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LETTER TO THE EDITOR

Component local densities of states for ordered TiNi

D A Papaconstantopoulos†, J W McCaffrey and D J Nagel

Naval Research Laboratory, Washington, DC 20390, USA

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Abstract. Densities of states for the ordered intermetallic compound TiNi, decomposed by site and symmetry, have been computed using the APW method. Of the fourteen valence electrons per unit cell, 7.2 were found to be in d like states localized on the Ni site. These results are useful for interpretation of the shapes and intensities of valence band x ray spectra.

The spatial or site distribution of the density of states (DOS) in solids, sometimes called the local density of states, has lately received increased attention. This interest comes from two sources: First, the problem of determining the spatial distribution of bonding charge is an important part of developing theories for disordered alloys (Schwartz *et al* 1971, Stocks *et al* 1971, Stern 1966). Secondly, interpretation of several kinds of experiments requires knowledge of the spatial arrangement of electrons with a particular symmetry character. For example, Knight shifts in nuclear magnetic resonance (Bennett *et al* 1971) and isomer shifts in Mössbauer spectroscopy (Shirley 1964) are related to the density of s like electrons at the nucleus. For calculating x ray band spectra, local DOS of particular symmetries are required in order to satisfy the angular selection rules (Nagel 1970). Conventional band theory (Conklin *et al* 1972) and multiple scattering theory (Babonev and Sokolov 1972, Gyorfyy and Stott 1973) are being used to calculate local DOS and x ray spectra from ordered compounds and disordered alloys, respectively.

In this letter we present the DOS for ordered TiNi, decomposed by site (Ti, Ni) and wavefunction symmetry (s, p, d like) calculated by the augmented plane wave (APW) method (Slater 1937, Mattheiss *et al* 1968). These results, while only an intermediate step in the full x ray spectrum calculation, are themselves a useful example of local DOS for both sites as obtained from conventional band calculations. The only other work of this nature for an intermetallic alloy is the calculation of the density of s and d like states at one site (Al) in AuAl₂ (Switendick 1971). TiNi was chosen for the present work because its unusual mechanical memory has led to considerable study of its properties (Wang *et al* 1968). Although TiNi usually exhibits a complex crystal structure, with proper heat treatment it can closely approach a pure CsCl arrangement (Wang *et al* 1972). Thus, a CsCl structure for TiNi was assumed for the purpose of the present calculation, since such a structure can be handled by the APW method in a straightforward manner. Figure 1 shows the arrangement of atoms and APW spheres.

The nonselfconsistent APW calculation was done using a potential computed from a superposition of Hartree-Fock-Slater charge densities (Herman and Skillman 1963)

†Permanent address: George Mason University, Fairfax, Virginia 22030, USA.

with the $4s^2$ configuration. Exchange was treated in the ' $\rho^{1/3}$ ' approximation (Slater 1951). An exchange coefficient of $\frac{5}{8}$ was used with this configuration since earlier calculations (Papaconstantopoulos and Nagel 1971) indicated that this choice would produce quantitative agreement with the peak separation in the NiM emission spectrum (Cuthill *et al* 1968). The APW sphere radii were determined by requiring the potentials to be equal at the contact points of the spheres (figure 1).

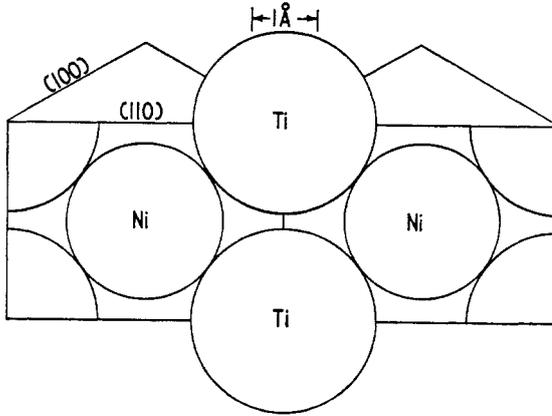


Figure 1. Ti APW sphere (radius = 1.38 Å) and Ni APW sphere (radius = 1.23 Å) arranged in a CsCl structure in TiNi (lattice constant = 3.015 Å). The constant potential in the plane wave region between spheres was -1.33 Ryd.

