Mössbauer investigations of the distribution and charge of the vacancies in the crystal lattice of α-leboite

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The Mössbauer spectra of Fe^{57} in α-leboite samples of various compositions, which are sharply asymmetrical doublets, are obtained. The spectra are interpreted on the basis of the assumption that the absorption lines are superimposed on quadrupole splitting, and that their parameters depend on the number and disposition of the vacancies in the first and second coordination spheres. The possible atomic characteristics corresponding to the obtained parameters are determined.

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The higher silicide of iron α-$Fe_{1-x}Si_2$ (α-leboite) has a tetragonal lattice (Fig. 1) and is a phase of variable composition with vacancies in the iron sublattice, the vacancy concentration increasing with increasing silicon content from 13% (at 69.5 at.% Si) to 23% (at 72.3 at.% Si).[1] X-ray structure investigations have shown that its vacancy distribution has no long-range order. The Mössbauer spectra (MS) of Fe^{57} in α-leboite[1–3] have the form of asymmetrical doublets. The interpretation of these spectra was either not carried out,[1] or was based on the assumption that the compounds contain at least three phases (FeSi, β-$FeSi_2$, and α-$FeSi_2$),[2] superpositions of which explained the different half-widths and intensities of the doublet lines. Such an assumption, however, contradicts the observed phase composition of the compounds. It is more realistic to attribute the peculiarity of the MS to the dependence of its parameters on the local surrounding of the Fe^{57} atoms, as a result of which the absorption spectrum should reflect the distribution of the vacancies and their charge characteristics.

In view of the foregoing, it was of interest to obtain the MS of Fe^{57} in α-$Fe_{1-x}Si_2$ compounds of various compositions, to attempt to represent them as superpositions of symmetrical doublets connected with various atomic configurations of the nearest surrounding of the resonant nuclei, and to determine the effective charges of the vacancies on the basis of the obtained parameters.

EXPERIMENTAL PROCEDURE AND RESULTS

The investigations were performed on six samples prepared by fusing high-purity components (carbonyl iron of brand VZ and semiconductor silicon) in a high-frequency hermetic furnace, with a composition corresponding to the region of homogeneity of the α-$FeSi_2$ phase. Finely ground powders were annealed at 1050 °C for ten hours in sealed quartz ampules and quenched in air. An x-ray analysis has shown the compounds to be single-phase, and the lattice periods determined with the aid of an RKU-114M camera and calculated by least squares with weighting coefficients (Table 1) were close to those reported earlier.[1]

The Mössbauer investigations were carried out on pellets of 2.5 cm diameter containing 10 mg of natural iron per cm^2, using a constant-acceleration spectrometer based on an NTA-512B analyzer. The γ-ray source was the isotope Co^{57} in a Cr matrix, with activity 20 mCi. The nonlinearity of the motion velocity (± 0.1%) was determined from the spectra of standard adsorbers ($Fe_2^{57}O_3$ and $Na[Fe(CN)_5NO]\cdot 2H_2O$).

The investigation has shown that the MS of all the obtained α-$Fe_{1-x}Si_2$ samples, regardless of the composition, are qualitatively similar to one another (Fig. 2). x is increased from 0.13 to 0.23, a regular variation of the general shape of the spectrum is observed, wherein the center of gravity of the right-hand peak shifts towards lower velocities.

INTERPRETATION OF SPECTRA

The observed asymmetry of the spectral lines can not be attributed to relaxation effects and to anisotropy of the Debye–Waller factor.[4] These effects depend strongly on the temperature, and this should lead to a temperature dependence of the shape of the MS. At the same time, it is noted in[1,3] that variation of the temperature of the α-leboite sample in the range 5–800 °K does not change significantly the form of the spectrum. The latter is apparently connected with the high Debye temperature of the α-leboite (533 °K[1]) and to the insignificant anisotropy of the Debye–Waller factor for iron atoms in the crystal under consideration.

