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ELASTIC PROPERTIES OF FeSi

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Measurements of the sound velocities in a single crystal of FeSi were performed in the temperature range 4–300 K. Elastic constants C_{11} and C_{44} deviate from a quasiharmonic behavior at high temperature; on the other hand, elastic constants C_{12} increases anomalously in the entire temperature range, indicating a change in the electron structure of this material.

The intermetallic compound with a cubic B20 crystal structure FeSi has attracted much attention over decades due to its unusual physical properties. A single crystal FeSi, being a semiconductor with a small energy gap about 0.05 eV at low temperatures, reveals metallic properties above 100 K [1–5]. Angle-resolved photoemission spectroscopy demonstrates the disappearance of an energy gap in FeSi at high temperatures [6–8]. One of the intriguing features of the physical properties of FeSi is that its magnetic susceptibility increases at temperatures above 100 K, reaching a broad maximum at 500 K, followed by the Curie–Weiss behavior at higher temperatures. The electrical conductivity of FeSi also increases steeply in the same temperature interval as the magnetic susceptibility. No magnetic ordering in FeSi was found at any temperature [9].

A number of theories and models have been suggested to explain the experimental observations, including a model of localized states at the Fermi level, a spin-fluctuation theory, and a Kondo model (see, e. g., [1, 3, 10]). According to recent studies, the Kondo scenario is not needed for the explanation of the physical properties of FeSi [8]. The concept of a strongly correlated semiconductor with an energy gap destroyed by correlations has gained acceptance as a general framework for interpreting the properties of FeSi. But, independently of any kind of theories, experimental data show that an insulator–metal crossover occurs in FeSi at elevated temperature, which should influence the interparticle interactions and hence the elastic properties of FeSi.

The main goal of this paper is to study the effects of gradual metallization on the elastic properties of FeSi. The significance of this study is enhanced by the importance of FeSi as a potential constituent of Earth's core. Previously, elastic properties of FeSi were studied in Refs. [11] and [12] in the temperature range 80–400 K, but, as we find, extending these measurements to lower temperatures provides a more complete interpretation of the origin of its elastic properties.

We report the results of ultrasonic studies of a single crystal of FeSi in the temperature range 4–300 K. The measurements were performed using a digital pulse-echo technique (see the details in Ref. [13]). The single crystal of FeSi was grown by the Chokhralsky method. The lattice parameter of the crystal, determined by powder X-ray diffraction, was equal to 4.483 Å, which corresponds well to literature values. Electron-probe microanalysis showed a small deficit (less than 0.1 at. %) of Si, which is generally typical of crystals of FeSi grown in different laboratories.

Electric and magnetic characteristics of the crystal are displayed in Figs. 1 and 2. Electrical measurements were made by a four-terminal dc method. Magnetic susceptibility was measured with a Quantum Design Magnetic Properties Measurement System. Figure 1 shows the temperature dependence of the conductivity σ and magnetic susceptibility χ of FeSi samples cut from the same batch as those used for ultrasound studies. We note that the steep increase in both the conductivity and magnetic susceptibility starts at about 100 K. Figure 2 *a* demonstrates that in the temperature regime below 100 K, the resistivity ρ can be approximated by the expression for variable-range hopping. In the narrow temperature region 100–150 K, the resistiv-

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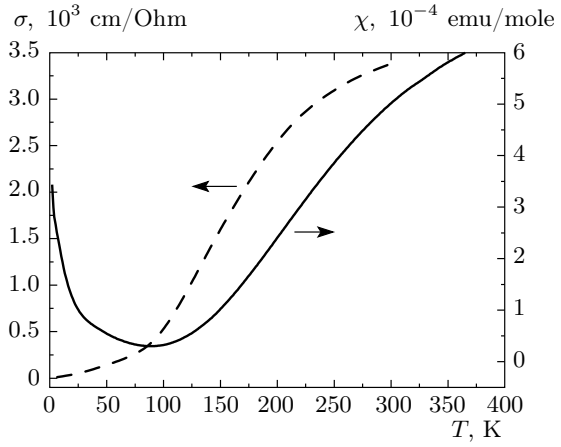

Fig. 1. The temperature dependence of the dc conductivity σ and magnetic susceptibility χ of FeSi

