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Temperature dependent high velocity resolution Mössbauer spectroscopic study of iron nickel phosphide microcrystals (rhabdites) extracted from Sikhote-Alin iron meteorite

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ABSTRACT

Iron nickel phosphide microcrystals (rhabdites) extracted from Sikhote-Alin iron meteorite fragment were studied using Mössbauer spectroscopy with a high velocity resolution at various temperatures. Mössbauer spectra of rhabdites demonstrated superparamagnetic behavior. Low temperature rhabdite spectra were fitted using a model with six magnetic sextets two pairs of which were related to crystallographically non-equivalent sites M1, M2 and M3 occupied by Fe and Ni atoms in different ways. Temperature dependencies of correspondent magnetic hyperfine fields were evaluated. On the basis of relative areas of spectral components and results of rhabdite chemical analysis the average numbers of Fe and Ni atoms occupied the M1, M2 and M3 sites, respectively, were evaluated.

1. Introduction

Rhabdites are iron nickel phosphides (Fe, Ni)$_3$P in the form of prismatic idiomorphic microcrystals precipitated in iron meteorite kamacite matrix. It is well known that artificial Fe_3P and meteoritic (Fe, Ni)$_3$P have the unit cell with 24 metal atoms in three crystallographically non-equivalent sites denoted as M1, M2 and M3 with 8 atoms in the each site. In the case of rhabdites these sites are occupied by Fe and Ni in different way [1]. Previous Mössbauer studies of synthetic Fe_3P and schreibersite (massive (Fe, Ni)$_3$P inclusions at kamacite grain boundaries) from Bocaiuva iron meteorite demonstrated complicated magnetic hyperfine structure with six magnetic sextets related to M1, M2 and M3 sites [2,3]. It was suggested that the magnetic moment splitting of about 0.1 μ_B for each site in phosphide as a reason of two sextets related to each site in Fe_3P [2]. Recently Mössbauer spectroscopy with a high velocity resolution demonstrated new possibilities in the study of various iron bearing phases in meteorites [4–8]. Our previous study of iron nickel phosphides demonstrated superparamagnetic Mössbauer spectrum of rhabdite at room temperature [9]. In this work we present new preliminary results of the study of iron nickel phosphide microcrystals extracted from Sikhote-Alin iron meteorite using Mössbauer spectroscopy with a high velocity resolution at various temperatures.

2. Materials and methods

Iron nickel phosphide microcrystals (rhabdites) were extracted electrochemically from the bulk fragment of Sikhote-Alin IIAB iron meteorite. Extracted phosphides were characterized by scanning electron microscopy (SEM) using Philips 30XL with EDX and X-ray diffraction (XRD) using STADI-P diffractometer with Cu $K_{\alpha 1}$ radiation.

Mössbauer spectra were measured using automated precision Mössbauer spectrometric system created on the basis of Mössbauer spectrometer SM-2201 with a high velocity resolution and modified liquid nitrogen cryostat with moving absorber (cryostat was made at the Research Institute of Physics, Southern Federal University, Rostov-on-Don). Mössbauer spectra are always registered in 4096 channels of analyzer. Details of this Mössbauer spectrometric system were given in [10,11]. Rhabdite sample had effective thickness of ~6 mg Fe/cm^2. The ~1.8 × 10^9 Bq ^{57}Co(Cr) source was used at room temperature. Mössbauer spectra were measured in transmission geometry with moving absorber in the cryostat to exclude parabolic distortion of the spectrum and contribution of the ^{57}Fe in the beryllium window of the detector. Mössbauer spectra were measured at 295, 220, 150 and 90 K and presented in 1024 channels by consequent summation of 4 neighbour channels. Spectra were measured with statistical rates of ~(1.1–2.2) × 10^6 counts per channel for the spectra presentation in 1024 channels. The spectra were computer fitted with the least squares procedure using UNIVEM-MS program (from the Research Institute of Physics, Southern Federal University, Rostov-on-Don) with Lorentzian line shape. Spectral parameters such as: isomer shift, δ, quadrupole splitting (quadrupole shift for magnetically split spectra), ΔE_Q, magnetic hyperfine field, H_{eff}, line width, Γ, relative subspectrum area, S, and statistical criterion, χ^2, were determined. Magnetic sextets were fitted using the ratio S_{16}:S_{25}:S_{34} = 3:2:1. Criteria of spectra fitting quality were χ^2, differential spectrum and physical meaning of parameters. Values of δ are given relative to α-Fe at 295 K.