The hypothetical defect-free structure of α-leboite should ensure a doublet character of the MS with a normal half-width, quadruple splitting, and isomeric shift due to the tetragonality of the lattice. The presence of vacancies in the iron sublattice leads inevitably to changes in the electric field gradient (EFG) and in the isomeric shift (IS), the values of which are determined by the number and by the arrangement of the vacancies in the nearest surrounding of the resonant Fe

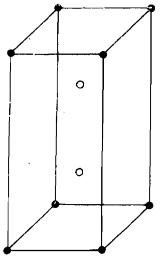

FIG. 1. Unit cell of α-leboite. ●—Fe, ○—Si.

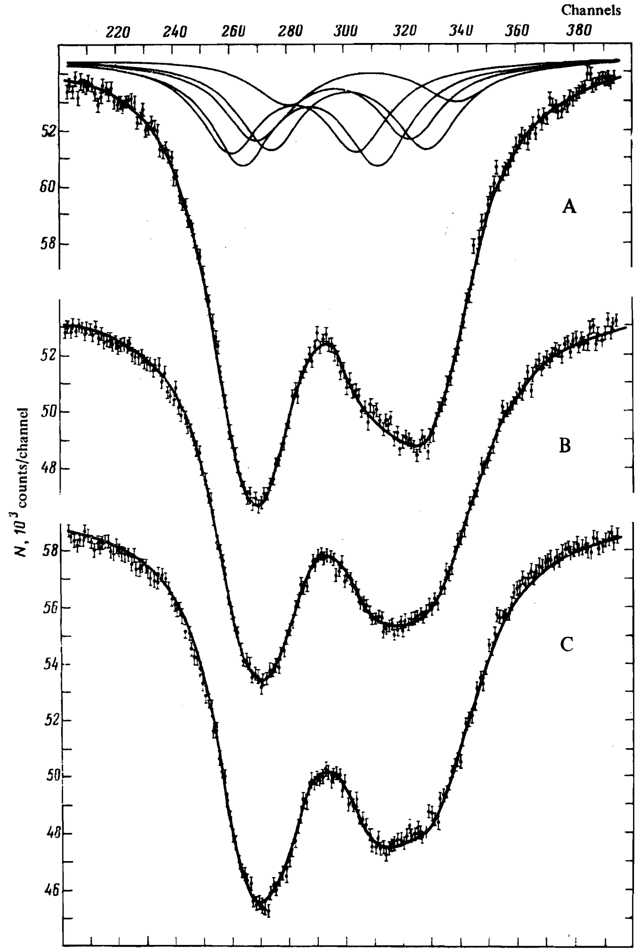

FIG. 2. Experimental (points) and theoretical (solid lines) spectra of Fe^{57} in α-$Fe_{1-x}Si_2$(A—α-$Fe_{0.87}Si_2$, B—α-$Fe_{0.80}Si_2$, C—α-$Fe_{0.77}Si_2$). Five (out of 12) components of the doublets (thin lines) are shown with the largest intensities for the sample A.

atoms. In the analysis of the experimental data, we took into account only the two nearest coordination spheres in the basal plane. We considered two models characterized 1) by the statistical distribution of the vacancies and 2) by the ordered (short-range order) distribution of the vacancies. For the first model, we calculated the statistical weights of 51 possible configurations corresponding to different numbers and dispositions of the vacancies satisfying the binomial distribution law:

$$P_i(k_1, k_2)=A\frac{n!}{k_1!(n-k_1)!}t^{k_1}g^{(n-k_1)}B\frac{n!}{k_2!(n-k_2)!}t^{k_2}g^{(n-k_2)},$$

where $P_i(k_1, k_2)$ are the probabilities of configurations containing k_1 and k_2 iron atoms in the first and second coordination spheres, respectively ($n=4$ is the total number of sites in each of these spheres), A and B are coefficients that take into account the arrangement of the vacancies, $t=1-x$ is the concentration of the iron atoms for disordered alloys, and $g=x$ is the concentration of vacancies in the iron sublattice.

TABLE 1. The periods of the α-leboite (α-$Fe_{1-x}Si_2$) lattice. The results are accurate to ±0.0005 Å.

x	a, Å	c, Å	x	a, Å	c, Å
0.13	2.6945	5.1453	0.20	2.6930	5.1415
0.14	2.6940	5.1437	0.21	2.6925	5.1402
0.16	2.6937	5.1424	0.23	2.6911	5.1391

TABLE 2. Values of the varied parameters, describing the influence of the vacancies on the MS of α-$Fe_{1-x}Si_2$ samples with different compositions within the framework of models 1 and 2. The results are accurate to ±0.005.

