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Self-consistent energy bands and bonding of $NiSi_2$

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The energy bands and cohesive energy of $NiSi_2$ are calculated with the use of the self-consistent linear combination of Gaussian orbitals method. Partial densities of states are calculated and integrated to obtain ionicities. Covalent bonding is displayed in a contour plot. The ^{29}Si nuclear-magnetic-resonance relaxation time is calculated and found to be in excellent agreement with experiment. All results are contrasted with those we recently obtained in a similar calculation of Ni_3Si.

I. INTRODUCTION

There are six nickel silicide compounds of which $NiSi_2$ and Ni_3Si form the two extremes in composition. Ni_3Si has a simple cubic lattice but is close packed, being identical to fcc nickel with each cube corner Ni replaced by a Si, whereas the fluorite structure of $NiSi_2$ is an fcc lattice consisting of a simple cubic array of Si atoms with every other cube containing a Ni at its center. In Table I we list the structures, lattice constants,[1] volume per atom and per unit cell, Ni—Si Ni—Ni, and Si—Si first-neighbor bond lengths, and major constituent second-neighbor bond lengths for the two crystals. Note that the more open fluorite structure has a shorter Ni—Si bond but longer major and minor constituent homopolar bond lengths than Ni_3Si.

In this paper we calculate energy bands, cohesive energy, partial density of states, ionicity, and ^{29}Si nuclear relaxation time of $NiSi_2$ using the same linear combination of Gaussian orbitals technique that we used[2] for Ni_3Si. Our basis set consists of all atomic orbitals up to Si 3*p* and Ni 4*p* plus two *p* and *d* and three *s* Gaussian orbitals on each atomic site. We calculated the charge density and Kohn-Sham-Wigner exchange-correlation potential at 841 points in the $\frac{1}{48}$th irreducible fcc unit cell; of these 385 are on a cubic mesh and the rest on four staggered radial meshes about each of the two independent atoms in the cell. The potential at these points was fitted using 40 (39) $e^{-\alpha r^2}$ functions centered on the Ni (Si), thirteen

$$[x^4+y^4+z^4-3(x^2y^2+y^2z^2+z^2x^2)]e^{-\alpha r^2}$$

on each atom and thirteen $(xyz)e^{-\alpha r^2}$ on the Si. The charge density is fitted with the Laplacians of

TABLE I. Lattice constant, cell and atomic volumes, bond lengths, calculated partial charges and ionicities (in electrons per ion), and calculated cohesive energy of Ni_3Si and $NiSi_2$.

	Ni_3Si	$NiSi_2$
Structure	Cu_3Au	Fluorite
a_0	3.507 Å	5.395 Å
Vol/unit cell	43.13 Å^3	39.26 Å^3
Vol/atom	10.783 Å^3	13.086 Å^3
Ni—Si bond length	2.480 Å	2.336 Å
Ni—Ni bond length	2.480 Å	3.815 Å
Si—Si bond length	3.507 Å	2.698 Å
Second neighbor	3.507 Å (Ni—Ni)	3.815 Å (Si—Si)
Si *s* charge	0.804	0.844
Si *p* charge	1.911	2.150
Si *d* charge	0.403	0.446
Ni *s* charge	0.385	0.451
Ni *p* charge	0.889	1.584
Ni *d* charge	9.019	9.084
Ni ionicity	+0.294	+1.119
Si ionicity	−0.882	−0.560
E_{cohesive}	5.51 eV/atom	5.23 eV/atom

these functions plus two $\nabla^2(e^{-\alpha r^2}/r)$ functions about each atom. To obtain the charge density we calculated the energy bands on a bcc (Ref. 3) mesh of 75 points within the $\frac{1}{48}$th irreducible Brillouin zone (BZ) generated by $(2\pi/a)\,(\frac{1}{12},\frac{1}{12},\frac{1}{12})$ vectors. The charge-density contribution of each eigenstate at the 16 primary points generated by $(2\pi/a)$ $(\frac{1}{6},\frac{1}{6},\frac{1}{6})$ vectors was calculated and interpolated[2] (taking symmetry into account) to the corresponding states at the remaining points. Each energy level was Gaussian broadened and weighted by the fraction of the Gaussian below the Fermi energy and by the number of equivalent points in the full BZ. The calculation was considered converged when the maximum deviation between input and output potentials was less than 0.0025 eV.

