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Bonding and structure of $CoSi_2$ and $NiSi_2$

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Self-consistent calculations of the electronic structure of $CoSi_2$ and $NiSi_2$ give insight into the nature of the bonding and suggest an explanation of the unique structure of these two compounds. A quasigap separates bonding and antibonding states. For $CoSi_2$ and $NiSi_2$, E_F falls in or near the quasigap. The Si atoms exhibit sp^3 hybridization, absent in many other silicides. Ionicity is negligible. Bonding is well described by a directed valence-orbital picture, except for free-electron (interstitial) character at higher energies.

Transition-metal silicides are of great current interest[1,2] largely because of electronic device applications of silicon-silicide interfaces. In this context the two compounds $CoSi_2$ and $NiSi_2$ are of particular theoretical interest. They both have a structure (the fluorite structure) where the local bonding geometry of the Si atom is similar to that in pure Si, except that its tetrahedral neighbors are Ni or Co instead of Si. The lattice match with Si is also remarkably close, so ideal epitaxial films and interfaces can be formed.[3,4]

Despite several electronic structure calculations for $NiSi_2$,[5-7] the theoretical understanding of the bonding in these two compounds is still uncertain.[2] In a recent review article Rubloff[2] states that the bonding in most transition-metal silicides[7-9] is well understood in terms of hybridization of Si *p* and Ni *d* orbitals, with the Si *s* orbital not participating. $NiSi_2$ is a puzzling exception,[2] with differing degrees of ionic, covalent, or simple-metal character attributed to the bonding by various authors.[5-7]

Here we show that the bonding in $NiSi_2$ and $CoSi_2$ is quite similar to that in Si, involving strictly covalent bonding, which is well understood in a directed valence-orbital picture. The presence of sp^3 hybridization distinguishes these compounds from other silicides studied to date,[7-9] as we illustrate by comparison with Ni_3Si. Contrary to results of previous work,[6] we find negligible ionicity.

Although $NiSi_2$ and $CoSi_2$ are metals, we find that they have a "quasigap" in the density of states near E_F separating bonding and antibonding states. This quasigap may be crucial in stabilizing the structure. Figures 1(b) and 1(c) show the density of states (DOS) of $CoSi_2$ and $NiSi_2$. The separation of bonding and antibonding states is most visible in the projected metal *d* DOS (lower lines) and is indicated by an arrow. Figure 1(a) illustrates schematically for the case of $CoSi_2$ how this split arises.

One of the interesting points here is that the bonding can be understood in terms of directed valence orbitals, even though no local-orbital assumption is made. At the center Γ of the Brillouin zone, the three Co *d* orbitals of $\Gamma_{25'}$ symmetry (symmetry *xy*, *yz*, and *xz*) are directed so as to overlap the eight Si neighbors, making a strong *p*-*d* bond. The Γ_{12}-symmetry orbitals (x^2-y^2, $3z^2-r^2$) are directed *away* from the Si and form a nonbonding state (corresponding to the very sharp peak near -2 eV in the DOS). (Similar behavior is seen in other silicides.[2]) The energetic position of these states is shown in Fig. 1(a); the corresponding charge densities are shown in Figs. 2(a) and 2(b).

At the point *X* on the edge of the Brillouin zone $[\vec{k}=(2\pi/a)(0,0,1)]$, each *d* complex is split. The x^2-y^2 orbital has lobes directed perpendicular to $\vec{k}$, and so the X_2 state remains nonbonding as at Γ. The $3z^2-r^2$ orbital is directed along $\vec{k}$, however, and forms an antibonding combination (X_1) with the free-electron-like interstitial charge. This state is shown in Fig. 2(c). Such a state cannot be described by methods with a minimum orbital basis such as extended Huckel.[7] A similar splitting occurs for the $\Gamma_{25'}$

