

Effect of pressure on the magnetic susceptibility of FeSi-CrSi and FeSi-NiSi monosilicide solid solutions

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The effect of hydrostatic pressure on the magnetic susceptibility of iron monosilicide and of some solid solutions based on it is investigated at room temperature. The derivatives with respect to volume are derived, within the framework of a simple model, for the main parameters of the FeSi electron spectrum (energy gap and band width). The possible role of the disordering of the potential in solid solutions is assessed.

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The peculiarities of the physical properties of the monosilicides of 3d metals and their mutual solid solutions is due to the singularities of the structure of the electronic spectra. However, in spite of the intensive study^[1,2], many properties of the electronic structure itself and the concrete form of its connection with the observed effects are not clear, and experiments in which the interatomic distance is varied may turn out to be quite useful for the understanding of these questions. We present below the results of an investigation of the magnetic properties of solid solutions of monosilicides of 3d metals with structure of the type B-20 under pressure.

EXPERIMENTAL PART

The magnetic susceptibility at hydrostatic pressures up to 4000 atm and at room temperature were measured by the method of free suspension of the metal by an inhomogeneous magnetic field^[3] in the single-phase solid solutions $Fe_{1-x}Cr_xSi$ ($0 \leq x \leq 0.7$) and $Fe_{1-x}Ni_xSi$ ($0 \leq x \leq 0.3$). The procedure for preparing the compounds and their solutions, and also of spherical samples of ~1 mm dia, are described respectively in^[4,5] and^[6]. The magnetic susceptibility of the samples of all the compositions decreased linearly under pressure (Fig. 1). The values of its logarithmic derivatives with respect to volume are shown in Fig. 2 (the compressibilities of the FeSi-CrSi solid solutions were obtained by linear interpolation of the data for the monosilicides of chromium^[7] and nickel^[8]; for FeSi-NiSi we assumed the same compressibility as for iron monosilicide). The largest effect of the pressure on the susceptibility is observed in pure iron monosilicide. Replacement of the iron by either chromium or nickel leads to an appreciable decrease of the magnitude of the effect.

DISCUSSION OF RESULTS

Iron monosilicide is a semiconductor with small energy gap ($2E_g \approx 0.05$ eV), which separates narrow bands ($2\Delta \approx 0.1$ to 0.3 eV) with high density of states $N(E)$ ^[1,2] (Fig. 3). Its magnetic susceptibility at low temperatures, i.e., in the absence of carriers, is close to zero, and consequently the appreciable paramagnetism observed at room temperature is entirely due to the pure spin contribution of the thermally excited carriers (the orbital diamagnetism is negligibly small, owing to the large effective masses, and the orbital paramagnetism is likewise small, owing to the closeness of the Fermi level to the top of the d band).

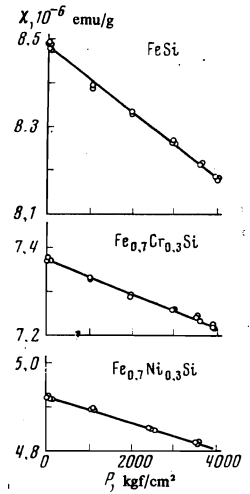


FIG. 1. Typical experimental plots of $\chi(P)$.

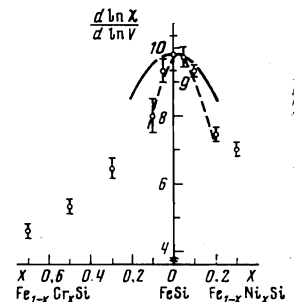


FIG. 2. Experimental values of $d \ln \chi / d \ln V$ as functions of the composition (points) and their model description with and without allowance for the scattering mechanism (dashed and solid lines, respectively).

To analyze the susceptibility of the iron silicide and of its alloys at finite temperatures, we use the approximate expression from^[9]

$$\chi(T) = \frac{2\mu_B^2}{5.55kT} \int_{\xi(T)-2.77kT}^{\xi(T)+2.77kT} N(E) dE. \quad (1)$$

The same reference gives a prescription for obtaining the chemical potential $\xi(T)$: its value is centered in the energy interval ~ 5.5 kT, in which the average value of the integral density of state, defined by

$$J(E, \xi_0) = \int_{\xi_0}^{\infty} N(E') dE' \quad (2)$$

is equal to zero; ξ_0 is the value of the chemical potential at $T = 0^\circ K$.

As the model spectrum in (1) we choose the scheme shown in Fig. 3, where both subbands are of the same form:

$$N(E) = \begin{cases} 0, & 0 < E < E_g, \\ 2\pi V \frac{(2m^*)^{3/2}}{\hbar^3} (E - E_g)^{1/2}, & E_g < E < E_g + \Delta, \\ 2\pi V \frac{(2m^*)^{3/2}}{\hbar^3} (E_g + 2\Delta - E)^{1/2}, & E_g + \Delta < E < E_g + 2\Delta. \end{cases} \quad (3)$$

The energy is reckoned from the center of the gap, and all the calculations performed for $+\xi_0$ are valid also for $-\xi_0$ by virtue of the symmetry of the spectrum.

Figure 4 shows the temperature dependence of the magnetic susceptibility of iron monosilicide, calculated from (1); it agrees well with experiment if we assume for the model parameters of the spectra the following values:

$$2\Delta = 0.12 \text{ eV}, \quad 2E_g = 0.05 \text{ eV}, \quad m^* \approx 80 m_0. \quad (4)$$

Their agreement with the results of the more rigorous theoretical analysis of the temperature dependence of the susceptibility^[2] confirms the validity of the employed approach.

