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Mössbauer effect investigation of the pentagonal approximant phase in the Fe-Nb system

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The formation of the pentagonal Frank-Kasper phase (μ phase) in the $\text{Fe}_{50+x}\text{Nb}_{50-x}$ system near $x=0$ has been investigated. The effects of composition and heat treatment on the phase diagram of this system have been studied. Only the as-cast $x=0$ alloy was found to consist of a pure μ phase. X-ray diffraction patterns indicate the existence of a phase with a high degree of structural order but considerable chemical disorder. A Mössbauer spectrum of the μ -phase material exhibits a room-temperature quadrupole split doublet with $\Delta=0.209$ mm/s and an isomer shift $\delta=-0.289$ mm/s relative to α -Fe. A shell model analysis of the spectrum indicates a structure with a high degree of order. Results are discussed in terms of measurements on related icosahedral and decagonal phase materials.

I. INTRODUCTION

Mössbauer effect studies of quasicrystals have been important for an understanding of the microstructure of these novel materials. A recent review of these studies has been presented by Dunlap and Lawther.¹ A number of methods for the interpretation of Mössbauer spectra of quasicrystalline materials have been presented in the literature and the information which can be obtained from these measurements depends crucially on the techniques applied to their analysis. The comparison of results from quasicrystalline materials and those of related crystalline phases has been important in understanding the relationship of Mössbauer spectral parameters and microstructural details. In the present work we have considered Mössbauer measurements of the pentagonal approximant phase in the Fe-Nb system. These results will be interpreted in the context of results for related quasicrystalline materials.

II. EXPERIMENTAL METHODS

Samples of $\text{Fe}_{50+x}\text{Nb}_{50-x}$ were prepared by melting high-purity elemental components in an argon arc furnace for compositions with $x=0,2$. Materials were studied as-cast and after annealing for four days at 1000 °C and water quenching. Room-temperature $\text{Cu } K_{\alpha}$ x-ray diffraction patterns were made of all samples using a Siemens D500 scanning diffractometer. Room-temperature ^{57}Fe Mössbauer effect studies were performed using a constant acceleration Wissell System II spectrometer and a $Pd^{57}\text{Co}$ source. The intrinsic linewidth of the spectrometer for ^{57}Fe is 0.23 mm/s (FWHM).

III. RESULTS

All alloys studied here showed the presence of the pentagonal μ phase. However, only the as-cast $x=0$ sample was free from the presence of impurity phases. This analysis is consistent with the phase formation studies of the Fe-Nb system reported by Raman.² Further investigations presented in the present manuscript are confined to the single-phase sample.

X-ray diffraction peaks for the μ phase were well defined with a typical linewidth of $\Delta(2\theta) \leq 0.2^\circ$ (FWHM), indicating a high degree of structural order. The peak locations

and relative intensities obtained in this work along with those calculated for the μ phase (W_6Fe_7 structure) with $a=4.928$ Å and $c=26.83$ Å are given in Table I. The peak locations are in excellent agreement with the calculated values³ for the lattice parameters as indicated above. The anomalies in the measured intensities for some of the diffraction peaks are an indication of the presence of substantial chemical disorder on the lattice sites.

The room-temperature ^{57}Fe Mössbauer effect spectrum of the pentagonal phase of Fe-Nb is illustrated in Fig. 1. This spectrum shows the existence of a symmetric quadrupole split doublet. Although the individual lines cannot be resolved, the shape and width of the absorption peak indicate that it is not a singlet. A fit to this spectrum using a Lorentzian doublet yields the mean quadrupole parameters as indicated in Table II. The linewidth of the component lines, 0.29 mm/s, is slightly greater than the intrinsic linewidth of the spectrometer but is substantially less than that found for similar fits to spectra of quasicrystalline materials; typically

TABLE I. X-ray diffraction scattering length and relative peak intensities for pentagonal $\text{Fe}_{50}\text{Nb}_{50}$ measured in the present work and calculated for the pentagonal Frank-Kasper phase.