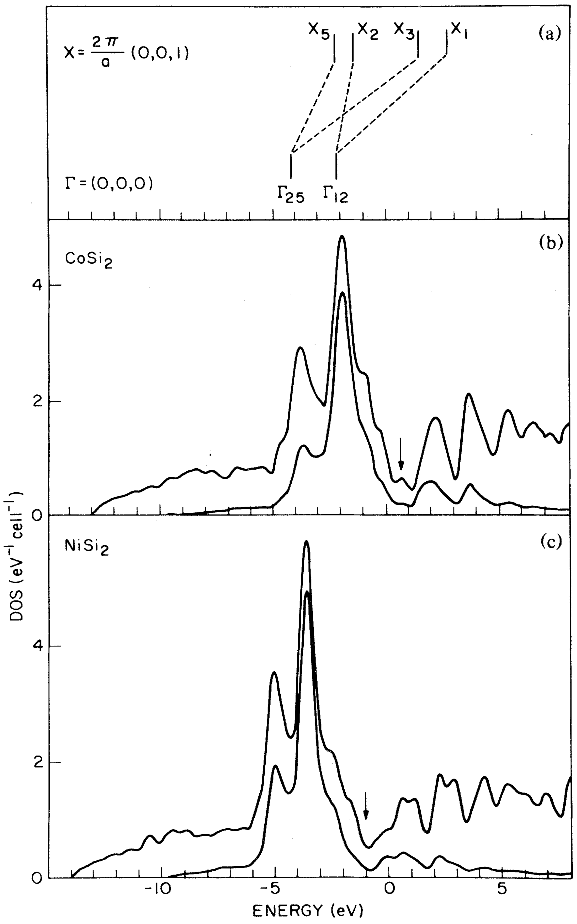

FIG. 1. Density of states of $CoSi_2$ and $NiSi_2$. Lower line in (a) and (b) shows projected *d* component in muffin-tin about metal atom. Arrow indicates approximate separation of *d* bonding and antibonding states. (a) shows characteristic states at Γ and *X* for $CoSi_2$, illustrating origin of bonding-antibonding structure in DOS. DOS is based on a discrete sample of 60 points in the irreducible Brillouin zone with Gaussian smoothing.

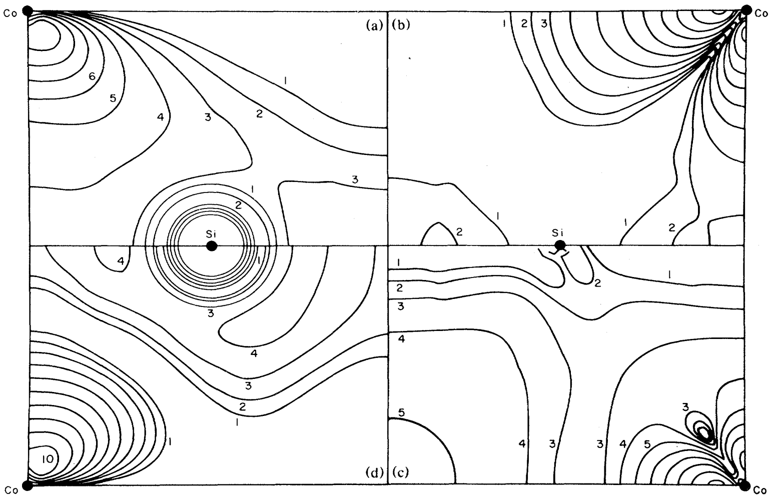

FIG. 2. Charge-density contours in (110) plane of $CoSi_2$ for four states of high symmetry, illustrating bonding [cf. Fig. 1(a)]. (a) p-d bonding state $\Gamma_{25'}$. (b) d nonbonding state Γ_{12}. (c) d-"free-electron" antibonding state X_1. (d) s-d antibonding state X_3. Charge has been symmeterized, i.e., averaged over inequivalent X points. Successive contours differ by a factor of 2; contour number 1 corresponds to 10^{-3} a.u.$^{-3}$, with normalization of two electrons per unit cell. The four panels together represent one unit cell of the (110) plane shown. Corner atoms are Co; central atoms are Si.

