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Abstract. We report magnetic susceptibility measurements on single crystals of very-high-purity VSi_2, $NbSi_2$ and $TaSi_2$ from 4 K to room temperature. VSi_2 is paramagnetic while $NbSi_2$ and $TaSi_2$ are diamagnetic. A systematic anisotropy of χ is observed for the three compounds. The results are in good agreement with previous investigations of the electronic properties of these materials. The different contributions of χ which account for these data are discussed.

1. Introduction

The silicides of the transition metals are widely studied owing to the variety of their physical properties and to their potential applications in VLSI technology. Of particular interest are VSi_2, $NbSi_2$ and $TaSi_2$ which are isoelectronic and crystallize in the same hexagonal C40 structure (space group, $P6_222$). Single crystals of very high purity have been grown [1]. Transport measurements on these metallic samples indicate that these materials are anisotropic [2, 3]. Low-temperature specific heat measurements are in good agreement with electronic density-of-state calculations which show that a narrow band is located near the Fermi level. The widths of this are around 0.15 eV, 0.4 eV and 0.5 eV for the vanadium, niobium and tantalum compounds respectively. $N(E_F)$ decrease with increasing atomic number of transition metal. From the γT term of the specific heat we deduced 2.58, 1.44 and 1.32 states eV^{-1}/formula unit for VSi_2, $NbSi_2$ and $TaSi_2$, respectively [4]. $NbSi_2$ and $TaSi_2$ are superconductors with transition temperatures of 130 mK and 353 mK, respectively [4]. For VSi_2 we found no indication of superconductivity for temperatures above 100 mK. These results are also in good accordance with optical data [5, 6].

Magnetic measurements are reported for only a few temperatures and on sintered materials [7]. We present here a systematic study of the magnetic properties of VSi_2, $NbSi_2$ and $TaSi_2$ carried out on single crystals from 4 K to room temperature.

2. Experimental details

Large single crystals of VSi_2, $NbSi_2$ and $TaSi_2$ were grown by a modified Czochralski technique. The crystals were pulled from a RF-levitated melt in a cold Hukin-type copper crucible [8, 9]. The alloys had previously been prepared by direct melting of purified metal rods (purity, greater than 99.99%) and high-purity (99.9999%) silicon lumps. Further details of this growth technique have been reported in [10]. By the above-described procedure we obtain large single crystals of cylindrical shape (4–5 cm long with a diameter of 8–10 mm). These rods were mounted with wax on a goniometer and oriented by Laue x-ray patterns. They are cut by mechanical grinding. Finally we obtained well oriented samples (precision, about 1°) with a suitable shape for magnetization measurements. In the case of VSi_2 and $TaSi_2$ we used the same samples which had already been studied by specific heat measurements [4].

Magnetic measurements were made with a commercial SQUID magnetometer from Metronique Instruments. The magnetic field is given by a superconducting coil; it can be varied up to 75 kG. The resolution of the magnetization is better than one part in 10^3. The precision of temperature regulation is about 5 mK at 4 K and 100 mK at 275 K.

The orientation of the crystallographic axis of the sample in the direction of the field is achieved with an accuracy of about 5°. This is not of crucial importance since the anisotropy of the magnetic properties is low. Furthermore several runs have given identical results with a reproducibility to within 0.5%. No thermal hysteresis was observed.

3. Results

Typical magnetization data are shown in figure 1 where we have plotted M versus B for VSi_2 and $TaSi_2$ at 4 and 275 K, with B parallel to the c axis. M varies proportionally to B up to the maximum field. At low fields and low temperatures, small deviations from linearity can be observed. They can be attributed to a very small number of residual impurities in the sample. In figure 1 for clarity we omitted to plot any data for $NbSi_2$, as they are very close to those of $TaSi_2$.

In figure 2 we have plotted $\chi = M/B$ at $B = 60$ kG versus temperature for the three compounds. χ_c and χ_{ab} refer to B parallel and perpendicular, respectively, to c.† The main results obtained from figure 2 can be summarized as follows.

(1) VSi_2 is paramagnetic while $NbSi_2$ and $TaSi_2$ are diamagnetic. As for the electronic specific heat and electrical resistivity the latter two compounds exhibit rather similar behaviours which are notably different from that of the vanadium compound.

(2) For the three silicides, the susceptibility is anisotropic. χ_c is larger than χ_{ac} by about $(40-50) \times 10^{-6}$ emu mol^{-1}.