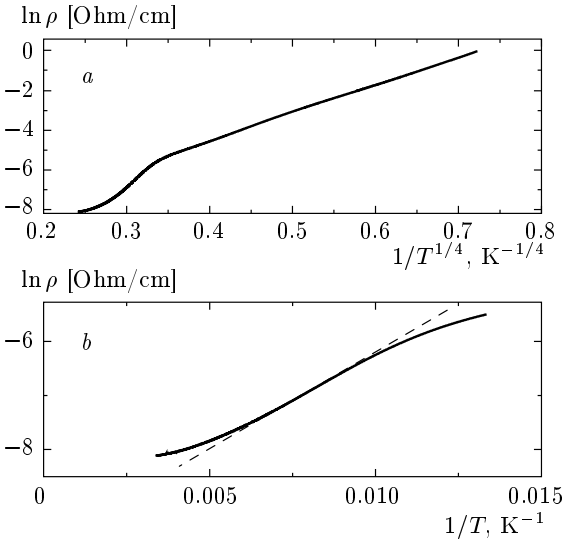

Fig. 2. Electric conductivity $\sigma = 1/\rho$ on a logarithmic scale as a function of $T^{-1/4}$ (a, $\rho \propto \exp(T_0/T)^{1/4}$, $T_0 \approx 40000$ K) and T^{-1} (b, $\rho \propto \exp(E_g/2kT)$, $E_g = 690$ K) for FeSi

ity ρ can be described by the standard activation formula with the energy gap $E_g = 0.06$ eV or $E_g = 690$ K (Fig. 2*b*). Close to room temperature, the resistivity crosses over into a saturation regime, which seems to be too early for a semiconductor with the indicated gap. This probably signifies the gap closure and entry into a metallic state, in agreement with Refs. [6–8]. All these observations generally agree with the data available in the literature (see, e. g., [5]).

For the ultrasonic studies, two samples of FeSi about 2 mm thick with orientations along [111] and

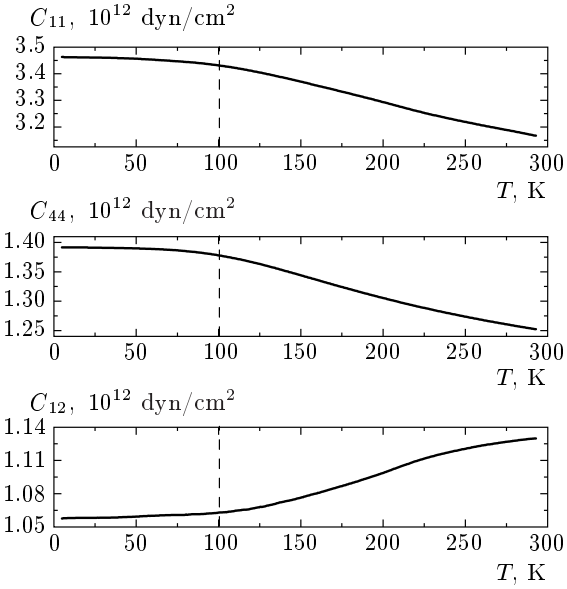

Fig. 3. Temperature dependence of the elastic constants of FeSi

[100] were cut from a big single crystal. The corresponding surfaces of the samples were made optically flat and parallel. The 36° Y (P-wave) and 41° X (S-wave) cut $LiNbO_3$ transducers were bonded to the samples with various adhesives, including silicon greases and superglue. The temperature was measured by a calibrated Cernox sensor with an accuracy of 0.02 K.

The speed of sound and the elastic constants C_{11}, C_{44} and C_{12} are calculated using the known thickness and density of the samples and the relations

$$\begin{aligned} C_{11} &= \rho V_l^2[100], \quad C_{44} = \rho V_s^2[100], \\ \rho V_l^2[111] &= \frac{1}{3}(C_{11} + 2C_{12} + 4C_{44}), \\ \rho V_s^2[111] &= \frac{1}{3}(C_{11} - C_{12} + C_{44}), \end{aligned} \tag{1}$$

where V_l and V_s are the velocities of longitudinal and transverse waves and indices in square brackets define propagation directions of sound waves. We note that the elastic constant C_{12} was evaluated using two different equations for the speed of the longitudinal and transverse sound waves. Both ways gave quite consistent results. Taking all the experimental uncertainties into account, the accuracy of the elastic constants obtained can be estimated as being of the order of 1 %, although the precision of the data displayed in Fig. 3 is significantly better.

Results of the measurements and calculations are shown in Fig. 3 and Table. Our data on FeSi generally agree with results in Refs. [11, 12] in the overlapping

Table. Elastic moduli of FeSi ($a = 4.483$ Å at $T = 298$ K)

C_{ij}, 10^{12} dyn/cm^2	$T = 4.8$ K	$T = 77.8$ K	$T = 292.8$ K
C_{11}	3.462	3.445	3.167
C_{44}	1.390	1.386	1.252
C_{12}	1.058	1.060	1.129