II. RESULTS

In Fig. 1 we display the energy bands of $NiSi_2$. Although there is only one Ni atom per unit cell, there are several levels at symmetry points in the BZ with large Ni d components. Making a Löwdin projection[2,4] we find that the Γ_{12} wave functions are 94% Ni d whereas the $\Gamma_{25'}$ wave functions at -5.29 eV are 70% Ni d and those at 1.72 eV are[5] 43% Ni d. The X_5 wave functions are 95% Ni d, whereas the X_3 function at -7.34 eV is 44% Ni d and that at -0.42 eV is 69%. The X_1 functions at -8.06, -3.43, and 1.48 eV are 14%, 74%, and 32% Ni d, respectively. In Fig. 2 we display the Löwdin projected valence density-of-states (DOS) and in Table I compare the s, p, and d contributions

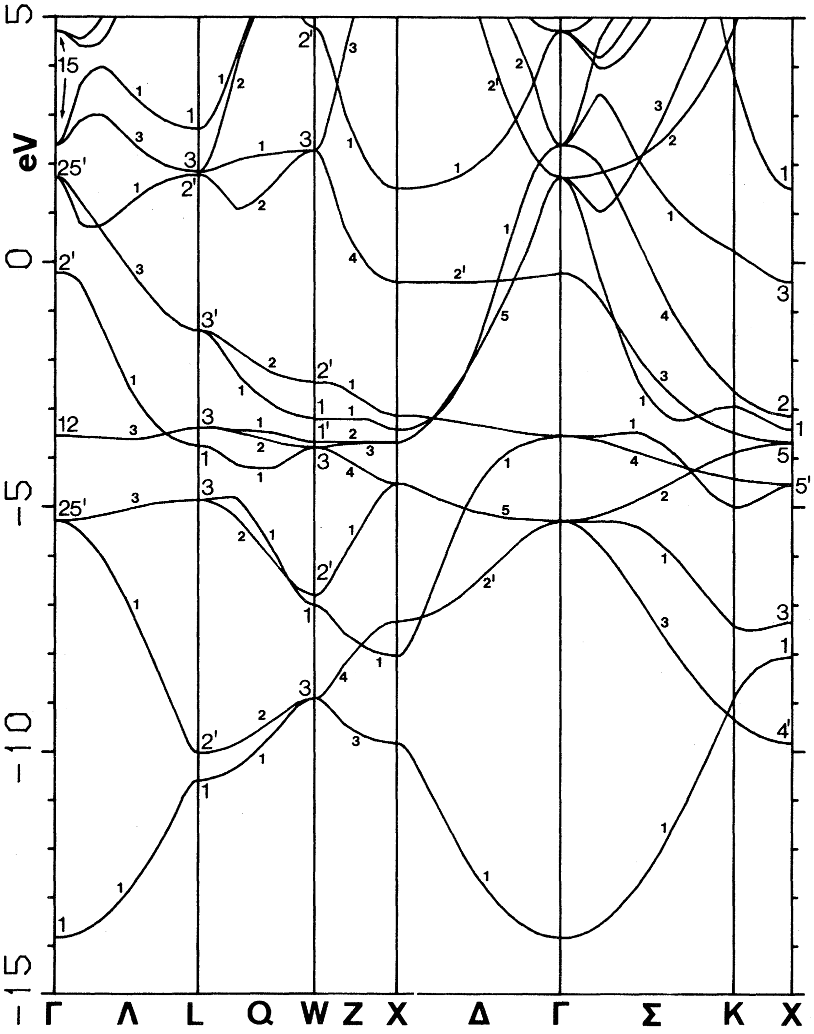

FIG. 1. Energy bands of $NiSi_2$ in eV from the Fermi energy.