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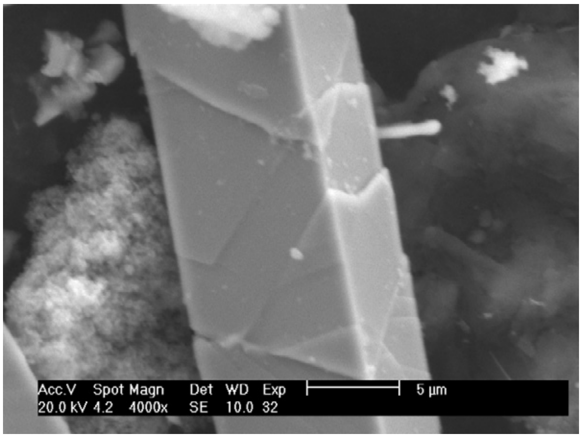

Fig. 1. SEM image of iron nickel phosphide microcrystal extracted from Sikhote-Alin iron meteorite.

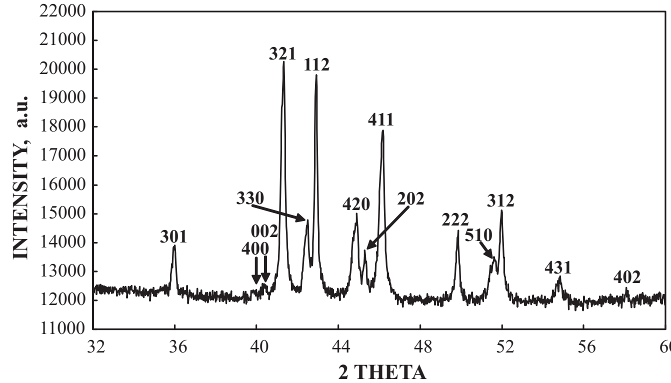

Fig. 2. XRD patterns of iron nickel phosphide microcrystals extracted from Sikhote-Alin iron meteorite.

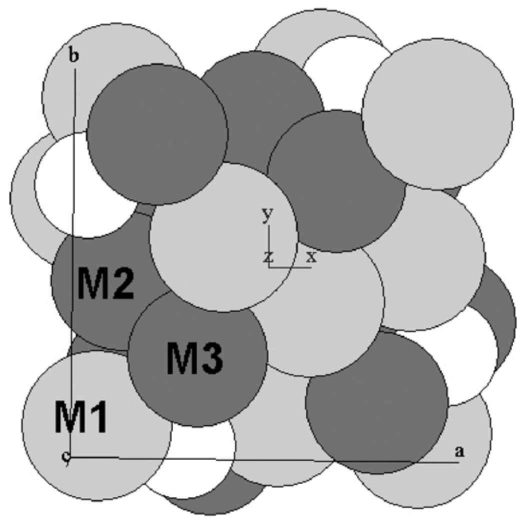

Fig. 3. Crystallographically non-equivalent metal sites M1, M2 and M3 in $(Fe, Ni)_3P$. ○ – P, ● – Fe, ● – Ni.

3. Results and discussion

Chemical analysis of 11 rhabdite microcrystals extracted from Sikhote-Alin iron meteorite using SEM with EDX demonstrated small variations of Fe and Ni content with average parts of Fe and Ni atoms as 52% and 48%, respectively (stoichiometric formula is $(Fe_{0.52}Ni_{0.48})_3P$). SEM image of rhabdite microcrystal is shown in Fig. 1. XRD patterns of rhabdites are shown in Fig. 2. XRD study showed that the unit cell had tetragonal structure I-4 with parameters a = 9.029(3) Å and c = 4.461(5) Å. Structure of a part of the iron nickel phosphide unit cell with different M1, M2 and M3 sites for metal atoms is shown in Fig. 3.

Mössbauer spectra of iron nickel phosphide microcrystals extracted from Sikhote-Alin iron meteorite measured with a high velocity resolution at 295, 220, 150 and 90 K are shown in Fig. 4. The room temperature spectrum of rhabdite microcrystals demonstrated superparamagnetic behavior (earlier we evaluated the Curie temperature for rhabdite by magnetization measurements of about 345 K [9]). It was better fitted using three magnetic sextets and one paramagnetic doublet. In contrast low temperature spec-

Table 1
Low temperature Mössbauer parameters for rhabdite microcrystals extracted from Sikhote-Alin iron meteorite.