The electronic charges within each sphere for each angular momentum component are (Mattheiss *et al* 1968):

$$Q_l = \frac{\Omega}{N} \sum_I \sum_J v^*(\mathbf{k}_I) v(\mathbf{k}_J) C_{IJl} \int_0^{R_s} \left(\frac{r u_l(r, E)}{R_s u_l(R_s, E)} \right)^2 dr$$

where Ω is the volume of the unit cell, N a normalization constant, C_{IJl} the probability of finding an electron within the APW sphere, $v(\mathbf{k}_I)$ the eigenvectors of the APW secular equation, u_l the radial wavefunction and R_s the radius of the APW sphere. The eigenvalues $\epsilon(k)$ together with the charges Q_l were determined at 64 points in the simple cubic Brillouin zone. Both $\epsilon(k)$ and Q_l vary smoothly in k space and were interpolated by Monte Carlo sampling of 96 000 points in the zone to obtain the total and component local densities of states.

Figure 2 shows the total DOS (both sites plus interstitial plane wave component), the total local (summed over l), and the component DOS for each site. Each of these DOS distributions will be discussed in turn in the rest of this letter.

The total DOS consists of sharp d electron structure on a smoother background made up of mixed s, p and d states, similar to elemental transition metals. However, instead of a single major peak of d like states, the alloy exhibits two large clusters of d states.

The local DOS for the Ni site in TiNi between -1.5 and -4.5 eV is somewhat similar in shape to the total density of states of Ni (Connolly 1967). However, this part of the Ni sphere DOS curve is narrower in TiNi because the Ni atoms are more widely separated in the CsCl structure of TiNi (see figure 1) than in the elemental Ni. Unlike the DOS of pure Ni, the local DOS in Ni in TiNi is split and has a high energy component with two prominent peaks.

The most pronounced structure in the local DOS for the Ti site is clearly associated with

major peaks in the Ni curve. The states predominantly localized on Ni atoms, which have the deeper potential, extend to the Ti sites, producing structure in the local DOS for Ti. Such sharing has been postulated previously for Al-Ag alloys (Marshall *et al* 1969). Similar sharing of bonding electrons between atoms, treated by molecular orbital theory is important in ordinary inorganic compounds and leads to the appearance of x ray bands which would be absent if it were not for the overlap (Urch 1970, Fischer 1973).

