

Local surroundings and the electronic state of the impurity in metastable alloys: Mössbauer spectra of ^{57}Fe in $\text{Ti}_{1-x}\text{Fe}_x$

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The Mössbauer spectra of ^{57}Fe in $\text{Ti}_{1-x}\text{Fe}_x$ ($5 \times 10^{-4} \leq x \leq 0.2$) were studied at temperatures $T = 295$ K, 100 K, 77 K, and 4.2 K. No correlation was found to exist in metastable phases between the local surroundings of Fe and the long-range crystal order (frustration). The relationship between the local distortions and the change in the electronic state of the impurity and the anomalous properties of titanium alloys is discussed.

An interest in the study of nonequilibrium metastable systems has recently increased sharply because of the considerable progress made in research on spin and ordinary glasses.^{1,2} An interesting class of such systems are the hardened titanium-based alloys³ which have, despite the crystal structure, several characteristic features typical of metallic glasses; in particular, they show evidence of the presence of two-level systems in the low-temperature properties.^{4,5} These alloys also display several anomalies of the electronic⁶ and lattice⁷ properties, of which the most unusual is the giant absorption of microwave electromagnetic field.⁸ The objective of our experiment was to study in detail the state of the impurities in metastable alloys $\text{Ti}_{1-x}\text{Fe}_x$ by measuring the Mössbauer spectra in the samples which were used in Refs. 7 and 8.

The procedure for preparing the samples and determining their characteristics (in the interval $5 \times 10^{-4} \leq x \leq 0.2$) was described elsewhere.^{7,9} In particular, an x-ray diffraction study showed that the samples with $x \leq 0.04$ had a hcp (α) structure and those with $x \geq 0.048$ had a bcc (β) structure. The methods used to measure the Mössbauer spectra and to analyze them were described in Ref. 9. In contrast with Ref. 9, our measurements were carried out at temperatures of the sample of 295 K, 100 K, 77 K, and 4.2 K (the source was held at room temperature). We studied samples with a small value of x ($x \approx 5 \times 10^{-4}$) and analyzed the results in a more consistent way.

Some of the spectra which we measured are shown in Fig. 1. At $x \approx 5 \times 10^{-4}$ (a value which is lower than the limit of equilibrium solubility, $x_e \sim 10^{-3}$ in α - Ti) the spectrum can be approximated by a singlet (or a slightly split doublet), consistent with the result of Ref. 10 (the α line). At $x \geq 0.08$, a doublet gives the best approximation (we refer to it below as the β doublet), consistent with Refs. 11 and 12. We found that the spectrum in the α phase ($0.02 \leq x \leq 0.04$) is described by nearly the same doublet (a doublet with the same parameters). In the region of "critical" concentrations, $0.05 \leq x \leq 0.07$, where many electronic properties (resistivity, magnetic susceptibility, magnetoresistance, etc.) and lattice properties (elastic moduli, damping of