T, K	Γ[a], mm/s	δ, mm/s	ΔE_Q, mm/s	H_{eff}, kOe	S[b], %	χ^2	Fe site[c]
220	0.582 ± 0.030	0.362 ± 0.018	0.011 ± 0.032	238.2 ± 1.9	9.71	0.911	M1
	0.582 ± 0.030	0.346 ± 0.015	0.019 ± 0.015	215.3 ± 1.0	34.20		M1
	0.582 ± 0.030	0.340 ± 0.015	−0.018 ± 0.016	194.1 ± 0.9	21.94		M2
	0.527 ± 0.077	0.409 ± 0.024	0.052 ± 0.036	159.5 ± 1.6	7.60		M2
	0.401 ± 0.066	0.587 ± 0.020	−0.340 ± 0.015	102.2 ± 1.7	5.84		M3
	0.582 ± 0.030	0.499 ± 0.017	−0.340 ± 0.015	69.8 ± 1.4	11.08		M3
	0.497 ± 0.035	0.204 ± 0.015	1.078 ± 0.017	–	9.63		(PM)
150	0.434 ± 0.030	0.358 ± 0.015	0.043 ± 0.016	261.9 ± 0.6	9.41	0.934	M1
	0.543 ± 0.030	0.380 ± 0.015	0.036 ± 0.015	246.4 ± 0.5	34.15		M1
	0.582 ± 0.030	0.380 ± 0.015	−0.036 ± 0.015	230.6 ± 0.7	23.97		M2
	0.582 ± 0.030	0.290 ± 0.043	0.139 ± 0.081	193.5 ± 2.2	4.08		M2
	0.582 ± 0.030	0.410 ± 0.016	−0.149 ± 0.034	120.1 ± 1.6	9.52		M3
	0.582 ± 0.030	0.400 ± 0.015	−0.079 ± 0.018	89.1 ± 0.9	12.96		M3
	0.448 ± 0.031	0.332 ± 0.015	1.084 ± 0.018	–	5.91		(PM)
90	0.272 ± 0.030	0.399 ± 0.015	0.010 ± 0.016	281.4 ± 0.8	4.35	1.014	M1
	0.486 ± 0.030	0.414 ± 0.015	0.033 ± 0.015	267.9 ± 0.5	39.70		M1
	0.506 ± 0.030	0.415 ± 0.015	0.002 ± 0.015	251.3 ± 0.5	22.42		M2
	0.558 ± 0.077	0.549 ± 0.026	−0.106 ± 0.049	210.8 ± 1.6	5.35		M2
	0.582 ± 0.030	0.397 ± 0.015	−0.219 ± 0.016	122.6 ± 0.9	12.78		M3
	0.582 ± 0.030	0.434 ± 0.015	−0.005 ± 0.022	91.5 ± 1.0	10.98		M3
	0.440 ± 0.039	0.323 ± 0.015	1.148 ± 0.023	–	4.40		(PM)

Indicated errors for Γ and hyperfine parameters were instrumental (systematic) or fitted errors if their values exceeded systematic errors.
[a] Line widths are given for the 1st and 6th lines of sextets.
[b] Relative error is less than 10%.
[c] PM is paramagnetic component.

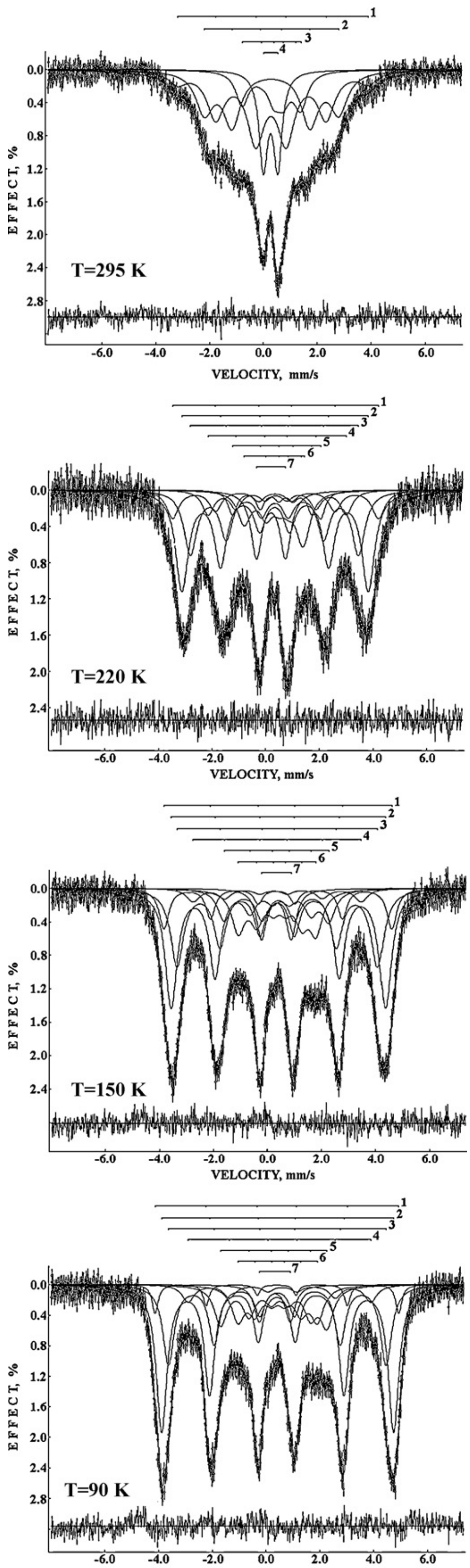

Fig. 4. Mössbauer spectra of iron nickel phosphide microcrystals extracted from Sikhote-Alin iron meteorite. Indicated components are the results of the better fit.