states, with the xy orbital forming an antibonding combination (X_3) with Si s orbital, as seen in Fig. 2(d). Empty s-d antibonding states preclude a separate filled Si s band as is seen in other silicides.[2]

This discussion has been limited to states at two points of high symmetry in the Brillouin zone. However, comparison of these states [Fig. 1(a)] with structure in the $CoSi_2$ DOS [Fig. 1(b)] suggests that these states exemplify the origin of the main features in the DOS. Our detailed examination of the bands confirms this. (The $CoSi_2$ band structure will be given elsewhere. It is very similar to that of $NiSi_2$ given by Chabal *et al.*[5])

Bylander *et al.*[6] have concluded that $NiSi_2$ is rather ionic, with a transfer of 1.12 electrons from the two Si atoms to the Ni. The analysis of Ref. 6 employed an intuitively reasonable but nonunique prescription for assigning all charge to specific sites; since much of the charge is in bonds midway between the Ni and Si sites, such an assignment is risky. We have instead examined the electronic structure within a sphere of radius 1 Å (almost the covalent bonding radius) about the Si atom; this sphere contains roughly half the Si valence charge. The net charge within this sphere is only 0.05 electrons less for $NiSi_2$ and $CoSi_2$ than for bulk Si, suggesting minimal ionicity. This is consistent with the similar electronegativities of Si, Ni, and Co. Moreover, the decomposition of charge within this sphere by s and p character is almost the same in the two silicides as in Si, indicating the similar formation of sp^3 hybrids.

A fundamental distinction between the bonding of Si and of many silicides is the absence of sp^3 hybridization in the silicides. To investigate the degree of sp^3 hybridization in some silicides, we have projected the DOS in a sphere of radius 1 Å about the Si atom. The s and p components of the DOS are shown in Fig. 3 for Si, $CoSi_2$, and Ni_3Si. Si shows the characteristic "signature" of sp^3 hybridization, a smooth crossover between s and p character, with enhanced s character just above E_F. The behavior of Si in $CoSi_2$ is in this respect, almost identical to that in pure Si, as is dramatically illustrated by the similarity of Si and $CoSi_2$ in Fig. 3. In Ni_3Si, however, the s and p orbitals dehybridize, with two electrons in a separate narrow s band far below E_F, and mostly p character throughout the rest of the band. Ni_3Si is typical of silicides studied theoretically to date[8,9] in that it is close packed and metal rich. (Results for $NiSi_2$ are almost identical to those shown for $CoSi_2$.)

We conclude that the bonding in $CoSi_2$ and $NiSi_2$ is remarkably similar to that in bulk Si in terms of sp^3 hybridization in the Si atoms, absence of ionicity, and presence of a quasigap at E_F, separating bonding and antibonding states. Here, however, the transition-metal d band plays a crucial role in the bonding. Any change in the position of the d band would move the "gap" away from E_F, which may explain why other silicides do not form in this structure.

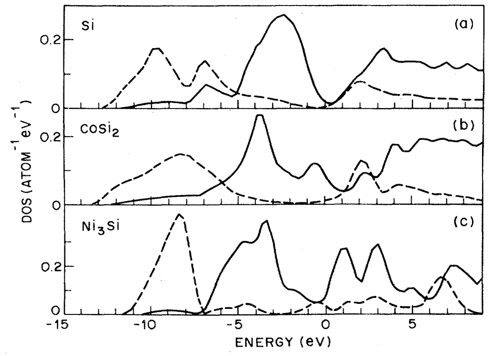

FIG. 3. Projected s (dashed line) and p (solid line) component of the "muffin-tin" DOS for (a) bulk Si, (b) Si atom in $CoSi_2$, and (C) Si atom in Ni_3Si. The projection is within a sphere of radius 1 Å about the Si atom (nearly the covalent bond radius). For Ni_3Si the projection is in a slightly larger sphere, hence the different scale; separate s band (-11 to -7 eV) contains two electrons (including portion outside muffin-tin).

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