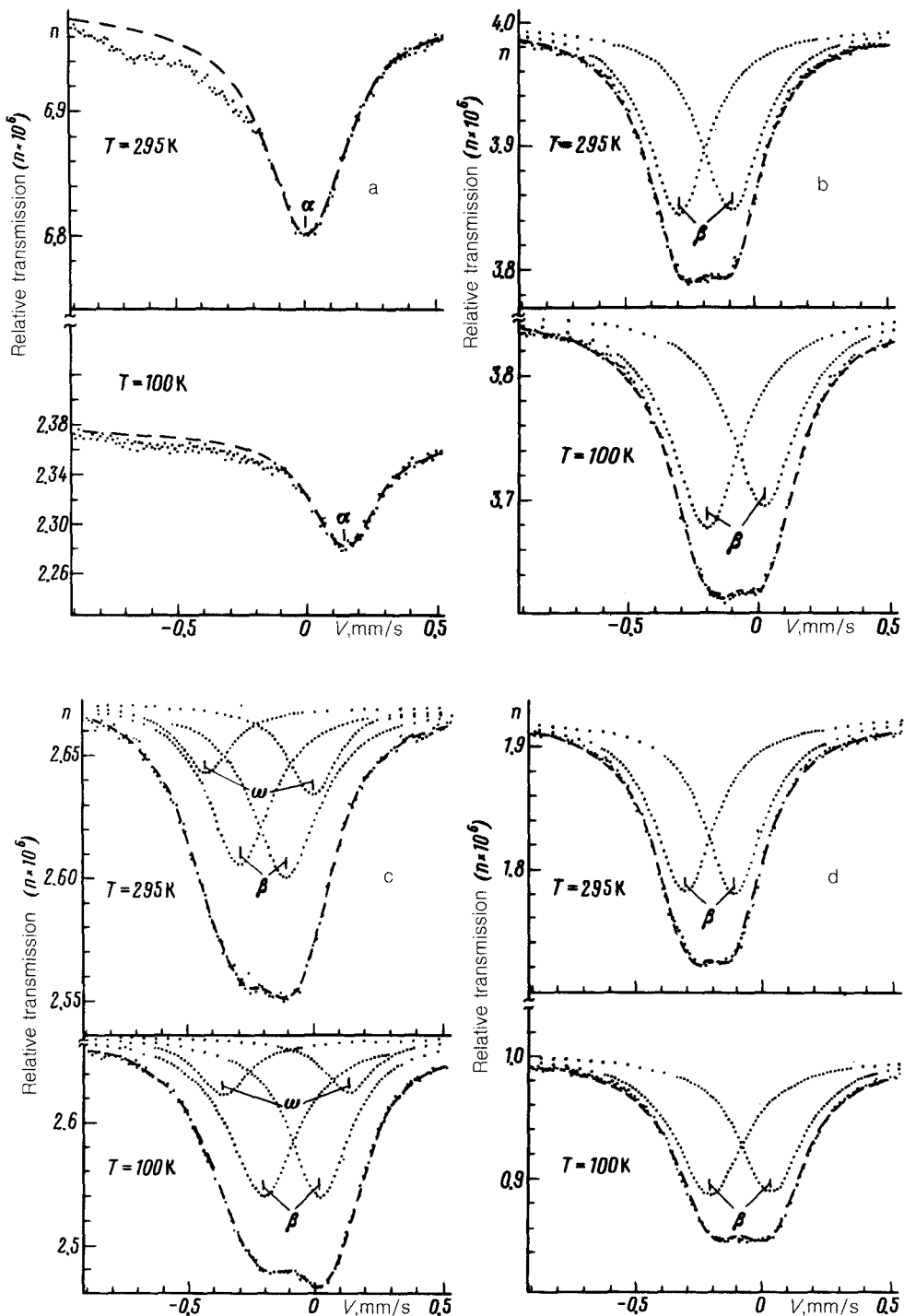


FIG. 1. The Mössbauer spectra of $Ti_{1-x}Fe_x$: (a) $x = 0.0005$; (b) $x = 0.029$; (c) $x = 0.048$; (d) $x = 0.101$, measured at two temperatures.