Parameters	x							
	Model 1		Model 2					
	0.13	0.20	0.13	0.14	0.16	0.20	0.21	0.23
Γ, mm/sec	0.310	0.302	0.312	0.301	0.303	0.325	0.330	0.309
Δ_0, mm/sec	0.537	0.508	0.523	0.531	0.522	0.505	0.504	0.505
β, mm/sec	0.076	0.068	0.065	0.063	0.058	0.073	0.070	0.065
δ_0, mm/sec	0.293	0.277	0.278	0.301	0.277	0.291	0.294	0.292
α_1, mm/sec	0.102	0.150	0.152	0.161	0.159	0.151	0.149	0.159
α_2, mm/sec	0.180	0.060	0.038	0.024	0.030	0.029	0.029	0.021
ε_1	—	—	0.073	0.062	0.041	0.002	—0.012	—0.033
ε_2	—	—	0.067	0.055	0.034	0.001	0.003	0.001

In the second model, to take the short-range order into account, we introduced independently variable correlation parameters ε_1 and ε_2' for the first and second coordination spheres, respectively.[5] In this case

$$t_{1,2}=(1-x)-\frac{\varepsilon_{1,2}}{1-x}, \quad g_{1,2}=x+\frac{\varepsilon_{1,2}}{1-x}.$$

In the reduction of the experimental data we took into account the fact that certain configurations produce identical effects, so that the spectrum could be described by a superposition of 12 doublets using 8 and 10 varied parameters in each for the first and second model, respectively. The absorption line shape was assumed Lorentzian:

$$I(V_{\text{chan}})=\sum_{i=1}^{12}\frac{P_iW\Gamma^2}{4\mathscr{P}_i},$$

$$\mathscr{P}_i=\left[V_{\text{chan}}-(\delta_0-c_i\alpha_1-d_i\alpha_2)+\sum_{n=1}(-1)^n\frac{\Delta_0+b_i\beta}{2}\right]^2+\frac{\Gamma^2}{4},$$

where the varied parameters are: Γ—the half-width, P_iW—the line intensity, δ_0, α_1, α_2—the isomeric shift and the concentration coefficients of its increment as functions of the number of vacancies in the first and second coordination spheres, Δ_0 and β—the quadrupole splitting and the additional contribution made to it by the defects in the structure; the quantities b_i, c_i, and d_i take into account the number and the disposition of the vacancies, while V_{chan} is the velocity of the source for a definite channel.

As the primary criterion for the applicability of the discussed model we have assumed constancy of the parameters Γ, δ_0, α_1, α_2, Δ_0 and β for compounds with different compositions. The results of computer minimization (by the Gauss-Seidel method) have shown that, within the framework of the model of the statistical distribution of the vacancies, the concentration-dependent changes in the coefficients α_1 and α_2 not only do not remain insignificant, but the influence of the second neighbors on the resonant atom (at $x=0.13$) becomes even much larger than the influence of the first nearest neighbors ($\alpha_2>\alpha_1$), an unreasonable result (Table 2, model 1). When the correlation parameters ε_1 and

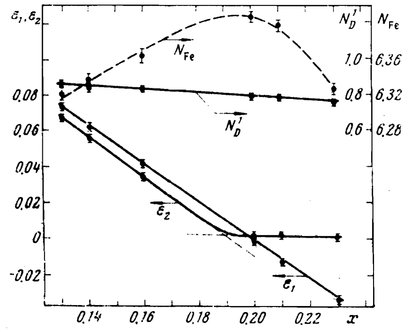

FIG. 3. Concentration dependences of the correlation parameters ε_1' and ε_2', of the number of vacancies in the first coordination sphere (N_D^1), and of the number of iron atoms in the two coordination spheres (N_{Fe}).

ε_2 are introduced, the values of the varied parameters actually changes little when x changes from 0.13 to 0.23 (Table 2, model 2). In addition, within the framework of the second model it becomes possible to approximate very accurately the concentration variations of the overall form of the spectrum (Fig. 2), thus confirming the admissibility of this model.

