Band parameters of FeSi single crystals determined by magnetic measurements

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The results of magnetization and magnetic-susceptibility measurements on FeSi single crystals are presented. The temperature dependence of the magnetic susceptibility in the range 5–300 K could be explained by contribution from the temperature-dependent parts due to paramagnetic centers and due to the carriers excited thermally in the intrinsic conductivity region. It is shown that the contribution to magnetic susceptibility of FeSi from single-occupied Anderson localized states is negligible. The values of the Curie-Weiss temperatures, an energy gap, as well as density-of-states effective mass were estimated. [S0163-1829(97)05213-2]

FeSi is a nonmagnetic narrow gap semiconductor with unusual features[1] and might represent the first d-electron material exhibiting Kondo-lattice behavior.[2,3] Band-structure calculations of FeSi predicted an indirect semiconducting gap of 100–110 meV,[4,5] and a value of a carrier effective mass m^*/m of the order of 5–10.[4,6] The resistivity[6,8] and optical-conductivity[6] measurements indicate a gap ε_g of about 54,[7] 60 meV.[6,8] A satisfactory fit of the susceptibility data was obtained using a fairly wide range of parameters: 80 meV$<\varepsilon_g<$130 meV and $0<B_w<$65 meV (where B_w is a bandwidth).[9] The photoemission spectra of FeSi indicates a surprisingly small gap of less than 5 meV.[10]

Reports on the value of m^*/m are fewer and the results obtained are also not in conformity with one another. The value of m^*/m was estimated using the Mott criterion ($m^*/m \leqslant 5.7$),[11] as well as on the base of optical-conductivity measurements ($m^*/m = 50$),[6] and data of the maximum magnetic susceptibility ($m^*/m = 80$–135).[12] Investigation of magnetic susceptibility has proved to be an effective method for studying the energy spectrum of electrons and holes in a semiconductor and can give information on its band structure.[13]

We report now on the results of the determination of the FeSi band parameters using the magnetization (M) and the magnetic-susceptibility (χ) measurements. The samples were cut from FeSi monocrystalline undoped ingots grown by the Czochralski technique.[14] The technological parameters were similar for all ingots, but silicon loss from the melt during crystal growth could lead to some differences in defects concentration in the samples studied. The magnetization was measured at 5 and 300 K in magnetic fields B up to 50 K G by using a superconducting quantum interference device magnetometer. Susceptibility measurements were performed at 1 K G in the temperature range of 5–300 K.

The magnetization (Fig. 1) is positive in the crystal studied. Magnetization measurements yielded a linear behavior in fields up to about 20 K G and deviation from linearity in

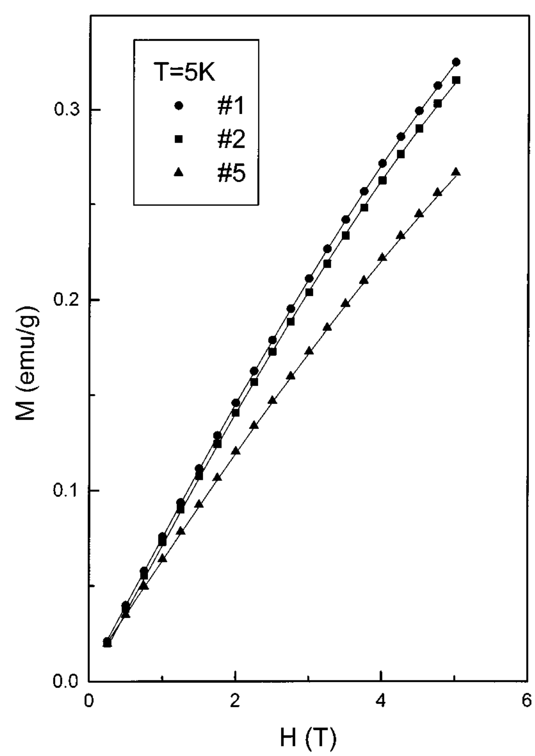

FIG. 1. Magnetization vs magnetic field.

TABLE I. Parameters of FeSi single crystals.