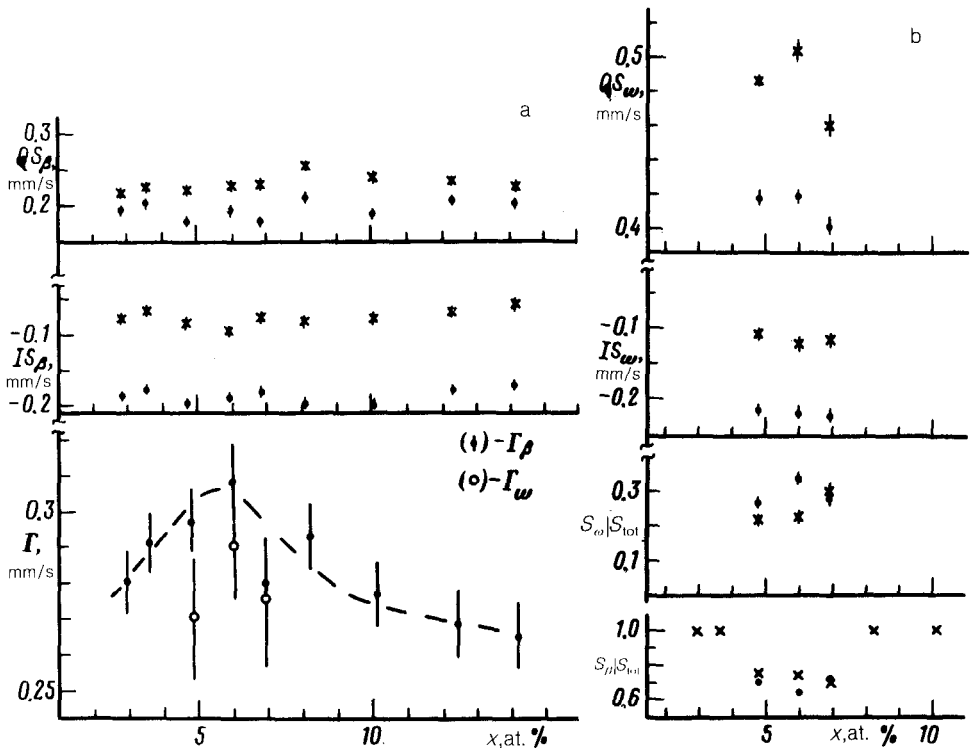


FIG 2. (a), (b)—The concentration dependence of the quadrupole splitting (QS_β , QS_ω), of the isomer shift (IS_β , IS_ω), of the width (Γ_β , Γ_ω), and of the area under the curve (S_β , S_ω), respectively, for the β and ω phases at the temperatures $T = 100$ K (x) and $T = 295$ K (●); ∇ —isomer shift for the intermetallic compound TiFe (see Ref. 11); the quadrupole splitting and isomer shift for the concentration $x = 0.0005$ at a temperature $T = 295$ K are respectively $QS_\alpha = 0.1$ mm/s and $IS_\alpha = -0.01$ mm/s for α -Fe.

sound, rigidity, etc.) exhibit critical anomalies,⁶⁻⁸ the best description is given by two doublets—the β doublet and an auxiliary doublet which apparently corresponds to the appearance of a second phase at these values of x . A comparison with the results of Ref. 11 and the data on the metastable phases in titanium alloys³ allow us to tentatively identify this phase as the ω phase and to call the new doublet the ω doublet. Figure 2 shows the concentration dependence of the parameters of these doublets. As can be seen in Fig. 2, Fe with $x \approx 0.06$ is in the ω phase when the impurities are in the range 25–30%. The temperature dependence of the parameters of the β doublet are shown in Fig. 3 (cf. Ref. 13).

The experimental results allow us to assert that the symmetry of the local surroundings and the electronic state of the iron impurity change dramatically upon transition from an equilibrium α solid solution ($x \lesssim 5 \times 10^{-4}$) to a nonequilibrium metastable α' phase³ ($x \gtrsim x_c$). The values of the quadrupole splitting, $QS_\beta(x)$, and of the isomer shift, $IS_\beta(x)$, which illustrate this assertion, are shown in Fig. 2. With an increase in x , these small and gradual changes have virtually no effect on the α - β transition ($x \approx 0.04$ – 0.05). The presence of a β doublet with $QS_\beta(x)$, which is nearly