(3) χ is almost temperature independent in the domain investigated for both orientations of $NbSi_2$ and for χ_{ab} of $TaSi_2$. For χ_c of the latter compound a maximum occurs at around 60 K with an overall variation in χ of about 10×10^{-6} emu mol^{-1} in the entire range of T. For the vanadium compound the components χ_c and χ_{ab} of the susceptibility decrease

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† To enable a comparison to be made with the results in the literature, χ is given in emu. To obtain values in SI units multiply by the factor $4\pi \times 10^{-6}$.
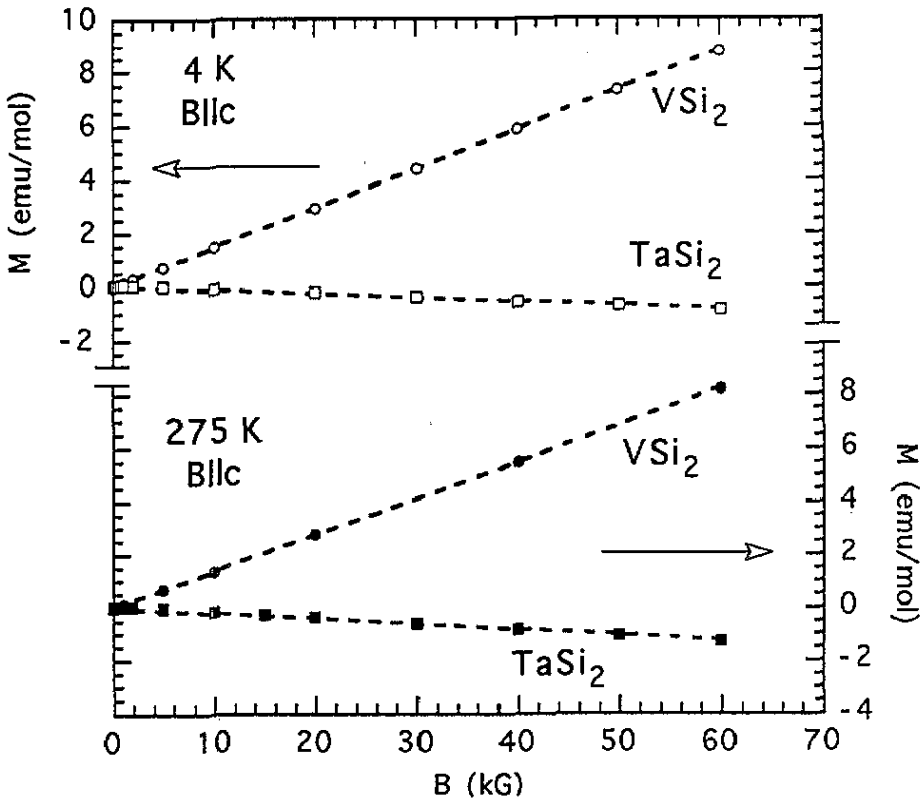
Figure 1. Magnetization M versus B for VSi$_2$ and TaSi$_2$ at 4 and 275 K with $B \parallel c$.

continuously from 4 to 275 K, both following roughly a T^2 law. The total variation is about 8×10^{-6} emu mol^{-1} for χ_c and about 10×10^{-6} emu mol^{-1} for χ_{ab}.

(4) Our results are in good agreement with old results on sintered samples [7] which were $+161$, -37 and -40×10^{-6} emu mol^{-1} for VSi$_2$, NbSi$_2$ and TaSi$_2$, respectively, at room temperature. A large decrease in the susceptibility with increasing temperature for VSi$_2$ is also reported. At 500 °C, χ has a value of 107×10^{-6} emu mol^{-1}.