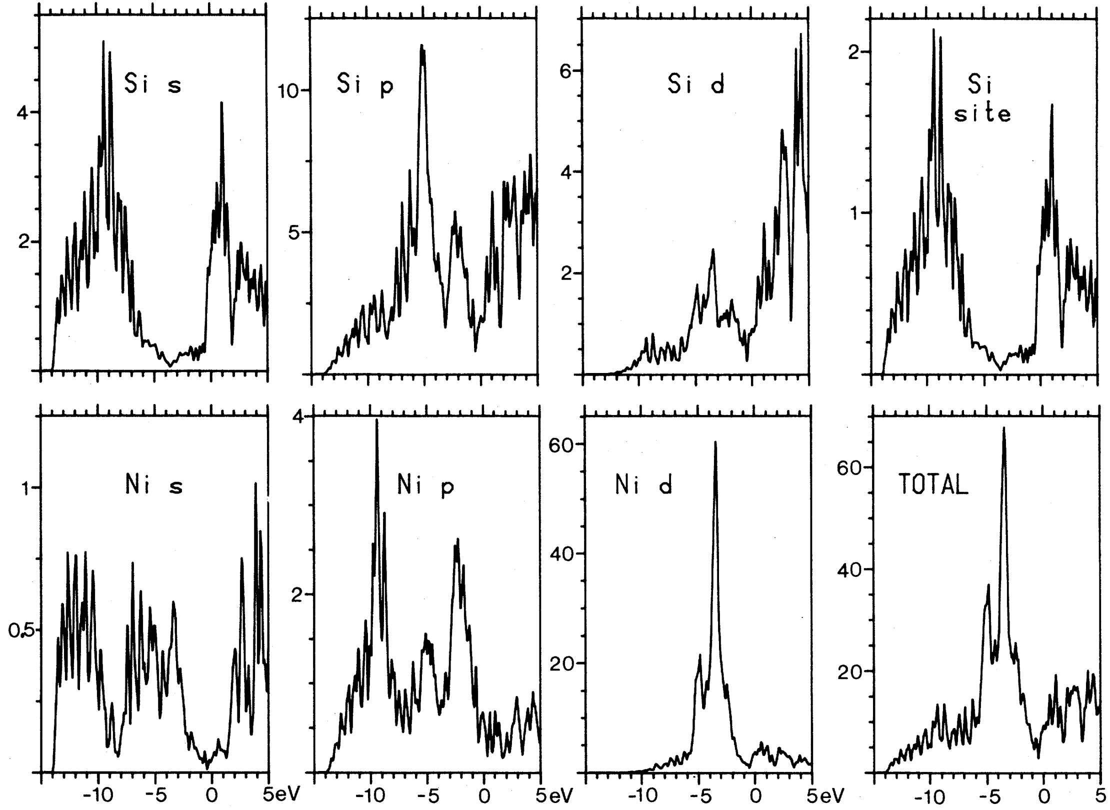

FIG. 2. Projected valence DOS in units of tenths of an electron per unit cell per eV. The panel labeled Si site is the valence DOS weighted with the square of the wave function at a Si nucleus in units of electrons per eV per cubic bohr.

to the charge on each ion with that of Ni_3Si. (The partial DOS are integrated up to E_F and divided by the number of Ni or Si atoms in the unit cell to obtain charge per atom.) The main peak of the Ni *d* DOS lies further below E_F in $NiSi_2$ than in Ni_3Si; however, because of the large hybridization, the Ni *d* electronic charge is only slightly larger in $NiSi_2$. The excess Ni ionicity in $NiSi_2$ arises mainly from the *p* component of the charge, and comes mainly from the bands running into the X'_4 and X'_5 levels. The larger ionicity in $NiSi_2$ is due to the fact that the Ni are completely surrounded by Si whereas in Ni_3Si the Ni have twice as many Ni nearest neighbors as Si nearest neighbors. The Madelung energy per unit cell for spherical nonoverlapping ions is $U=Mq^2/a_0$, where q is the smaller of the two ionic charges, a_0 is the cubic lattice constant, and $M=11.636\,56$ for fluorite[6] and 13.528 for the Cu_3Au structure. Substituting from Table I and dividing by the number of atoms per cell yields $U=1.20$ eV per atom for Ni_3Si and $U=3.24$ eV per atom for $NiSi_2$. Although these numbers are only meant to be suggestive, a comparison with the cohesive energy per atom listed in Table I indicates the relative importance of the ionic contribution to the binding in the two structures.

The graph labeled "Si site" in Fig. 2 represents a DOS with each energy level weighted with the square of the wave function evaluated at one of the Si nuclei. As in Ref. 2, this graph, which is unique, is very nearly proportional to the Si *s* DOS, thus demonstrating that the Löwdin projection scheme yields meaningful results. The value of the Si-site DOS at E_F is 0.783 electrons per eV per cubic bohr. According to the Korringa[7] relation this yields a ^{29}Si nuclear relaxation time of 1.1 s. The measured value[8] is 0.9 ± 0.2 s. This good agreement may be fortuitous since in Ni_3Si it required a shift of the Si-site DOS of 0.3 eV relative to E_F (or equivalently a shift of the Si *s* bands relative to the Ni *d* bands) to obtain agreement between the calculated and measured ^{29}Si nuclear relaxation times.

