Magnetic properties of β-$FeSi_2$ single crystals

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(Received 2 August 1995)

The results of magnetization and magnetic susceptibility measurements on n- and p-type β-$FeSi_2$ single crystals are presented. The magnetic susceptibility in the studied crystals are determined by the temperature-independent contribution from the lattice, lattice defects and/or neutral impurities, and by the temperature-dependent parts due to paramagnetic centers as well as due to the carriers excited thermally at high temperature. The temperature variation of the paramagnetic terms are in agreement with the Curie-Weiss law. The values of the Curie-Weiss temperatures, activation energy of the donor and acceptor levels, and the upper (lower) limit of the density of state electron (hole) effective masses were estimated.

Beta-iron disilicide (β-$FeSi_2$) as a direct energy gap semiconducting silicide[1] has received considerable attention as a very attractive material for light detectors, photovoltaic applications[2] and for development of new optoelectronic devices.[3] The recently reported high value of the Hall mobility [at low temperatures the hole mobility is up to 1200 cm^2/Vs (Ref. 4) and the electron mobility is up to 48 cm^2/Vs (Ref. 5) in single crystals, i.e., up to 25–50 times higher than maximum values previously reported[6–8]] as well as observation of the photoconductivity in β-$FeSi_2$ (Ref. 9) increased interest in this material and the possibility of its application.

A relatively large number of investigations have been made on the transport and optical properties of β-$FeSi_2$ thin films, polycrystalline samples, and single crystals (see Ref. 1–9 and references therein), but reports on the magnetic properties are fewer and results obtained are not in conformity with one another. Birkholz and Frühauf[10] measured the magnetic susceptibility of the powdered-metallurgically prepared β-$FeSi_2$ samples. On the base of the results obtained the conclusion was made that pure β-$FeSi_2$ shows diamagnetism at low temperatures.

According to Ref. 11, Hall effect measurements of β-$FeSi_2$ polycrystalline films indicate that β-$FeSi_2$ behaves as a ferromagnetic material at temperatures below 100 K. Magnetization measurements on n-type β-$FeSi_2$ single crystals[5] show a small positive susceptibility. The analysis of these results show no evidence of a ferromagnetic phase transition mentioned in Ref. 11.

We report now results of magnetization (M) and magnetic susceptibility (χ) measurements on p- and n-type β-$FeSi_2$ single crystals. β-$FeSi_2$ needlelike crystals were grown by chemical vapor transport.[12] The typical parameters of n- and p-type β-$FeSi_2$ single crystals are given in Tables I of Refs. 5 and 4, respectively.

The magnetization was measured at 5 (Fig. 1) and 300 K in magnetic fields up to 20 000–40 000 Oe using a superconducting quantum interference device (SQUID) magnetometer. Susceptibility measurements were performed at 3000 Oe in the temperature range of 5–300 K. As the resolution of the experimental technique used did not allow us to investigate individual β-$FeSi_2$ needlelike single crystals the obtained magnetization and magnetic susceptibility curves represent measurements of several similarly oriented along [010] axis single crystals grown by the same conditions.

The values of M (Fig. 1) are positive and quite small for crystals studied. The temperature dependencies of the magnetic susceptibility are different in n- and p-type samples (Fig. 2).

The observed magnetic susceptibility $\chi(T)$ for a semiconductor is given by[13]

$$\chi(T)=\chi_0+\chi_p(T)+\chi_c(T), \tag{1}$$

where $\chi_0=\chi_1+\chi_n$. χ_1 is the contribution from the lattice, which is temperature independent. χ_n is the temperature-independent contribution to χ from lattice defects[14] and/or any neutral impurities[13] that may be present in the crystal. χ_p