4. Discussion

The calculation of the magnetic susceptibility of solids is a very difficult task, since one needs a detailed knowledge not only of the band structure but also of the electronic orbitals localized around the atoms. χ can be modified by the lattice potential as well as by electron interactions. Different contributions to the susceptibility can be distinguished. The values of these contributions are generally of the same order of magnitude; their signs can be either positive or negative. Thus it is sometimes difficult to predict whether a material will be
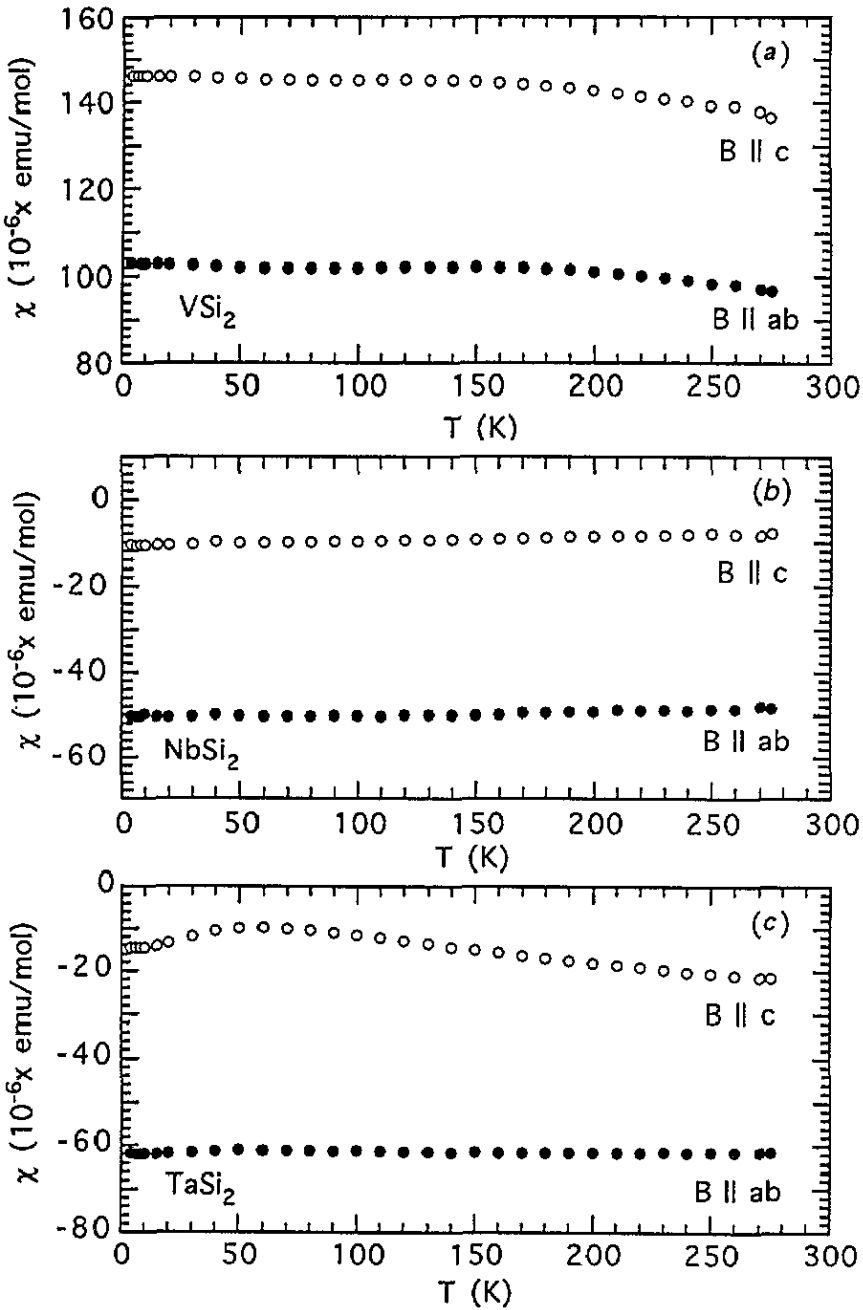
Figure 2. (*a*) Magnetic susceptibility versus T for VSi$_2$, χ_c with $B \parallel c$ and χ_{ab} with B in the basal plane. (*b*) Magnetic susceptibility versus T for NbSi$_2$, χ_c with $B \parallel c$ and χ_{ab} with B in the basal plane. (*c*) Magnetic susceptibility versus T for TaSi$_2$, χ_c with $B \parallel c$ and χ_{ab} with B in the basal plane.

diamagnetic or paramagnetic. The separation between these different contributions is also

more or less arbitrary.

We do not know the electronic structures of VSi_2, $NbSi_2$ and $TaSi_2$ sufficiently accurately to perform such a calculation of χ. However, from our knowledge of the electronic properties of these compounds that we have obtained in our previous studies, we try to describe the main trends of the magnetic data with a simplified model.