Index	Measured		Calculated	
	d (Å)	I	d (Å)	I
1 1 0	2.470	86	2.471	72
0 1 10	2.273	67	2.278	46
0 0 12	2.238	18	2.242	18
1 1 6	2.163	100	2.165	75
2 0 1	2.131	45	2.133	35
1 0 11	2.120	53	2.124	43
2 0 4	2.037	17	2.039	16
0 2 5	1.987	31	1.985	29
1 1 9	1.903	15	1.905	15
0 1 13/2 0 7	1.867	11	1.866	15
3 0 0	1.426	16	1.426	20
2 1 10	1.385	15	1.386	33
3 0 6	1.359	22	1.359	32
0 1 19/1 2 13	1.348	22	1.348	48
0 0 21/1 1 18	1.278	20	1.279	60
0 2 17	1.270	9	1.273	21
2 2 0	1.236	20	1.236	100

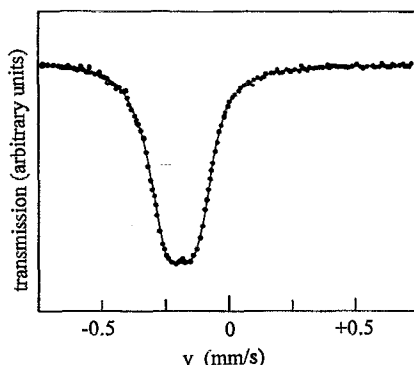


FIG. 1. Room-temperature ^{57}Fe Mössbauer effect spectrum of the pentagonal phase of $\text{Fe}_{50}\text{Nb}_{50}$. The solid line is a least-squares fit to the shell model.

about 0.36 mm/s .¹ This excess linewidth is, presumably, the result of local disorder in the structure as evidenced by the anomalous x-ray peak intensities and which produces a corresponding distribution of local Fe environments. This behavior can be accounted for in the analysis of the Mössbauer effect spectrum by fitting the data to a shell model distribution of quadrupole splittings of the form^{1,4}

$$P(\Delta) = \left(\frac{\Delta}{\sigma}\right)^n \exp\left(-\frac{\Delta^2}{2\sigma}\right), \quad (1)$$

where n and σ are fitted parameters. The symmetric nature of the spectrum indicates the lack of correlation between isomer shift and quadrupole splitting distributions. A detailed computer analysis confirms this assumption. The results of the shell model analysis for this spectrum are given in Table III and the calculated $P(\Delta)$ is illustrated in Fig. 2.

IV. DISCUSSION AND CONCLUSIONS

The existence of a decagonal⁹ and icosahedral¹⁰ phase in the Fe-Nb system has been demonstrated by electron diffraction studies of rapidly quenched samples; although single-phase materials have not yet been prepared. Table I compares the mean quadrupole parameters of the pentagonal Fe-Nb phase with several other icosahedral and decagonal materials. The mean quadrupole splitting of Fe-Nb is somewhat less than in Al-based icosahedral⁹ and decagonal⁷ alloys where Fe atoms are believed to exist in a highly anisotropic environment analogous to the transition metal site environments in the outer shell of the MacKay icosahedra of a cubic approximant phase (e.g., $\alpha\text{-AlMnSi}$) or in the sites of a two-dimensional Penrose tiling, respectively. On the other hand, the quadrupole splitting of Fe-Nb is much greater than that in

TABLE II. Results of room-temperature Mössbauer effect studies of some quasicrystalline and related materials; i =icosahedral, d =decagonal, p =pentagonal, *=this work.

Alloy	Structure	Δ (mm/s)	δ (mm/s)	Reference
$\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$	i	0.369	+0.234	5
$\text{Ti}_{56}\text{Ni}_{23}\text{Fe}_5\text{Si}_{16}$	i	0.06	-0.170	6
$\text{Al}_{75}\text{Pd}_{15}\text{Fe}_{10}$	d	0.372	+0.185	7
$\text{Fe}_{50}\text{Nb}_{50}$	p	0.209	-0.289	*

TABLE III. Comparison of shell model parameters for pentagonal Fe-Nb (p) and some icosahedral (i) alloys. *=this work.

Alloy	Phase	n	σ (mm/s)	Reference
$\text{Al}_{70}\text{Ta}_{10}\text{Fe}_{20}$	i	1.14	0.363	8
$\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$	i	1.44	0.283	5
$\text{Al}_{80}\text{Fe}_{11}\text{Mo}_9$	i	1.48	0.351	8
$\text{Al}_{86}\text{Fe}_{0.28}\text{Mn}_{13.72}$	i	1.70	0.144	1
$\text{Fe}_{50}\text{Nb}_{50}$	p	5.2	0.088	*

typical Ti-based icosahedral alloys.^{11,12} where the Fe atoms are believed to reside in highly symmetric sites at the center of an icosahedral cluster.

The negative isomer shift observed in this alloy is indicative of an anomalously high electron density at the Fe probe sites. This is expected on the basis of the presence of a large concentration of early transition metal (M) atoms in the alloy. The value of δ observed here is consistent with measurements of dilute $M\text{Fe}$ alloys and near neighbor effects of dilute M impurities in Fe (see Ref. 13 and references therein).

