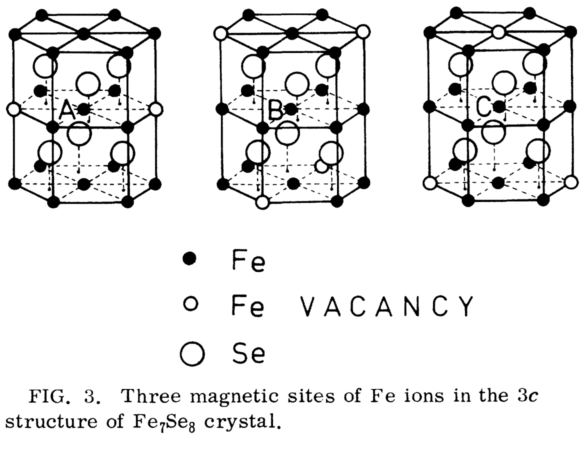

FIG. 3. Three magnetic sites of Fe ions in the 3*c* structure of Fe_7Se_8 crystal.

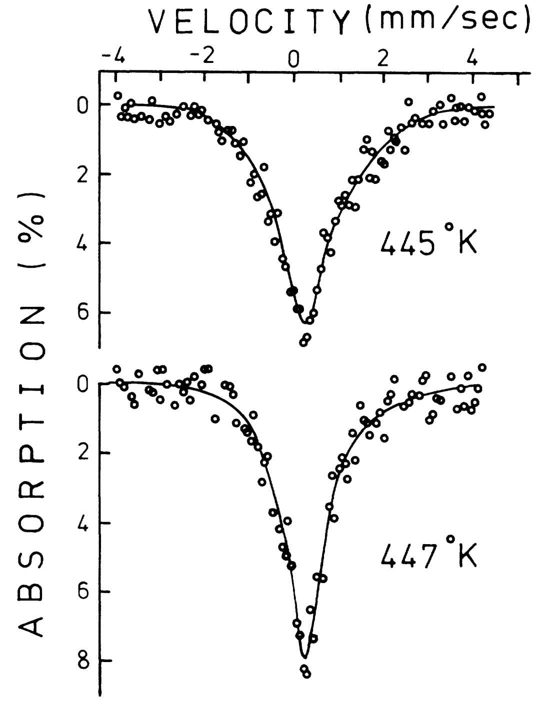

FIG. 4. Mössbauer spectra near the Néel temperature.

TABLE I. Experimental data for Fe_7Se_8 at 78 and 298 °K. The isomer shifts (IS) are relative to Fe metal. σ is the distance between the two outermost lines on the right of the spectrum minus the distance between the two outmost lines on the left divided by 2, which is equal to $e^2qQ/2$ for an axially symmetric electric field gradient lying along the direction of the magnetic hyperfine field H.

T (°K)	Subspectrum	Intensity ratio	H (kOe)	IS (mm/sec)	σ (mm/sec)
78	A	3.0 ± 0.1	274 ± 3	0.83 ± 0.03	0.00 ± 0.04
	B	2.1 ± 0.1	228 ± 7	0.81 ± 0.04	-0.13 ± 0.05
	C	2.1 ± 0.1	206 ± 7	0.76 ± 0.04	-0.04 ± 0.05
298	A	3.0 ± 0.1	237 ± 3	0.70 ± 0.03	0.05 ± 0.04
	B	2.4 ± 0.2	193 ± 8	0.67 ± 0.05	0.04 ± 0.05
	C	2.4 ± 0.2	172 ± 8	0.65 ± 0.05	0.11 ± 0.06

charges for all three sites are nearly equally reduced from the charge of Fe^{3+}.

The three magnetic hyperfine fields can be interpreted to originate from three magnetically nonequivalent sites in the orthorhombic superstructure as shown in Fig. 3; the A site is in the c plane with no Fe vacancies, and the B and C sites in the c plane with Fe vacancies. Actually, the A sites consist of two kinds of sites, say, A_1 and A_2 sites, taking into account the next-nearest-neighbor ferromagnetic c planes. A, B, and C sites have 18, 14, and 13 interplanar superexchange links (Fe-Se-Fe), respectively (Fig. 3), and may be expected to have magnetic-hyperfine-field magnitudes in the proportion of $18:14:13$, neglecting all intraplanar and all cation-cation interactions which are supposed to be much weaker than interplanar interactions.[8,12] The relative ratio of the numbers of A, B, and C sites in the superstructure are $3:2:2$. Since the three experimental magnetic hyperfine fields at 78 °K are in the relative ratios of magnitudes of $274:228:206 = 18.0:15.0:13.5$, and the intensity ratio is $3.0:2.1:2.1$, as shown in Table I, we may conclude that the largest magnetic hyperfine field originates from A sites and the smallest one from C sites.

As shown in Fig. 3, each Fe ion is surrounded by 6 Se ions in an almost perfect octahedral coordination. The angle between the two Fe-Se bonds was calculated to be 90°, within 0.15°, using the following values[3] of a and c : $a = 3.617$ Å and $c = 5.883$ Å. This may be the reason why we have very small values for the quadrupole splittings listed in Table I. To detect the spin rotation[4] that has been reported near 130 °K, we increased the temperature and observed the change of sign of σ that seems to be due to the spin rotation as shown in Table I, though the quadrupole splittings are very small because of the above-mentioned nearly perfect octahedral coordination. σ is defined to be one-half of the distance between the two outermost lines on the right of the six-line Mössbauer spectrum minus the distance between the two outermost lines on the left. The Néel temperature was determined to be (447 ± 1) °K, as shown in Fig. 4. This is a little higher than the 443 °K of the magnetic torque measurement,[2] but lower than the 455 °K obtained by the neutron-diffraction method.[4] It may be mentioned that our values of the three magnetic hyperfine fields at room temperature shown in Table I are much less than the 310 and 225 kOe of Fatseas[6]. However, it should be noted that the Mössbauer spectrum of Fatseas's sample prepared using natural iron showed only about 1% absorption and large baseline distortion, while that of our sample showed 3% absorption and no baseline distortion and could be fitted with Lorentzian curves using an electronic computer.

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