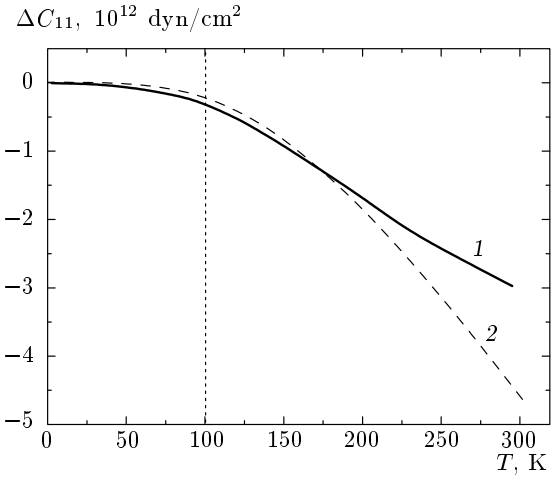

Fig. 4. Temperature dependence of $\Delta C_{11} = C_{11}(T = 0) - C_{11}(T)$: *1* — experimental data; *2* — extrapolation from low temperatures with Eq. (2)

region of temperatures, although a lack of numerical data in Ref. [11, 12] and the relatively lower resolution in Ref. [11] do not allow a detailed comparison.

As can be seen from Fig. 3, the elastic constants C_{11} and C_{44} of FeSi decrease with temperature at a rate rapidly increasing at about 100 K. This behavior can be explained most straightforwardly by a simple model of solids. According to the quasiharmonic theory, a temperature dependence of the adiabatic elastic constants is defined by the expression [14]

$$C_{ij} = C_{ij}(T = 0)(1 - D\bar{\epsilon}), \qquad (2)$$

where C_{ij} are harmonic values of the elastic constants, D is a parameter defined by the crystal structure, and $\bar{\epsilon}$ is the mean energy per oscillator ($3sN\bar{\epsilon} = U$, where U is thermal energy, N is the number of atoms, and s is the degree of freedom).

Using values of the elastic constants from Table, we estimate the Debye temperature of FeSi, which turned out to be $\Theta_D = 690$ K, and calculated the corresponding thermal energy U. Simple calculations illustrated

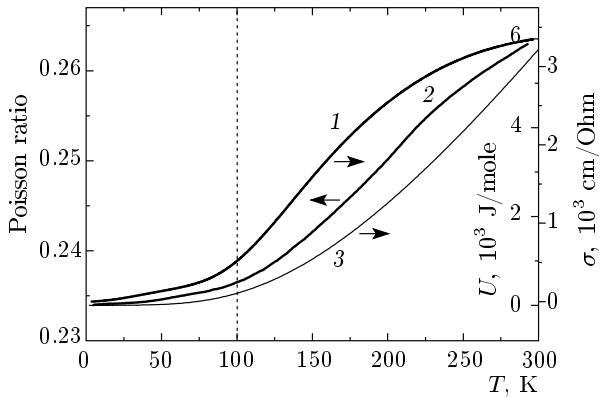

Fig. 5. The conductivity σ (curve *1*), Poisson's ratio $C_{12}/(C_{12} + C_{11})$ (*2*), and thermal energy U (*3*) for FeSi versus temperature. The thermal energy is calculated in the Debye approximation ($\Theta_D = 690$ K)

in Fig. 4 show that the Debye model of solids can account for the behavior of C_{11} and C_{44} to at least 170 K. At the same time, these calculations reveal anomalous stiffening of C_{11} and C_{44} at higher temperatures (see in this connection Ref. [12]). The increase in C_{12} (see Fig. 3) and hence a steady increase in the Poisson ratio $C_{12}/(C_{12} + C_{11})$ (Fig. 5) in the entire temperature range is another specific feature of the elastic properties of FeSi. This was not properly recognized in Ref. [12], although an anomalous behavior of C_{12} can be seen after a careful analysis of the figures in [12].

An explanation of that highly "anharmonic" behavior of the elastic constants of FeSi apparently lies in the specifics of its electronic subsystem. The emergence of a metallic state implies generation of an electron liquid in FeSi that would normally give a positive contribution to its bulk modulus and modify the interatomic interaction. Both factors are expected to inluence the elastic constants, and certainly could lead to a deviation from a simple quasiharmonic model.

Remarkably, the energy gap and the Debye temperature Θ_D in FeSi have practically the same values. This fact is reflected in a rapid increase in the charge carrier and phonon populations, obviously occurring in the same temperature interval around 100 K, as follows from behavior of the electric resistivity, magnetic susceptibility, and elastic constants of FeSi. It is worth recalling that the conductivity mechanism in FeSi changes from hopping to activation also around 100 K (see Fig. 2). However, whether this is a simple coincidence or there is hidden physics in the background remains to be seen.

To conclude, we note that the anharmonic behavior of elastic constants suggests changes in the character of interatomic interactions in FeSi, as is evidenced by the metal–insulator crossover. The anomalous behavior of C_{12} and the Poisson ratio can probably serve as indicators of a qualitative change in the electronic structure of materials. Indeed, Fig. 5 explicitly shows the generic connection between variations in conductivity, the Poisson ratio, and thermal energy in FeSi.

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