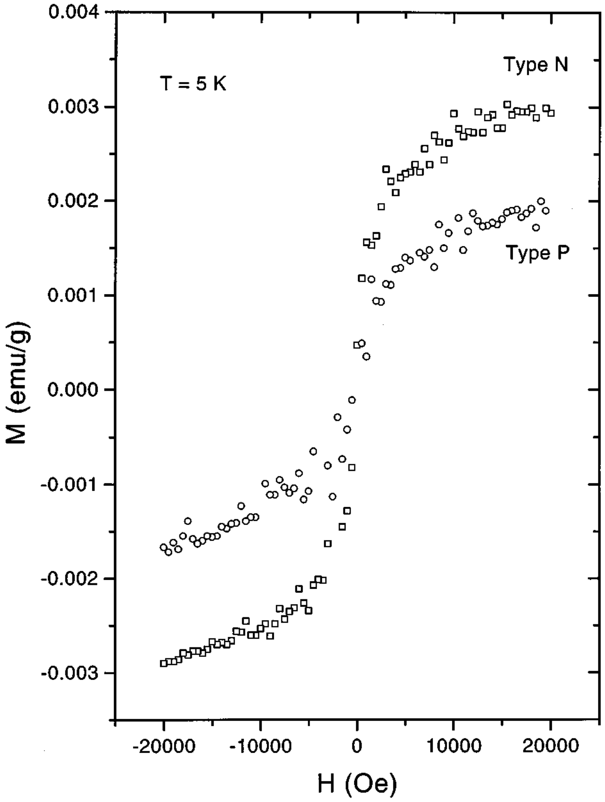

FIG. 1. Magnetization vs magnetic field.

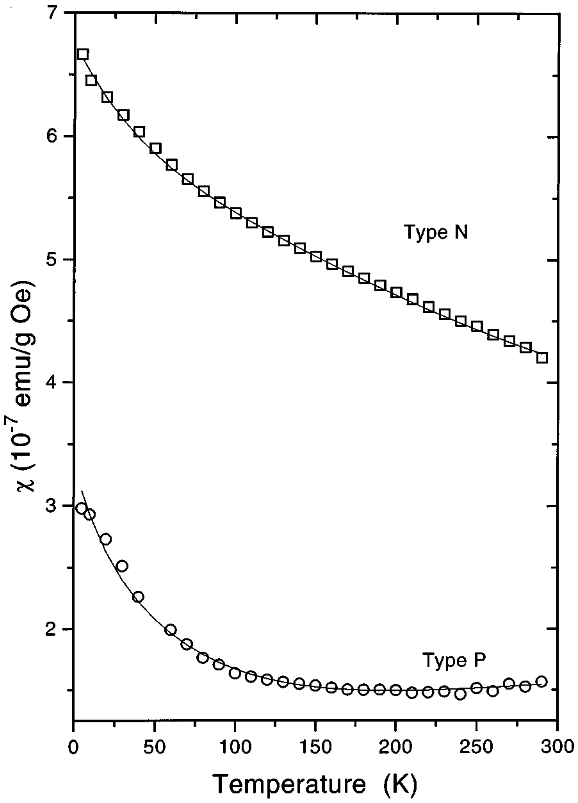

FIG. 2. Magnetic susceptibility vs temperature.

is the temperature-dependent susceptibility due to paramagnetic impurities. χ_c is the magnetic susceptibility due to free carriers. Therefore the observed temperature variation of the susceptibility is due to terms $\chi_p(T)$ and $\chi_c(T)$. The expression for ξ_c, if only one type of carriers is present, is given by[14,15]

$$\chi_c=\frac{n\mu_B^2}{\rho\kappa T}\left[\frac{g^2}{4}-\frac{1}{3}\left(\frac{m}{m^*}\right)^2\right]\frac{F_{-1/2}(\eta)}{F_{1/2}(\eta)}, \tag{2}$$

where μ_B is the Bohr magneton, ρ is the density of the substance, n is the electron (hole) concentration, g is the Landé factor of the electrons (holes), m^* is the density-of-state electron (hole) effective mass, $F_{-1/2}(\eta)$, $F_{1/2}(\eta)$ are Fermi integrals and η is the reduced Fermi level. The latter could be determined using the equation[16]

$$n=N_\nu F_{1/2}(\eta), \tag{3}$$

where

$$N_\nu=2(2\pi m^*kT/h^2)^{3/2} \tag{4}$$

if values of n and m^* are known; N_ν is the density of states in the conduction (valence) band.