The parameters obtained from shell model fits to several quasicrystalline alloys are compared with the data for pentagonal Fe-Nb in Table III. The present results are anomalous in two respects; an unusually large value of the parameter n and an unusually low value of the parameter σ , when compared with all results for quasicrystalline alloys reported to date.¹ The relationship of these parameters to the detail of the microstructure has been discussed by Dunlap *et al.*⁸ Specifically, n near unity and a large value of σ are characteristic of a highly disordered (e.g., amorphous) structure, while increasing values of n (and correspondingly smaller values of σ) are characteristic of an increase in the degree of microstructural order. This inverse correlation between the values of n and σ is characteristic of the relationship between the shell model and the distribution of local Fe environments in the material and is illustrated for typical data for quasicrystalline and related materials in Fig. 3. Typically quasicrystalline materials have values of n in the range of 1–2, with more highly ordered materials (as evidenced from other ex-

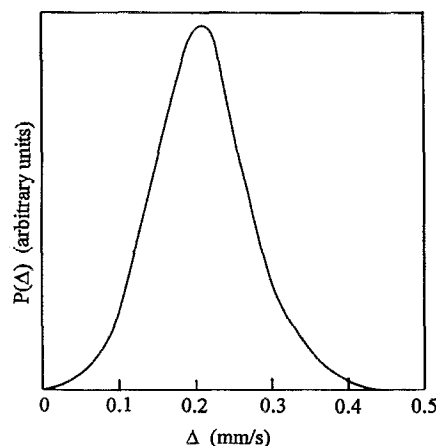


FIG. 2. Quadrupole splitting distribution, $P(\Delta)$, for the spectrum of Fig. 1 as obtained from the shell model.

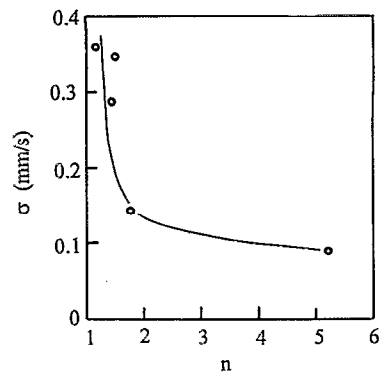


FIG. 3. Relationship between the shell model fitting parameters n and σ for several quasicrystalline and related materials.

perimental techniques) giving $n \approx 2$. The value of $n = 5.2$ obtained in the present work for pentagonal Fe-Nb indicates a much greater degree of order in this crystalline approximant phase than in similar quasicrystalline phases. This, presumably, is indicative of the existence of translational symmetry in the approximant phase which is lacking in the quasicrystalline phase. In more specific terms, n is related to the number of independent distortion vectors d , which are necessary

to describe the structure as $n = d - 1$. The present studies clearly point to the differences which exist between the microstructure of quasicrystals and their crystalline approximants.

ACKNOWLEDGMENTS

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- ¹R. A. Dunlap and D. W. Lawther, *Mater. Sci. Eng. Rep. R* **10**, 141 (1993).
- ²A. Raman, *Proc. Ind. Acad. Sci. A* **65**, 256 (1967).
- ³P. I. Kripyakevich, E. I. Gladyshevskii, and R. V. Skolozdra, *Sov. Phys. Crystall. XPhys. Crystall.* **12**, 525 (1968).
- ⁴G. Czjzek, *Phys. Rev. B* **25**, 4908 (1982).
- ⁵D. W. Lawther and R. A. Dunlap, *J. Non-Cryst. Solids* **153/154**, 45 (1993).
- ⁶D. Bahadur, V. Srinivas, R. A. Dunlap, R. C. O'Handley, and M. E. McHenry, *Philos. Mag. B* **60**, 871 (1989).
- ⁷D. W. Lawther and R. A. Dunlap, *J. Non-Cryst. Solids* **153/154**, 49 (1993).
- ⁸R. A. Dunlap, R. C. O'Handley, M. E. McHenry, and V. Srinivas, *Struct. Chem.* **2**, 501 (1991).
- ⁹A. Q. He, Q. B. Yang, and H. Q. Ye, *Philos. Mag. Lett.* **51**, 69 (1990).
- ¹⁰A. Q. He, H. Q. Ye, and K. H. Kuo, *Scr. Metall.* **23**, 533 (1989).
- ¹¹R. A. Dunlap, M. E. McHenry, R. C. O'Handley, V. Srinivas, and D. Bahadur, *Phys. Rev. B* **39**, 1942 (1989).
- ¹²R. A. Dunlap, R. C. O'Handley, M. E. McHenry, and R. Chatterjee, *Phys. Rev. B* **37**, 8484 (1988).
- ¹³R. Ingalls, *Mössbauer Isomer Shifts* (North-Holland, Amsterdam, 1978), p. 361.