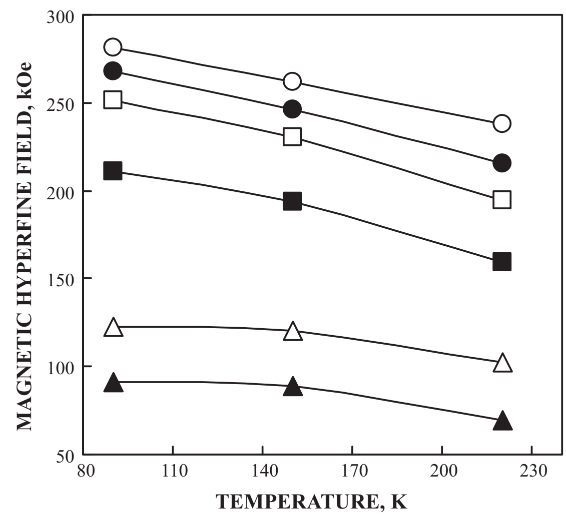

Fig. 5. Temperature dependences of magnetic hyperfine fields related to the each site in iron nickel phosphide microcrystals extracted from Sikhote-Alin iron meteorite: ●, ○ – M1 sites, ■, □ – M2 sites and ▲, △ – M3 sites.

tra were better fitted using six magnetic sextets based on model [2] and one paramagnetic doublet. These six sextets were related to the ^{57}Fe nuclei in the M1, M2 and M3 sites in rhabdite microcrystals, two sextets per one site. Two sextets with the largest values of magnetic hyperfine fields were related to the M1 site, two sextets with medium values of magnetic hyperfine fields were related to the M2 site and two sextets with the lowest values of magnetic hyperfine fields were related to the M3 site in agreement with [3]. Mössbauer parameters of all components in the low temperature spectra are presented in Table 1.

Temperature dependencies of H_{eff} for Fe atoms in the M1 and M2 sites appeared to be different from those for Fe atoms in the M3 sites (Fig. 5). An analysis of the relative areas of spectral components showed that total S values for sextet pairs related to the both M1 and M2 sites were the same within the error at 220, 150 and 90 K while that for sextet pair related to the M3 site increased with decrease of doublet area (Table 2). In this case we can assume that at low temperatures Fe atoms remained in paramagnetic state in the M3 sites only. Therefore, average relative areas for spectral components related to the M1, M2 and M3 sites in rhabdite microcrystals were about 44%, 28% and 28%, respectively, in the temperature range of 220–90 K. Different total relative areas of spectral components related to the M1, M2 and M3 sites in rhabdites may be a result of different numbers of Fe atoms occupied the each type sites. Using the results of chemical analysis (relative parts of Fe and Ni) and ratio of Fe atoms in the M1, M2 and M3 sites we calculated numbers of Fe and Ni atoms in the each site of the unit cell. Evaluation of average numbers of Fe and Ni atoms showed that the M1 sites were occupied by 5.5 Fe and 2.5 Ni atoms while the M2 and M3 sites were occupied by 3.5 Fe and 4.5 Ni atoms.

Table 2
Relative areas of spectral components related to the M1, M2 and M3 sites.

Spectral components	S^a, %		
	220 K	150 K	90 K
M1 sextets	43.91	43.56	44.05
M2 sextets	29.54	28.05	27.77
M3 sextets	16.92	22.48	23.76
Paramagnetic doublet	9.63	5.91	4.42

[a] Relative experimental error is ±10%.

4. Conclusion

Study of iron nickel phosphide microcrystals (rhabdites) extracted from Sikhote-Alin iron meteorite using Mössbauer spectroscopy with a high velocity resolution permitted us demonstrate superparamagnetic behavior of Mössbauer spectra patterns in the temperature range of 295–90 K. Mössbauer spectra were fitted with a model of six sextets two pairs of which were related to the crystallographically non-equivalent sites M1, M2 and M3 sites in rhabdites. Temperature dependencies of magnetic hyperfine fields for the spectral components related to the M1 and M2 sites were different from those for the M3 sites. Based on the total relative areas of the spectral components related to the M1, M2 and M3 sites and results of chemical analysis of rhabdite microcrystals we evaluated average number of Fe and Ni atoms occupied the M1, M2 and M3 sites in the unit cell of iron nickel phosphide extracted from Sikhote-Alin iron meteorite

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