Sample	χ 10^{-7} emu/g G	A 10^{-5} K/g G	B 10^{-6}emu k$^{1/4}$/g G	Mo emu/g	To K	ε_g^0 MeV	$-\theta$ K	N_p 10^{20} cm^{-3}		m^*/m
1	3.18	15.1	2.0	0.0035	9.5	71	11	0.89[a]	1.23[b]	31
2	1.65	13.7	1.94	0	8.6	70	10	0.83[a]	1.16[b]	31
5	21.6	13.4	1.77	0.006	10.2	68	12	0.75[a]	1.13[b]	30

[a]Estimated from Eq. (1).
[b]Estimated from Eq. (5).

higher magnetic fields (Fig. 1). The dependence of $M(B)$ was analyzed on the basis of Eq. (1)

$$M(B)=M_0+\frac{N_p g S \mu_B}{\rho} B_s(x), \tag{1}$$

where

$$B_s(x)=\frac{2S+1}{2S}\coth\left[\frac{(2S+1)x}{2S}\right]-\frac{1}{2S}\coth\left(\frac{x}{2S}\right),$$

$$x=\frac{gS\mu_B}{k(T+T_0)}B,$$

with N_p the concentration of the paramagnetic centers, g is the Lande' factor, S is the spin of the paramagnetic center, μ_B is the Bohr magneton, ρ is the density, and $B_s(x)$ is the Brillouin function.[15]

A satisfactory fit of the $M(B)$ dependence could be achieved for $S=5/2$ (Fig. 1). The value of $S=5/2$ is attributable to Fe^{3+} ions. The estimated value of Np is about 10^{20} cm^{-3} (Table I). The latter as well as the value estimated by Schlesinger *et al.*[6] is much higher (40–100 times) than that reported by Hunt *et al.*[11] The observed very small but nonzero value of M_0 (sample 1, sample 5; Table I) indicate their weak ferromagnetic behavior.[16]

The value of the magnetic susceptibility decreases with increasing temperature (by a factor of 2.5–4), shows a minimum at about 90–100 K and a strong increase (a few times) up to room temperature (Fig. 2). This is in agreement with the literature data.[1,6,8]

The observed magnetic susceptibility $\chi(T)$ in the case of a semiconductor is given by[17]

$$\chi(T)=\chi_0+\chi_p(T)+\chi_c(T), \tag{2}$$

where $\chi_0=\chi_l+\chi_n$. χ_l is the contribution from the lattice, which is temperature independent. χ_n is the temperature-independent contribution to the magnetic susceptibility from lattice defects[18] and/or any neutral impurities.[19] χ_p is the temperature-dependent susceptibility due to paramagnetic impurities. χ_c is the magnetic susceptibility due to free carriers.

Analyses of $\chi(T)$ were performed assuming that the observed temperature dependences of the susceptibility are caused by the terms $\chi_p(T)$ and $\chi_c(T)$. Transport measurements on our FeSi single crystals in the temperature range of 1.5–300 K show intrinsic conductivity in the high-temperature region ($T>100$ K). The value of the gap obtained (50 ± 5 meV) is close to those found in Refs. 6–8. Using Eq. (2) a fit of our experimental curves $\chi(T)$ has been made. $\chi_p(T)$ is determined according to a Curie-Weiss law

$$\chi_p=A/(T-\theta), \tag{3}$$

where

$$A=\frac{N_p\mu_B^2 p_{\mathrm{eff}}^2}{3\rho k}, \quad p_{\mathrm{eff}}^2=g^2S(S+1). \tag{4}$$

θ is the Curie-Weiss temperature, ρ is the density of the material (for FeSi $\rho=6.15$ g/cm^3, Ref. 20), and p_{eff} is the effective number of Bohr magnetons.

In the region of the intrinsic conductivity χ_c is determined as[22]

$$\chi_c=\frac{n\mu_B^2}{3\rho kT}\left[6-\left(\frac{m}{m_n^*}\right)^2-\left(\frac{m}{m_p^*}\right)^2\right], \tag{5}$$

where m_n^* (m_p^*) is the density-of-states electron (hole) effective mass. The value of the g factor is assumed to be equal to 2 for both types of the charge carriers.[22]

The concentration of free electrons (holes) is given by[23]

$$n=\frac{(2kT)^{3/2}(m_n^*m_p^*)^{3/4}}{4\pi^{3/2}\hbar^3}\exp\left[-\frac{\varepsilon_g}{2kT}\right], \tag{6}$$