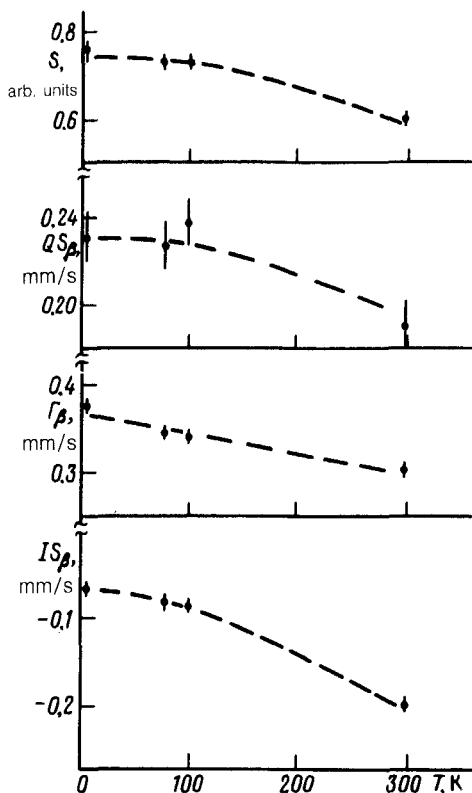


FIG. 3. Temperature dependence of the area under the curve (S_{tot}), of the quadrupole splitting (QS_{β}), of the linewidth (Γ_{β}), and of the isomer shift (IS_{β}) for $Ti_{1-x}Fe_x$ at $x = 0.101$.

independent of x , suggests that the cubic symmetry of the local surroundings of iron in the β phase (more precisely, the $\beta + \omega$ phase) is disrupted, while a comparison of the spectra with $x \approx 0.02-0.03$ and with $x \approx 0.08$ shows that these surroundings are similar in the α' and β phases. These surroundings differ appreciably (the QS is large) from those in an undistorted hpc structure (the α line in Fig. 1).

The absence of an appreciable dependence $IS_{\beta}(x)$ (Fig. 2) confirms the validity of the hypothesis, proposed in Ref. 6, that the electronic impurity subsystem is an "independent" subsystem (there is no appreciable redistribution of electrons between Ti and Fe at $x \approx x_c$). The results for $IS_{\beta}(x)$, on the other hand, determine the concentration range of this subsystem, while the results for $\theta S_{\beta}(x)$ show that the structural state of Fe impurities is an independent state (in the sense that the surroundings do not depend on the long-range crystal order). We can assume (see Fig. 2) that these two results are related and that the transition through the equilibrium solubility limit causes the electronic structure of the impurity to change and the lattice to be locally distorted (an effect similar to the Jahn-Teller effect or a trapped-polaron effect occurs). In this sense, the impurity state is a "frustrated" state² (the short-range order does not correlate with the long-range order). The presence of such frustrations is apparently a feature which is common to metastable crystal alloys. A possible prerequisite for the appearance of local distortions is that a substitution of Fe for Ti in each

ideal structure is energetically unfavorable. According to the microscopic calculations,¹⁴ for example, this energetic disadvantage amounts to approximately 4.5×10^3 K for the hcp phase and 2.5×10^3 K for the bcc phase. Since a local distortion can occur in more than one way, the physical model proposed above constitutes a microscopic foundation for the existence of two-level systems in crystalline titanium alloys^{4,5} and in other metastable systems such as Zr-Nb (Ref. 15).

The slight asymmetry of the β doublet may be yet another characteristic feature of the experimentally observed Mössbauer spectra (Fig. 1). The trivial origin of this asymmetry (a slight admixture of another phase) cannot be ruled out. If it is nonetheless assumed to be an intrinsic property, then this asymmetry could be the result of the Blume effect¹⁶: the result of QS fluctuations of frequency $\nu \gg \Gamma$ (where Γ is the linewidth). Since Shcherbakov et al.⁸ observed the absorption of an electromagnetic microwave field at $\nu \sim 10$ GHz and $x \approx 0.06-0.07$, it would be reasonable to assume the existence of such characteristic frequencies. We can assume that two-level systems of the type described above have dipole moments whose interaction under conditions of reduced electron screening^{7,8} ultimately accounts for the absorption reported in Ref. 8. Since the Mössbauer spectra we obtained suggest that the local distortions and their dynamics (if it is linked with the doublet's asymmetry) are conserved when the temperature is lowered to $T = 4.2$ K, even the effect⁸ which was observed at room temperature apparently should also be observed at low temperatures. It would be very interesting to verify this assumption experimentally. Since the region in which the effect observed by Shcherbakov et al.⁸ coincides with the region in which the ω doublet appears, it would be of interest to determine whether there is a correlation between the observation of this effect and the appearance of the ω phase or the phase boundaries.

The application of the "local" method to the study of the impurity subsystem in metastable alloys thus proved to be highly informative. It would be of considerable interest to study the state of the titanium subsystem by, for example, the nuclear-quadrupole-resonance method.

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