At low carrier concentration, Boltzmann statistics applies, and the magnetic susceptibility amounts to

$$\chi_c=\frac{n\mu_B^2}{\rho kT}\left[\frac{g^2}{4}-\frac{1}{3}\left(\frac{m}{m^*}\right)^2\right] \tag{5}$$

which in the degenerate case changes to

$$\chi_c=\frac{\mu_B^2}{\rho}\frac{4m^*}{h^2}(3\pi^2 n)^{1/3}\left[\frac{g^2}{4}-\frac{1}{3}\left(\frac{m}{m^*}\right)^2\right]. \tag{6}$$

Formulas (2), (5), and (6) seem only applicable if the g value of the carriers is not too far from 2, otherwise spin-orbit effects are important and the susceptibility formula may be much more complicated.[17]

The first term in formulas (2), (5), and (6) in square brackets (the paramagnetic contribution) is due to the fact that free carriers have an intrinsic magnetic moment and its relative importance is governed by the value of the g factor. The second term in the square brackets (diamagnetic contribution) depends strongly on the effective mass.

The value of the g factor is determined as[16]

$$g=2\left[1+(1-m/m^*)\frac{\Delta}{3E+3E_g+2\Delta}\right], \tag{7}$$

where E is the energy of electrons (holes) from the bottom (top) of the conduction (valence) band, E_g is the energy gap, and Δ is the spin-orbit splitting. The analysis of experimental curves of $\chi(T)$ was performed assuming that the observed temperature dependence of $\chi(T)$ is caused by terms $\chi_p(T)$ and $\chi_c(T)$. In fact, electron paramagnetic resonance was applied to β-$FeSi_2$ ceramics and revealed a variety of paramagnetic centers.[18] We suppose that paramagnetic centers exist in β-$FeSi_2$ single crystals as well as in β-$FeSi_2$ ceramics and these centers could be responsible for the observed temperature dependence of $\chi(T)$.

Transport measurements on our n- and p-type β-$FeSi_2$ single crystals between 30–300 K (Refs. 5 and 4) show ex-

TABLE I. Parameters of β-$FeSi_2$ single crystals.

Sample	$-\chi_0$ 10^{-7} emu/g Oe	A 10^{-5} emu K/g Oe	B 10^{-6} emu $K^{1/4}$/g Oe	ε meV	$-\Theta$ K	$N_p p_{\mathrm{eff}}^2$ 10^{20} cm^{-3}
n-type	4±0.2	2.7±0.3	−1.4±0.1	95±10	100±10	6.5±0.5
p-type	0.8±0.04	1.3±0.1	0.9±0.1	90±10	50±5	3±0.3

trinsic behavior. The electron (hole) concentration in n-type (p-type) β-$FeSi_2$ single crystals at room temperature is about 10^{18} cm^{-3} (10^{19} cm^{-3}) decreasing exponentially with decreasing temperature. The value of the activation energy of the donors (acceptors) is about 0.08 eV (Ref. 18) [0.10±0.01 eV (Ref. 4)] and mainly determines the temperature variation of the carrier concentration in the high-temperature region.

Using Eq. (1) a fit of our experimental curves $\chi(T)$ has been made. $\chi_p(T)$ is determined according to a Curie-Weiss law

$$\chi_p = A/(T-\Theta), \tag{8}$$

where

$$A = \frac{N_p \mu_B^2 p_{\mathrm{eff}}^2}{3\rho k}. \tag{9}$$

Θ is the Curie-Weiss temperature, N_p is the concentration of the magnetic centers, ρ is the density of the material (in β-$FeSi_2$ ρ=4.93 g/cm^3, Ref. 20), and p_{eff} is the effective number of Bohr magnetons.

χ_c, the magnetic susceptibility due to free carriers, is determined by Eq. (5), taking into account that in the samples studied the electron (hole) gas is nondegenerate ($\eta<0$). Estimation of the reduced Fermi level has been done using Eq. (3), assuming that $m_p^*/m = 1.0$ (Ref. 4) and $m_n^* = m_p^*$.[19]

The concentration of free electrons (holes) is given by[4]

$$n = \left[\frac{N_\nu}{\gamma} N\right]^{1/2} \exp\left[-\frac{\varepsilon}{2kT}\right], \tag{10}$$

where N and ε is the concentration and the activation energy of donor (acceptor) levels respectively, γ is the degeneracy factor [γ=2 (Ref. 4)].