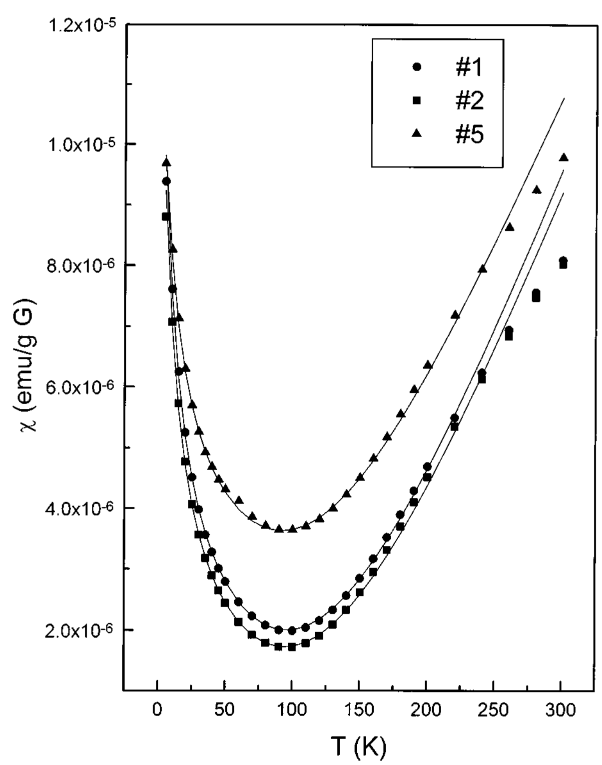

FIG. 2. Magnetic susceptibility vs temperature.

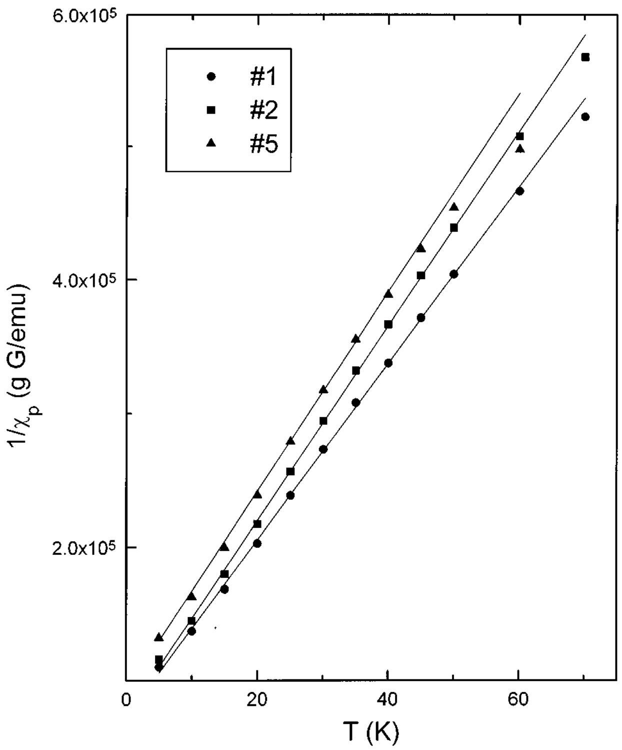

FIG. 3. Dependence of χ_p vs temperature.

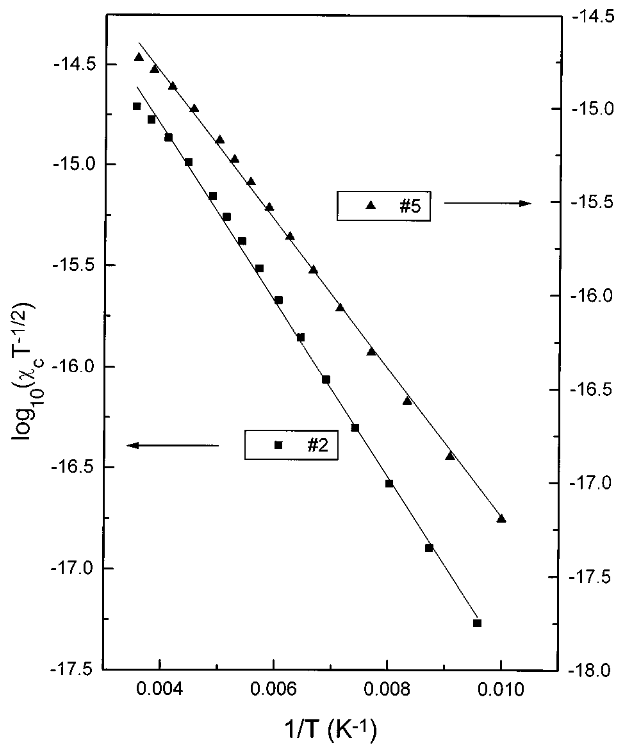

FIG. 4. Dependence of $\chi_c T^{-1/2}$ vs $1/T$.

