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OBSERVATION OF SMALL POLARONS IN β-FeSi WITH THE AID OF THE MOSSBAUER EFFECT

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The semiconducting nature of the low-temperature modification of the higher silicide of iron (β-$FeSi_2$) has been investigated in a number of papers [1 - 5]. The widths of the forbidden band in its energy spectrum is $\sim$0.9 eV. The impurity conductivity and the optical absorption of β-$FeSi_2$ doped with cobalt (n-type) have been interpreted in the small-polaron model [2, 5].

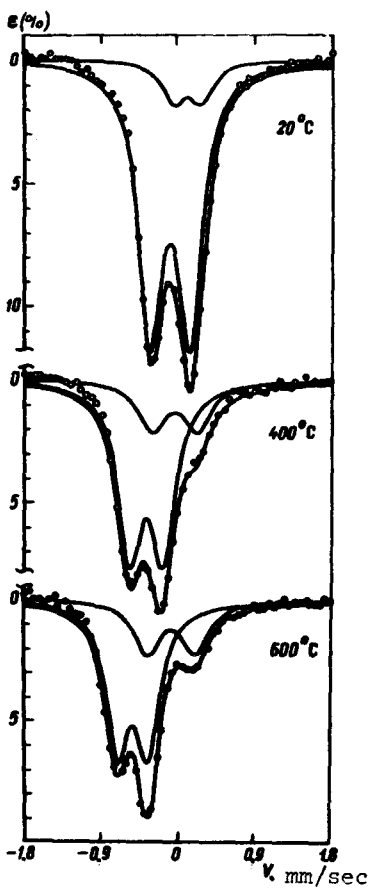

Fig. 1. Mossbauer spectra of Fe^{57} in β-$FeSi_2$ at different temperatures.

The crystal structure of β-$FeSi_2$ was determined in [6], viz., Cmca, rhombic lattice, a = 9.763 Å, b = 7.797 Å, c = 7.833 Å, the Fe atoms occupy the positions 8d and 8f, and the Si the positions 16g with two sets of structure parameters. Different data, however, are given in [7] concerning the space group of the silicide in question.

The Mossbauer spectrum of Fe^{57} in β-$FeSi_2$ [8] was investigated earlier at the nitrogen boiling temperature and at room temperature.

To obtain new information on the electronic structure of β-$FeSi_2$, we investigated the Mossbauer effect in the temperature region from -196 to 600°C. The samples were prepared by direct fusion of high-purity components in a hermetically sealed high-frequency furnace. The obtained alloy was annealed at 950°C for 100 hours. Metallographic and x-ray structure analyses have confirmed the single-phase character of the compound.

The Mossbauer absorber was prepared by deposition of β-$FeSi_2$ powder from an alcohol suspension onto a beryllium disk. The thickness of the absorber was 15 mg/cm^2. The radiation source was Co^{57} introduced into Pd. The spectra were processed with a "Mir" computer assuming a Lorentz line shape.

Figure 1 shows the Mossbauer spectra of β-$FeSi_2$ at three temperatures. At room temperature the absorption line is an almost symmetrical doublet. With increasing temperature, the spectrum

assumes an asymmetrical form. This is connected with the transition of part of the iron atoms into other electronic states, characterized by other values of the quadrupole splitting and isomer shifts. The figure shows the simplest resolution of the spectrum into two pairs of lines with quadrupole splitting.

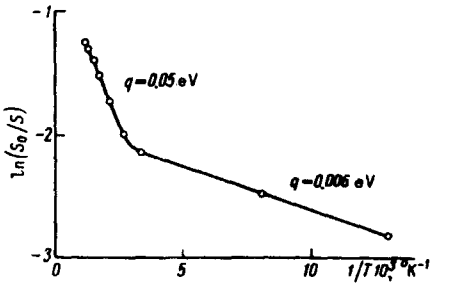

Fig. 2. Relative area of the additional Mossbauer-absorption line, produced upon increase of temperature, vs. T^{-1}.

The area under the line corresponding to the new states of the iron depends linearly on exp(-q/kT), as is seen from Fig. 2, and reaches ∿30% of the total area of the spectrum at 600°C.

The following is a probable interpretation of the obtained data. The appearance of a new line in the Mossbauer spectrum with increasing temperature is evidence of the production of new electronic states not belonging to the entire crystal, but localized near part of the atom during a time greatly exceeding the time of interaction of the γ quanta with the Fe^{57} nuclei. The fraction of the nuclei near which the state of the electrons is measured is relatively large (on the order of 30% at 600°C), making it necessary to connect the excited localized states with the main atoms of the matrix, rather than with the atoms of the possible small impurities. It is tempting to identify the observed localized states with small polarons of two types with characteristic production energies 0.006 and 0.05 eV. The value q = 0.05 eV turns out to coincide with the position of the sharp maximum in the IR absorption spectrum of β-$FeSi_2$ [5]; the temperature corresponding to the singular point on Fig. 2 coincides approximately with the temperature of the kink on the plot of ln σ- T^{-1} [2], and the ratio of the activation energies is the same in both cases.

If the observed local states are actually small polarons then, judging from the values of q and the values of the quadrupole spectrum, their radius is unusually small compared with the radius of the atom.

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RELAXATION AND NONCOLLINEARITY OF THE SPINS OF IRON IN THE FERRITE $Li_{0.5}Fe_{1.7}Al_{0.8}O_4$

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It was proposed in [1] that the spin configuration of the ferrite $Li_{0.5}Fe_{1.7}Al_{0.8}O_4$ is not collinear.