The magnetic susceptibility of a normal metal (without local magnetic moment) can be decomposed into different contributions:

$$\chi = \chi_{core} + \chi_P + \chi_{LP}.$$

χ_{core} is the diamagnetic susceptibility of the core electrons, χ_P is the Pauli spin paramagnetism of the conduction electrons and χ_{LP} is the Landau–Peierls term resulting from the orbital motion of the conduction electrons. Other terms can also be introduced to account for the experimental data if necessary.

χ_{core} is temperature dependent and can be calculated if the electronic distribution is known [11]. So we have to assume the electronic configuration of the ion in the solid in order to evaluate this term. For the silicon ions, a reasonable assumption is to suppose an intermediate value between the two extreme $3s^23p^2$ ($\chi = -26 \times 10^{-6}$ emu mol^{-1}) and $2p^6$ ($\chi = -2 \times 10^{-6}$ emu mol^{-1}) electronic configurations [12]. The former corresponds to the neutral free atom of Si and the latter to the Si^{4+} ionized atom. This leads to -14×10^{-6} emu mol^{-1} for each Si ion core. The value corresponding to the two Si atoms in the molecule is indicated by an arrow in figure 3 where we have plotted the values of χ measured at low temperatures for the three compounds and for both orientations against the atomic number of the metallic element in the silicide. The diamagnetic susceptibilities are -21, -47 and -69×10^{-6} emu (g atom)$^{-1}$ for the $3d^4$, $4d^4$ and $5d^4$ configurations of the V, Nb and Ta ions, respectively [13]. They correspond to an M^+ ion. The total (2 silicon atoms + transition metal atom) χ_{core} contributions are shown in figure 3.

At low temperatures, χ_P is given for non-interacting electrons by

$$\chi_{P0} = \mu_B^2 N(E_F).$$

Using the density $N(E_F)$ of states deduced from specific heat measurements we can calculate χ_{P0}. We have plotted $\chi_{core} + \chi_{P0}$ in figure 3. We see that with only these two contributions reasonable agreement with the measured value has already been achieved in particular the decrease in χ from vanadium to tantalum has been accounted for.

However, we note that the measured susceptibility of VSi_2 is about twice the χ obtained by taking account of these two contributions. We have seen that a narrow band is located at E_F in this compound, leading to a large value for the electronic density of states. Such a result is favourable to strong electron–electron interactions which, as discussed in [4], can be a reason for the lack of superconductivity of VSi_2 at temperatures above 100 mK. Electron–electron interactions enhance the spin susceptibility by the Stoner factor $1/[1 - IN(E_F)]$, where I is the exchange integral.

By using quite a reasonable $IN(E_F)$-value of 0.5 [14], we can easily achieve good agreement between the data for VSi_2 and the two contributions of the susceptibility: $\chi_{core} + \chi_{P0}/[1 - IN(E_F)]$. Assuming that I is the same for the other two silicides we can calculate the enhancement in χ_P for $NbSi_2$ and $TaSi_2$. They are much smaller owing to the smaller $N(E_F)$. The results for the two contributions are shown in figure 3. They are in quite good agreement with experimental data for the three silicides.
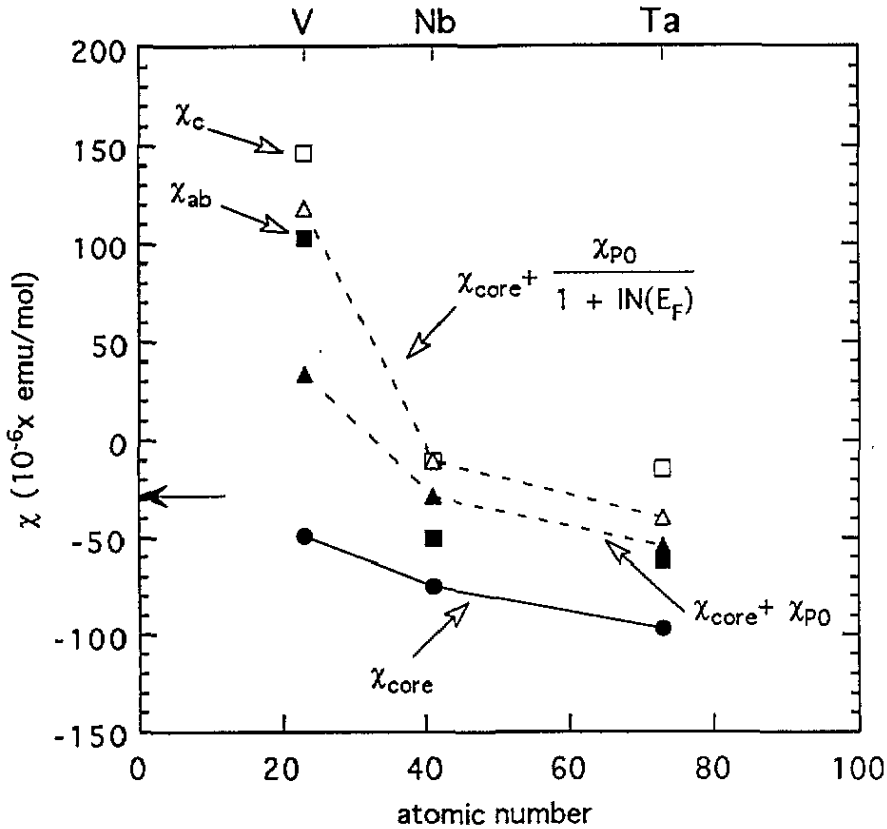
Figure 3. χ versus atomic number of the metallic element in the disilicide: $\square$, measured χ_c; $\blacksquare$, measured χ_{ab}; $\bullet$, c_{core}; $\blacktriangle$, $\chi_{core} + \chi_{P0}$; $\triangle$, $\chi_{core} + \chi_{P0}/[1 + IN(E_F)]$. For detailed explanation see text.