where $\varepsilon_g=\varepsilon_g^0-\alpha T$, ε_g^0 is the energy gap value at 0 K. If we take into account Eqs. (5) and (6), $\chi_c(T)$ could be written as

$$\chi_c=BT^{1/2}\exp(-\varepsilon_g^0/2kT), \tag{7}$$

where

$$B=\frac{(2k)^{1/2}(m^*/m)^{3/2}m^{3/2}\mu_B^2}{\pi^{3/2}\hbar^3\rho}\left[3-\left(\frac{m}{m^*}\right)^2\right]\exp\left(\frac{\alpha}{2k}\right), \tag{8}$$

assuming that $m_n^*=m_p^*=m^*$.[12]

The experimental curves $\chi(T)$ for samples studied could be satisfactorily fitted, using Eqs. (2), (3), and (7) with χ_0, A, θ, B, and ε_g^0 as adjustable parameters (Fig. 2). The latter are presented in Table I. The values of χ_0 are different in samples studied probably due to differences in the concentration of lattice defects and/or neutral impurities. However, the measurements performed do not permit us to identify lattice defects and neutral impurities as well as to separate their contribution from the lattice contribution.

The dependences $1/\chi_p$ vs T [where χ_p is equal to $(\chi-\chi_0-\chi_c)$] in accordance with Eq. (3) are straight lines indicating the Curie-Weiss law (Fig. 3). The values of θ and A determined from their intersection (along T axes) and slope, respectively, are in agreement with the values estimated from the fitting of the experimental curves. The Curie-Weiss temperature is negative as well as in Ref. 8 ($\theta=-10$ K) and Ref. 21 ($\theta=-25$ K) and indicate antiferromagnetic interactions in FeSi crystals. The value of A permits us to estimate N_p assuming that $S=5/2$. The obtained value of N_p is in satisfactory agreement with that estimated from Eq. (1) (Table I).

It is worth mentioning that the Kamimura-Kurobe mechanism,[8] which takes into account the intrasite interactions between the Anderson-localized electrons, was used to explain the low-temperature Curie-Weiss behavior in FeSi. Our calculations (see the Appendix) show that the contribution to the magnetic susceptibility from the single-occupied Anderson-localized states in our FeSi samples is negligible.

m^*/m was estimated using Eq. (8). The coefficient α was taken equal to 2×10^{-4} eV/K taking into account that the gap [60 meV (Refs. 6 and 8)] disappear entirely near 300 K.[6] The obtained value of m^*/m is about 31 (Table I) which is lower than the value reported by Schlesinger *et al.* [$m^*=50$ m (Ref. 6)] and much higher than those of Ref. 11 as well as the theoretically estimated value of m^*/m.[4,6] The plot of $\ln(\chi_c T^{-1/2})$ vs $1/T$ yields straight lines in the high-temperature region (Fig. 4), where exponential increase of the electron (hole) concentration takes place. Its slope permits us to determine the value of ε_g^0 in agreement with Eq. (7). The obtained value as well as the value estimated as an adjustable parameter to fit the susceptibility measurements, are in agreement, and equal to 70 meV and close to those determined on the base of the transport measurements.[6–8,14]

In conclusion, the temperature dependence of χ in the range of 5–300 K could be explained by the contribution from the temperature-dependent parts due to paramagnetic centers and due to the carriers excited thermally in the intrinsic conductivity region. The contribution to magnetic susceptibility of FeSi from single-occupied Anderson localized states is negligible. The values of θ, ε_g^0, and m^*/m were estimated.

APPENDIX

According to the Kamimura model[24] at low temperatures the single-occupied Anderson-localized states (N_s is the concentration per unit volume V) give rise to Curie-type magnetic susceptibility $\chi_s = \mu_B^2 N_s/\rho kT$.