If we take into account Eqs. (6) and (10), $\chi_c(T)$ can be written as

$$\chi_c = BT^{-1/4} \exp(-\varepsilon/2kT), \tag{11}$$

where

$$B = \frac{\mu_B^2}{\rho k}\left(\frac{N_\nu}{\gamma} N\right)^{1/2}\left[\frac{g^2}{4} - \frac{1}{3}\left(\frac{m}{m^*}\right)^2\right]. \tag{12}$$

The experimental curves $\chi(T)$ for n- and p-type samples can be fitted satisfactorily, using Eqs. (1), (8), and (11) and χ_0, A, Θ, B, and ε as adjustable parameters (Fig. 2). The latter are presented in Table I.

The values of χ_0 are different in n- and p-type samples probably due to a difference of lattice defect concentration 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.

In the studied samples the dependencies $1/\chi_p$ vs T [where χ_p is equal to $(\chi-\chi_0-\chi_c)$] in accordance with Eq. (8) are straight lines indicating the Curie-Weiss law (Fig. 3). The values of Θ and A determined from their intersection with the T axes and slope, respectively, are in agreement with the values estimated from a fit of the experimental curves.

The Curie-Weiss temperature is negative, similar to iron monosilicide,[21] and indicates antiferromagnetic interactions in β-$FeSi_2$ single crystals. The value of A (see Table I) allows the estimation of $N_p p_{\mathrm{eff}}^2$ in both n- and p-type samples. However, our lack of knowledge about the nature of the paramagnetic centers does not allow separation of N_p and p_{eff}.

The determined value of B (Table I) is positive (negative) in p-type (n-type) β-$FeSi_2$ single crystals. The g factor in β-$FeSi_2$ is equal to 2 according to Eq. (7), if we take into account that $m_p^*/m = 1$ (Ref. 4) and $m_p^* = m_m^*$.[19] Therefore, spin-orbit effects are not important and formulas (2), (5), and (6) are applicable. It leads also to the conclusion in accordance with Eq. (13) that the paramagnetic and diamagnetic

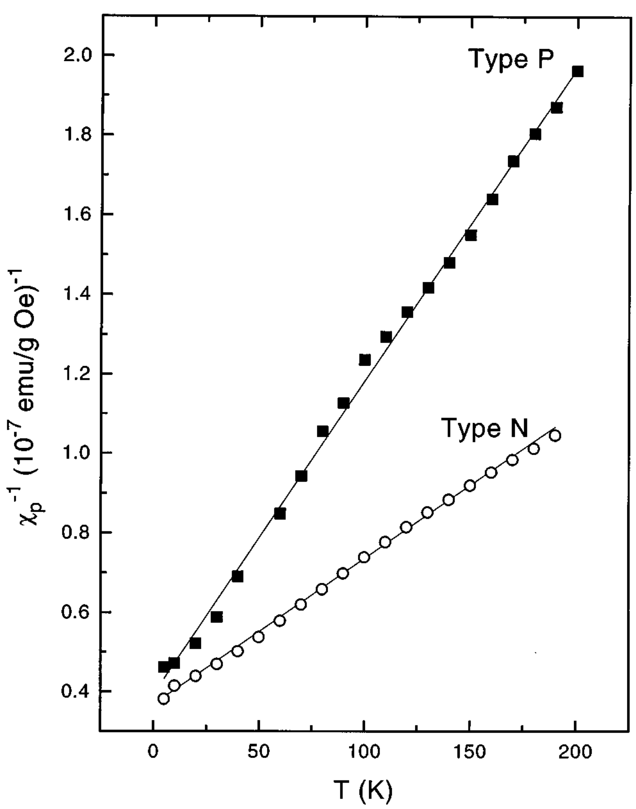

FIG. 3. Dependence of $1/\chi_p$ vs temperature.