The concentration dependences of the correlation parameters ε_1 and ε_2 are shown in Fig. 3. The linearity of $\varepsilon_1(x)$ (approximated by the relation $\varepsilon_1 = -1.052x + 0.210$) indicates that the number of vacancies in the first coordination sphere (N_D^1) is practially independent of the composition of the compound. At the same time, the number of iron atoms in the two nearest spheres (N_{Fe}) varies in accordance with an extremal law, reaching 6.41 at $x \approx 0.20$ (Fig. 3).

VACANCY CHARGE

In accordance with the data of Table 2, each vacancy produces in the EFG a change determined by the coefficient $\beta \approx 0.065$ mm/sec. In addition, the appearance of a vacancy in the first coordination sphere changes the IS by $\alpha_1 \approx +0.16$ mm/sec, and in the second coordination sphere by $\alpha_2 \approx +0.03$ mm/sec. This information enables us to estimate the charge of the vacancy by two independent methods: a) from the change of the IS and b) from the change of the EFT.

a) The IS of the defect-free structure α-FeSi$_2$ ($\delta_0 = 0.271 \pm 0.005$ mm/sec relative to Cr) is close to the IS of pure iron ($\delta_{Fe} = 0.257$ mm/sec).[6] An increase of the IS usually is interpreted as a result of an increase of the number of $3d$ electrons or a decrease of the number of $4s$ electrons per iron atom. The positive sign of the Fe atoms relative to the Si atoms[1] and the weak dependence of the MS parameters and of the magnetic susceptibility on the temperature[1,2] make it possible to attribute the observed change of the IS following the appearance of vacancies in the nearest surrounding of the resonant atoms primarily to a decrease in the number of the $4s$ electrons. From the plot of the IS against the number of $4d$ and $4s$ electrons[6] we obtain the following values of the charges e_{Fe}, e'_{Fe}, and e''_{Fe} (for the defect-free structure and in the presence of vacancies in the first and second coordination spheres, respectively) of the iron atoms: $e_{Fe} = +0.02$, $e'_{Fe} = +0.12$, and $e''_{Fe} = +0.05$ (the electron charge is assumed equal to unity here and below).

From the expression[5]

$$N_{Fe}^{1,2} = N[x(1-x) + \varepsilon_{1,2}]/x,$$

where N is the number of neighbors of the resonant atom, we can determine the number of iron atoms in the first and second coordination spheres ($N_{Fe}^1 \approx N_{Fe}^2 \approx 3.2$), and also the number per unit cell (~0.80). Assuming further that the total charge of the iron sublattice does not change when vacancies are produced, we obtain $e_D/e'_{Fe} \approx -3.2$ and $e_D/e''_{Fe} \approx -7.2$. These values make it possible to calculate the charge e_D of the vacancy, which amounts to -0.37 ± 0.01 regardless of the disposition of the vacancies in the two nearest coordination spheres. A close value (-0.374) was obtained also from the condition of the electroneutrality of the unit cell:

$$e_{Si}n_{Si} + e_{Fe}'n_{Fe} + e_D n_D = 0,$$

where n_{Si}, n_{Fe}, and n_D is the number of Si and Fe atoms and of vacancies per unit cell, while $e_{Si} = -0.5$ and $e_{Fe} = -0.01$ (from the condition that the hypothetical defect-free structure be electrically neutral).

b) The EFG components in spherical coordinates as functions of the distribution of the electric charges around the resonant nucleus can be determined from the expression[4]

$$V_{zz} = \sum_a e_a \frac{3\cos^2\vartheta_a - 1}{r_a^3},$$

where r_a and ϑ_a are the spherical coordinates of the charge e_a. In the calculation of the EFG we took into account not only the iron atoms and the vacancies in the basal plane, but also the contribution from 16 silicon atoms, located 2.356 and 4.205 Å from the considered nucleus. Termination of the series with the last value $r = 4.205$ Å is accurate enough, since $V_{zz} \propto r^{-3}$. The quadrupole-splitting values obtained from the MS for a defect-free structure (Δ_0) and for different surroundings of resonant atoms ($\Delta_0 + b_i\beta$) make it possible to determine the charge of the vacancy at known values of e_{Si} and e_{Fe} from the relation