Figure 3 is a plot of constant valence-electron charge-density contours in the (110) plane of $NiSi_2$. The Ni atom at the lower left corner is in the center of a cube of Si atoms. Proceeding along the [001]

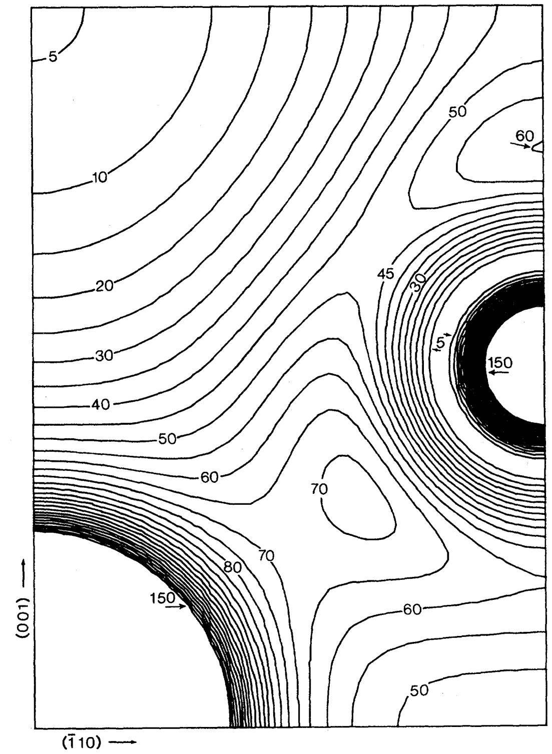

FIG. 3. Contours of constant valence charge density in steps of 5 millielectrons per cubic bohr in the (110) plane containing Ni and Si atoms.

direction to the upper left corner one arrives at the center of an empty cube of Si atoms. The lower right corner is the intersection of Ni—Ni and Si—Si bonds; so is the upper right corner but here the Ni—Ni bond is perpendicular to the plane of the figure. Note that the charge contours intersect the right-hand edge of the figure symmetrically about the Si atom, as they must because all Si—Si bonds are equivalent. Figure 4 is a plot of the valence-electron charge density along the Ni—Si bond. It appears very similar to the bond in Ni_3Si except that the minimum in the charge density near the center of the bond is 68.0 millielectrons per cubic bohr here and only 51.0 in the Ni_3Si bond. Thus we conclude that $NiSi_2$ is both more ionic and more covalent than Ni_3Si (in the same sense that GaAs is more ionic and more covalent than Al). It therefore is less metallic (i.e., jelliumlike) in its binding as is demonstrated by a comparison of the ratios of the minimum interstitial charge density to the minimum bond charge density in the two crystals: $29.4/51.0=0.576$ in Ni_3Si and $4.6/61.0=0.075$ in $NiSi_2$.

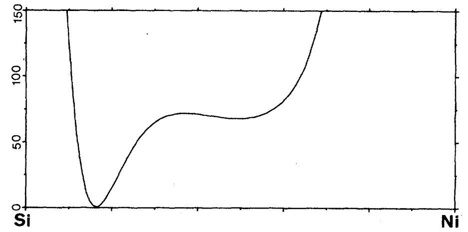

FIG. 4. Plot of the Si—Ni covalent bond charge density in millielectrons per cubic bohr.

The total energy per $NiSi_2$ unit cell, calculated as in Ref. 2, is 4161.878 Ry and subtracting the previously calculated[2] atomic energy of Ni and twice that of Si we obtain a cohesive energy of 1.152 Ry per unit cell or 5.23 eV per atom compared with 5.51 eV per atom in Ni_3Si. We previously argued[2] that a crude estimate of the zero-temperature heat of formation of Ni_mSi_n could be obtained by subtracting the cohesive energy per Ni_mSi_n unit cell from n times the experimental Si cohesive energy plus m times the calculated Ni cohesive energy. Using[9] 4.64 eV per atom for Si and[10] 5.617 eV per atom for Ni we obtained a heat of formation of -0.55 eV per unit cell for Ni_3Si. Making the same subtraction here we obtain -0.78 eV per unit cell for $NiSi_2$. The experimental room-temperature heats of formation are[11] -0.90 eV per Ni_3Si and[12] -0.88 eV per $NiSi_2$. One might expect differences of the order of a few tenths of an eV between the Ni cohesive energy calculated by Moruzzi, Janak, and Williams[10] and that which would be obtained using our technique. Note that a reduction of only 0.11 eV in the Ni cohesive energy makes the calculated heats of formation of both crystals agree with experiment. The important point is not to see how well we can get our errors to cancel and thus obtain agreement with experiment but rather to see how two different nickel silicides which bond in vastly different ways can end up having essentially identical heats of formation.

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We used the $NiSi_2$ lattice constant given by R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1973), Vol. 1, p. 242. A value 0.011 Å larger is given in Ref. 11.

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[3] Our interpolation scheme requires a bcc mesh of points in $\vec{k}$ space, which happens to be the reciprocal space to our fcc lattice. Thus even though our generating vector is larger (in units of a_0) than the one we used for Ni$_3$Si, we have more mesh points within this BZ than we had in the simple cubic BZ of Ni$_3$Si.

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[5] The fact that the two $\Gamma_{25'}$ states sum to more than 100% Ni d indicates a small admixture of $4d$ with the $3d$.

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