We shall use this approach to analyze the effects of pressure. Differentiating (1) with respect to the volume at constant capacity of the bands of type (3), we obtain

$$\frac{d \ln \chi}{d \ln V} = \alpha_1 \gamma + \alpha_2 \frac{\partial \ln E_g}{\partial \ln V}, \quad (5)$$

where $\gamma = -\partial \ln \Delta / \partial \ln V$, and the coefficients α_1 and α_2 for small ξ ($|\xi| / (2.77kT - E_g) < 1$) and temperatures on the order of room temperature take the following form:

$$\alpha_1 = \frac{3}{2} \left[1 - \frac{3}{4} \left(\frac{\xi}{2.77kT - E_g} \right)^2 \right], \quad (6)$$

$$\alpha_2 = -\frac{3}{2} \frac{E_g}{(2.77kT - E_g)} \left[1 - \frac{3}{4} \left(\frac{\xi}{2.77kT - E_g} \right)^2 \right].$$

It follows from (6) that the dependences of the coefficients on the level of the chemical potential are identical and that it is unfortunately impossible to separate the contribution to (5) by using the data for alloys of variable valence at fixed temperature. However, the value of the first of the contributions, which is connected with the deformation of the bands, can be estimated from theoretical calculations for narrow bands of the resonant type and from the experimental data for the d-bands of transition metals.^[10] Assuming according to^[10] that $\gamma = 2 \pm 1$ and comparing (5) with experiment for FeSi ($\xi = 0$), we obtain

$$\partial \ln E_g / \partial \ln V = -9 \pm 3, \quad \text{or} \quad \partial (2E_g) / \partial \ln V \approx -0.5 \text{ eV}.$$

Expression (5) with the assumed values of the parameters γ and $\partial \ln E_g / \partial \ln V$ describes only qualitatively the behavior of the susceptibility of the alloys near Fe Si (Fig. 2, solid line), under the assumption

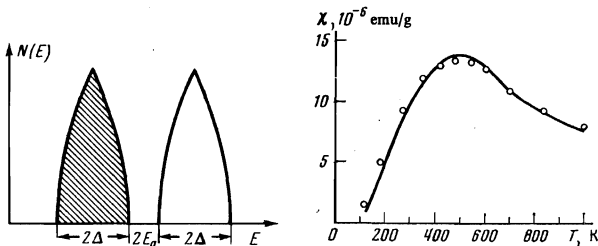


FIG. 3

FIG. 3. Diagram of energy bands in iron monosilicide.

FIG. 4. Calculated (solid) and experimental functions $\chi(T)$ for iron monosilicide.

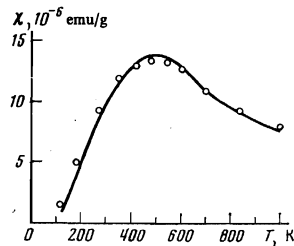


FIG. 4

that the effect of melting consists only in a change of the level of the chemical potential given by (3) and (2) in accordance with the average valence of the alloy. Actually, there is also a smearing of the spectrum because of the scattering of the electrons by the inhomogeneities of the potential in the alloys. At small values of X, this mechanism can be approximately accounted for in terms of the effective temperature $T^* = \beta X$,^[11] which we add to the real temperature in (6). It must be borne in mind that in the real spectrum of FeSi, first, the parameters of the upper and lower subbands can differ noticeably if their mean values corresponds with the models (3) and (4); second, an initial shift of the level of the chemical potential is possible, owing to the impurities or the presence of defects. A certain asymmetry of the observed peak in the pressure effect relative to pure FeSi (Fig. 2) can be attributed precisely to these factors, and not only to peculiarities of the impurities themselves. We can therefore demand of the model theory only a satisfactory description of the shape of the peak, and not a disclosure of the differences between the scattering abilities of the impurities. And such a description can indeed be obtained by introducing for chromium and nickel an identical value $\beta \approx 4 \text{ deg/at.}\%$. For greater clarity, the calculated curve (dashed in Fig. 2) is shifted along the concentration axis until it coincides with experiment (this is equivalent to an excess of acceptor impurity in the initial FeSi). The value of β is in reasonable agreement with the typical values of the Dingle factor^[12] and should lead to a washing out of the gap at $X \approx 0.25$. The character of the temperature dependence of the conductivity of the solid solutions $\text{Fe}_{1-x}\text{Mn}_x\text{Si}$ ^[13] and $\text{Fe}_{1-x}\text{Ni}_x\text{Si}$ ^[5] is evidence of the vanishing of the gap at precisely this concentration, regardless of the type and valence of the third component.

The foregoing analysis is valid on the whole only near FeSi. At a larger content of the third component in the solutions ($X \approx 0.5$), the chemical-potential is located far from the gap, and the state-density curve seems to be maximally smoothed out as a result of scattering, so that the decisive factor in the behavior of the magnetic susceptibility under pressure should be the deformation contribution. This prediction agrees qualitatively with experiment.

The obtained behavior of the gap agrees in sign and in magnitude with the gap between levels of different symmetry, if the lower is referred to the edge of the filled d-band.^[10] This is precisely the situation characteristic of the considered compounds, where the d-band is preferably almost filled or already filled, and the gaps have a hybridization nature (see the NiAl spectrum by way of illustration^[14]).

We have left out in the analysis the exchange correction to the spin paramagnetism, which not known for the considered systems. In analogy with the palladium alloys, we can expect its participation in the pressure effects to be negligible,^[15] although it is not clear whether this exchange property is general enough. Further refinements call for extending the temperature range and the use of additional information, particularly the electric conductivity under pressure. But even in the form presented here, the parameters that characterize the properties of the energy spectrum of the electrons in monosilicides of 3d metals may turn out to be useful for the clarification of the genesis of the spectrum and the

connection of various effects with its singularities, and also for the correction of the form of the lattice potential.

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