$$\frac{\Delta_0}{\Delta_0 + b_{i\beta}} = \frac{a}{b}$$

$$a = C\left[\sum_{16} e_{Si}\frac{3\cos^2\vartheta_{Si} - 1}{r_{Si}^3} + \sum_{8} e_{Fe}\frac{3\cos^2\vartheta_{Fe} - 1}{r_{Fe}^3}\right],$$

$$b = C\left[\sum_{16} e_{Si}\frac{3\cos^2\vartheta_{Si} - 1}{r_{Si}^3} + \sum_{7} e_{Fe}\frac{3\cos^2\vartheta_{Fe} - 1}{r_{Fe}^3} + e_D\frac{3\cos^2\vartheta_D - 1}{r_D^3}\right]$$

where C is the quadrupole-interaction constant and does not depend on the local surrounding of the resonant atom.[4]

The calculated values of e_D for the case when one vacancy is located in the first and second coordination spheres (−0.39 and −0.38 respectively) correlate well both with each other and the values given above for the vacancy charge (−0.37±0.01) obtained from variation of the IS.

CONCLUSION

The investigations of the high-temperature phase of the higher iron silicide with the aid of the Mössbauer effect indicate that a relation exists between the parameters of the spectrum and the distribution of the vacancies, and makes it possible to determine the short-range order parameters for the first two coordination spheres. This enables us, in turn, to calculate the number of iron atoms in the nearest surrounding of the resonant atoms and to determine the charges of the vacancies.

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On the Drude formula for semiconductors

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Intraband absorption of light in semiconductors is investigated. It is shown that the classical Drude formula for the mean rate of change of the energy of a conduction electron in a high-frequency electric field is valid for both one-photon and many-photon changes in the electron energy in individual scattering events. Formulas are obtained which describe the effect of the ordered, uniform translational and vibrational motions of the current carriers on the intraband absorption coefficient for different scattering mechanisms.

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1. It is well known that the processes of absorption and stimulated emission are possible in electron scattering in the presence of an electromagnetic wave. In recent years bremsstrahlung absorption and stimulated bremsstrahlung emission have been considered in connection with the problems of plasma heating and electronic cumulative ionization in gases and crystalline dielectrics under the action of high-power laser radiation. Of greatest interest for both of these problems is the derivation of a formula for the mean (over a large number of collisions) rate of change of the energy of an electron under the action of a field.

From the quantum-mechanical point of view, an electron can, in the course of a scattering process in the presence of an electromagnetic wave of angular frequency Ω, absorb or emit a whole number of the quanta $\hbar\Omega$. Zel'dovich and Raĭzer[1] have considered the variation of the energy of an electron only as a result of one-photon processes, which, for sufficiently fast electrons, occur in the case when

$$eEp/m\hbar\Omega^2 \ll 1, \tag{1a}$$

(where E is the electric-field intensity, e and m are the electron charge and mass, and p is the electron momentum), and have shown that for

$$2\hbar\Omega m/p^2 \ll 1 \tag{1b}$$

the rate of change of the energy of an electron is given by the classical Drude formula

$$\frac{d\varepsilon}{dt} = \frac{e^2E^2}{2m\Omega^2}\nu_{\rm eff}(p), \quad \Omega \gg \nu_{\rm eff}, \tag{2}$$

where $\nu_{\rm eff}$ is the effective collision rate. This result was of great importance, as it meant that, since in gases and crystalline dielectrics the ionization potential $I_{\rm ion} \gg \hbar\Omega$, the problem of cumulative ionization can be solved classically.

On the other hand, according to the classical picture, the change in the energy of an electron in a single scattering event under the action of a field is, in order of magnitude, equal to $\pm eEp/m\Omega$. In the author's paper[2] it was shown that Drude's formula turns out to be also valid when

$$eEp/m\hbar\Omega^2 \gg 1, \tag{3a}$$

$$eE/\Omega p \ll 1. \tag{3b}$$

The inequality (3a) implies that the elementary processes of emission and absorption have a multiphoton character.

On the face of it, the result of the cited papers[1,2]