terms for n- and p-type β-$FeSi_2$ are of the same order of magnitude. However, taking into account the sign of B, the absolute value of the diamagnetic term is somewhat higher or smaller than the paramagnetic term in n- and p-type samples, respectively. The latter indicates that values of the g factor and/or m^* do not coincide for n- and p-type samples. Assuming that in samples studied the difference in g factor is smaller than differences in m^* and values of the g factor are close to 2, the upper (lower) limit of m^*/m in n-type (p-type) β-$FeSi_2$ could be estimated assuming that the term in square brackets of Eq. (12) is equal to zero. The obtained value of m^*/m is about 0.6 which is in reasonable agreement with previous estimates of the density of states of the electron (hole) effective mass ($m_n^*/m=0.8$,[19] $m_p^*/m=0.8$,[19] $m_p^*/m=1.0$ (Ref. 4)].

The plot $\ln \chi_c T^{1/4}$ vs $1/T$ is linear in the high-temperature region (Fig. 4), where an exponential increase of the electron (hole) concentration takes place in n-type (p-type) samples, according to the temperature-dependent Hall coefficient.[4,5] Its slope permits us to determine the value of the donor (acceptor) level activation energy in agreement with Eq. (11). The obtained value as well as the value estimated as an adjustable parameter to fit the susceptibility measurements, are in agreement and equal to 0.095 ± 0.010 eV (0.09 ± 0.01 eV) and close to those derived from transport measurements [0.08 eV (Ref. 18) and 0.09–0.11 eV (Ref. 4) is the activation energy of the donors and acceptors, respectively]. Some deviation from good linearity observed in the dependence of $\ln \chi_c T^{1/4}$ vs $1/T$ (Fig. 4) as well as in dependence of $1/\chi_p$ vs T and M vs H (Fig. 1, fields up to about 4000 Oe) could be caused by quite small values of M and χ in samples studied as well as by the resolution of the used technique.

In conclusion, the magnetic susceptibility in n- and p-type β-$FeSi_2$ single crystals is determined by the temperature-independent contribution from the lattice, lattice defects and/or neutral impurities, and by the temperature-dependent parts due to paramagnetic centers as well as due to the carriers excited thermally in the high-temperature region.

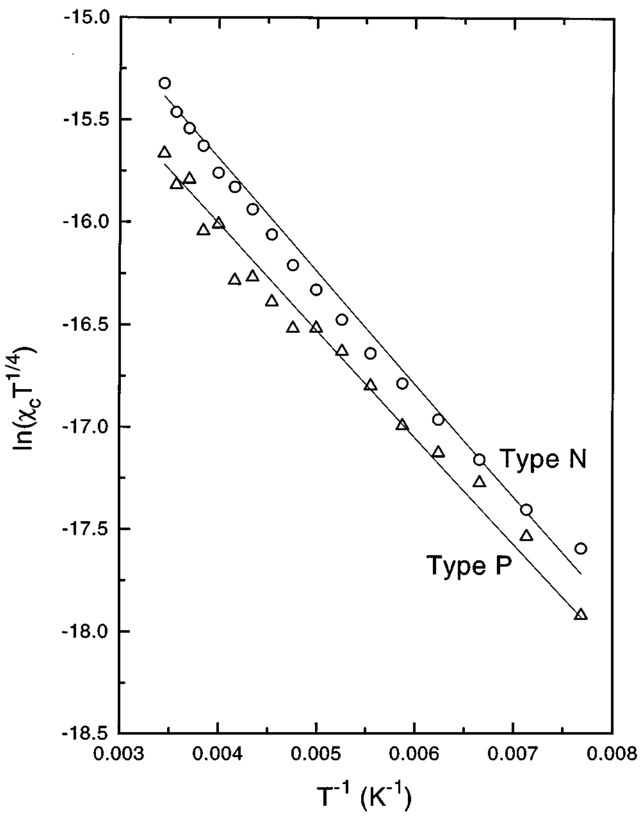

FIG. 4. Dependence of $\chi_c T^{1/4}$ vs $1/T$.

The temperature variation of the paramagnetic terms are in agreement with the Curie-Weiss law. The values of the Curie-Weiss temperatures, activation energy of the donor and acceptor levels, and the upper (lower) limit of the density of state electron (hole) effective masses were estimated.

The authors are indebted to Professor J. Cisowski and Dr. L. Brossard for useful discussion.

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