At $\langle U\rangle/W\langle 0.3, N_s \approx N\langle U\rangle/W$, where N is the concentration of localized states, W is the width of the Anderson band with nonzero density of localized states (DOS) and $\langle U\rangle$ is the correlation energy, or the energy of interaction of two electrons at one site, averaged over the width of the Anderson band. Hence the Curie constant $A = \mu_B^2 N\langle U\rangle/\rho k$.

To calculate $\langle U\rangle$ we use

(i) the model of the DOS proposed in Ref. 25 (symmetric nonzero DOS inside the gap, constant within stripe $\Delta\varepsilon$, and decreasing outside $\Delta\varepsilon$ down to zero at the edge of the gap);

(ii) the energy dependence of the localization radius ξ following from the results of Ref. 25:

$$\xi(\varepsilon) = \begin{cases} \text{const}, & \dfrac{\varepsilon_g}{2} \leqslant \varepsilon \leqslant \dfrac{\varepsilon_g + \Delta\varepsilon}{2} \\ \left[\dfrac{\varepsilon_g - \Delta\varepsilon}{2(\varepsilon_g - \varepsilon)}\right]^{\nu}, & \dfrac{\varepsilon_g + \Delta\varepsilon}{2} \leqslant \varepsilon \leqslant \varepsilon_g ; \end{cases}$$

(iii) the result of Kamimura[24]

$$U(\varepsilon) \sim 1/\xi^3(\varepsilon).$$

Then we get

$$U(\varepsilon) = U_{\max} \times \begin{cases} 1, & \dfrac{\varepsilon_g}{2} \leqslant \varepsilon \leqslant \dfrac{\varepsilon_g + \Delta\varepsilon}{2} \\ \left[\dfrac{2(\varepsilon_g - \varepsilon)}{\varepsilon_g - \Delta\varepsilon}\right]^{3\nu}, & \dfrac{\varepsilon_g + \Delta\varepsilon}{2} \leqslant \varepsilon \leqslant \varepsilon_g . \end{cases}$$

For the average value we obtain

$$\langle U\rangle = \frac{2}{\varepsilon_g} \int_{\varepsilon_g/2}^{\varepsilon_g} U(\varepsilon)\, d\varepsilon = U_{\max} \frac{\Delta\varepsilon}{\varepsilon_g} \left[1 + \frac{1}{3\nu + 1}\left(1 - \frac{\Delta\varepsilon}{\varepsilon_g}\right)\right]$$

and for the Curie constant

$$A = \frac{\mu_B^2 N_t}{k\rho} \frac{N}{N_t} \frac{U_{\max}}{\varepsilon_g} \frac{\Delta\varepsilon}{\varepsilon_g} \left[1 + \frac{1}{3\nu + 1}\left(1 - \frac{\Delta\varepsilon}{\varepsilon_g}\right)\right],$$

where $N_t = 1.9 \times 10^{22}$ cm^{-3} is the concentration of atoms in FeSi. Taking into account that $\mu_B^2 N_t/k\rho = 1.9 \times 10^{-3}$ emu K/g G and values of $\Delta\varepsilon$, ε_g, and ν according to Ref. 25 are equal to 7.5 meV, 60 meV, and 0.75, respectively, we obtain

$$A = 3.04 \times 10^{-4} \frac{N}{N_t} \frac{U_{\max}}{\varepsilon_g} \text{ (emu K/g G)}.$$

The experimental value for sample 5 is $A = 1.34 \times 10^{-4}$ emu/g G (Table I). The value of N is about N_d, the concentration of defects. Hence, to achieve agreement we have to assume that $N_d \approx N_t$ and $U_{\max} \approx \varepsilon_g$. Both assumptions are contradictive by themselves, meaning enormous amount of defects in FeSi and no electrons in localized states inside the gap. In real conditions, $N_d \ll N_t$ (at least 0.1–0.01) and $U_{\max} \ll \varepsilon_g$. According to Ref. 25 $U_{\max} = 17$ K, so $U_{\max}/\varepsilon_g \approx 0.024$. This means that the calculated value of A is lower than the experimental value at least by three orders of magnitude. Therefore, the contribution to the magnetic susceptibility of FeSi from single-occupied Anderson-localized states is negligible.

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