The anisotropy of the susceptibility can be ascribed to the Landau–Peierls term which is given by [15]

$$\chi_{LP} = -\tfrac{1}{3}\chi_{P0}(m_0/m^*)^2$$

where m^* is the effective mass of the carriers and m_0 the free-electron mass. The electrical conductivity at room temperature is anisotropic [3]. σ is systematically larger when the current flows along the c direction than when it flows in the hexagonal plane. The anisotropy of σ can be related to the anisotropy of the effective mass tensor. For a hexagonal crystal the two values M and m are sufficient to define this tensor [16]. So the component m of the effective-mass tensor along the c axis is smaller than M in the a–b plane.

For the susceptibility the effective masses to consider are the components in the directions perpendicular to the field. χ_{LP} can be taken to be proportional to $-1/M^2$ for χ_c and to $-1/mM$ for χ_{ab}. This simple argument explains well that χ_c is larger than χ_{ab} for a given silicide.

A thermal dependence of the Pauli susceptibility occurs when the electronic density of states varies significantly on an energy scale of the order of kT. For a simple parabolic band we have

$$\chi_P(T) = \chi_{P0} \left[1 - \tfrac{1}{12}\pi^2 (kT/E_F)^2 \right].$$

A more general expression can also be used for other shapes of the electronic density of state [17]. In the simplified case, applying this formula to VSi₂, we obtain $E_F \simeq 0.06$ eV and $E_F \simeq 0.08$ eV from χ_c and χ_{ab}, respectively, which is of the order of magnitude of the width of the narrow band present in that compound. So the thermal variation in χ for VSi₂ can be explained by the thermal variation in the Pauli paramagnetism. In the cases of NbSi₂ and TaSi₂ the widths of the narrow band located at E_F are four and five times, respectively, that of VSi₂. Thus the thermal variation in the Pauli paramagnetism for NbSi₂ and TaSi₂ should be about a twentieth of that for VSi₂. It is more probable that the observed thermal variation in χ_c for TaSi₂ has another cause.

Thermal dilatation of the lattice gives small variations in the susceptibility even in simple metals such as Cu, Ag or Au [18]. Even in simple systems the variations are not easily predictable. For copper and gold, χ decreases with increasing T. A minimum is observed for silver. In the case of systems such as hexagonal zinc or cadmium the more complex band structure gives a variety of effects which can be explained only if one knows in great detail the Fermi surface topology [19]. The effect of the lattice dilatation could very probably explain the thermal variation in χ shown by TaSi₂.

5. Conclusion

We measured the magnetic susceptibilities of VSi₂, NbSi₂ and TaSi₂ single crystals from 4 K up to room temperature. VSi₂ is paramagnetic while NbSi₂ and TaSi₂ are diamagnetic. Using the information obtained from specific heat measurements and from band-structure calculations we can explain the magnetic measurements as the sum of the core diamagnetism of the localized ions and the enhanced Pauli paramagnetism due to the conduction electrons. We observe a systematic anisotropy in χ for the three compounds. We can explain this by a Landau–Peierls diamagnetic term and we can correlate it to the anisotropy of the transport properties.

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