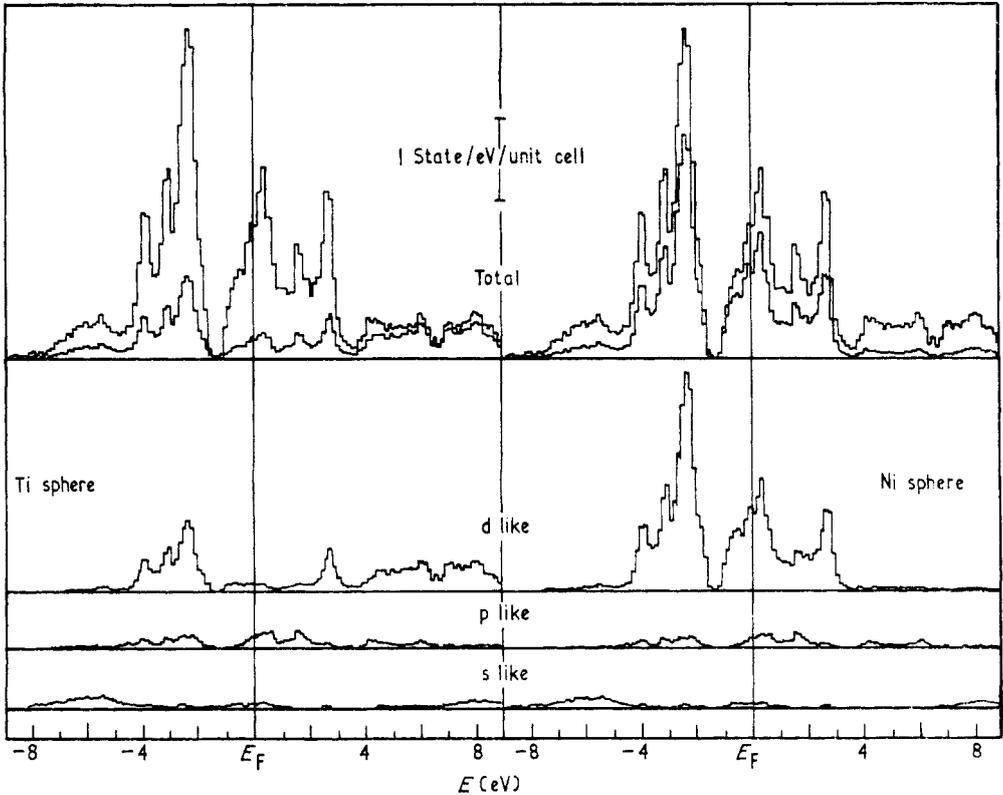


Figure 2. Density of states histograms for TiNi. The total DOS (Ti plus Ni spheres, plus plane wave region) is given by the heavy lines at the top of both halves of the figure for comparison with the total local DOS (sum of s, p, and d like components) shown underneath by light lines for the Ti (left) and Ni (right) APW spheres. Component distributions are given at the bottom for both sites.

Total local DOS curves shown by the light lines at the top of figure 2 were obtained for an ordered alloy in this APW calculation. Local state densities can be computed for disordered alloys by the use of scattering theories, such as the coherent potential approximation (CPA) or averaged T matrix approximation (ATA) (Schwartz *et al* 1971, Stocks *et al* 1970). This raises the possibility of comparing local state densities calculated for an ordered alloy from band theory with the local DOS for disordered alloys of similar composition as obtained from the CPA or ATA approaches. However, no such comparisons can be made now because the two classes of calculations have yet to be applied to the same alloy system.

Turning now to the component (s, p, d) state densities shown in figure 2 and the charges listed in table 1, it is clear that the d like states dominate the other symmetries for both atoms. The filled d like states are mainly localized on the Ni atoms. The empty d like states have a relatively high value within the Ti spheres above about 3 eV. The p like DOS are very similar in shape for both sites, with that for the Ti site being consistently 22% greater than for the Ni site. Thus, in contrast to the strong localization of d like electrons on Ni sites, there is a weak localization of p like states on the Ti sites. This occurs even though structure in the histograms for the filled p like states is generally related to structure in the d like histograms. The s like state densities are essentially identical. States with s like character tend to be excluded from the energy range of the lower (filled) d bands but do overlap the unfilled d states.

Table 1. Charges for s, p and d components

	Ti site			Ni site			Plane wave
Component	s	p	d	s	p	d	
Charge	0.56	0.76	2.30	0.52	0.62	7.16	2.08

The DOS curves in figure 2 can be used to partially interpret the shapes of x ray valence band spectra. Because the radial matrix element introduces little structure into computed band spectra, structure in TiNi x ray spectra should follow that in the appropriate DOS curves in figure 2 (p like for K spectra, s and d like for L and M spectra). Fine structure in the DOS curves will not occur in the spectra because of lifetime and spectrometer broadening. Preliminary calculations of TiNi x ray emission spectra including matrix elements and broadening effects, show good agreement with experiment for the NiK spectrum but exhibit a peak separation in the NiM_{2,3} spectrum which is smaller than that measured (Papaconstantopoulos *et al* 1972).

The charge localization values in the table provide information concerning the ratio of integrated intensities for valence band x ray spectra. For example, below E_F , $Ni(s + d)/Ti(s + d) = 2.7$. Hence, aside from differences in radial matrix elements and effects such as self absorption (Birks 1969), the integrated intensity ratio for the Ni and TiL_{2,3} (4s + 3d → 2p) valence band x ray spectra should be different from the weight fraction ratio. It is this sensitivity of valence band spectra to the local charge distribution which complicated spectrochemical analysis using these spectra (Nagel 1970), but makes possible the use of such spectra to study charge redistribution upon alloying (Wenger *et al* 1971).

The present results are given to demonstrate the type of information on alloys which can be obtained from conventional band calculations for both components, and which can be compared with results of scattering theories of alloying. A more rigorous discussion of component densities of states and charge distributions in alloys will require self-consistent band calculations. Such a calculation is in progress for TiFe (Papaconstantopoulos 1973).

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