



ELECTRONIC STRUCTURE OF THE INTERMETALLIC COMPOUND TiNi

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We present the results of self-consistent band structure calculations for the intermetallic compound TiNi in the CsCl structure. The calculated Fermi surface shows nesting features that appear to be consistent with the suggestion of an incommensurate charge density wave.

I Introduction

The intermetallic compound TiNi is one of a number of β -phase alloys which undergo a reversible martensitic transformation upon cooling.^{1,2} Early work of Wang et al.³ and of Mitchell et al.⁴ suggested that this transformation, which is at about 300 K, is from the B2 or cubic CsCl structure to a B19 structure accompanied by a substantial shift of the s-band relative to the d-band.

Recently Shabalovskaja et al.⁵ from measurements of optical and x-ray photoelectron spectra and from their magnetic susceptibility data, argued that the martensitic transformation is accompanied by a Fermi surface change. Finally, Salamon et al.⁶ have studied the premartensitic phases of TiNi(Fe) by neutron diffraction, specific heat measurements, and electron microscopy. They conclude that the premartensitic transformation proceeds in two distinct stages. The first is a second order transformation from the B2 higher temperature form to an intermediate structure having incommensurate superlattices, while the second is a first-order transformation to a rhombohedrally distorted cubic form having commensurate superlattices. Further, Kelly and Stobbs⁷ constructed a Landau theory of martensitic phase transformations that accounts for precursor phenomena and low temperature structures observed in β -phase alloys.

In view of this renewed interest in the electronic structure of TiNi, we are presenting here a self-consistent augmented plane wave (APW) calculation of the band structure of this material that supercedes our earlier reports.^{8,9}

II Computational Procedure

These calculations were performed in the usual muffin-tin approximation using a symmetrized non-relativistic APW program adapted for the CsCl structure. The exchange potentials were constructed using the $X\alpha$ method.¹⁰ The APW sphere radii were determined by the condition of matching potentials at the point of contact of the Ti and Ni spheres. This prescription for determining the radii was applied in each cycle of our self-consistent calculation and the final radii were $R_{Ti} = 2.664$ a.u. and $R_{Ni} = 2.271$ a.u., corresponding to a lattice constant of 5.698 a.u. This calculation was carried out to self-consistency after five iterations with an eigenvalue convergence criterion of 3mRy. In each iteration the core levels 1s, 2s, and 2p were calculated atomic-like using the corresponding crystal potentials for Ti and Ni and a suitably modified version of the Herman-Skillman computer code.¹¹ The "soft-core" levels 3s and 3p together with the conduction bands were calculated, for each iteration, on a mesh of 10 k-points in the irreducible Brillouin zone by the APW method.

Our final self-consistent potentials were used to calculate the energy eigenvalues $E_n(\vec{k})$ and the electronic charges inside the muffin-tin spheres $Q_{n,\ell}(\vec{k})$ (needed for the site and angular momentum decomposition of the density of states). $E_n(\vec{k})$ and $Q_{n,\ell}(\vec{k})$ were calculated on a mesh of 35 k points in the irreducible zone or, equivalently, 512 k points in the full zone. We then used the interpolation method recently proposed by Boyer¹² to generate $E_n(\vec{k})$ and $Q_{n,\ell}(\vec{k})$ on

a mesh of 969 k points in the irreducible zone. These results were finally used in the tetrahedron method¹³ to obtain the total density of states (DOS) and its muffin-tin components for each site and for each angular momentum ℓ .

III Energy Bands and Densities of States

Our energy bands and DOS are shown in Fig. 1. Careful inspection of both the energy bands and the DOS panels reveals that the bottom of the first band starting at Γ_1 has about equal amounts of

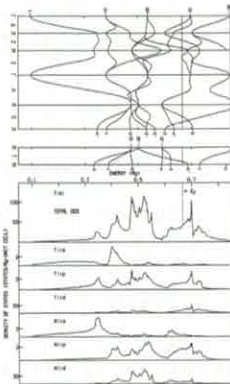


Fig. 1 Energy bands and densities of states for TiNi.

s-Ti and s-Ni character and mixes with Ti p-like states at the top (X_4'). At the lower Γ_{12} and Γ_{25}' points we find the d-like states associated mainly with the Ni atom. The higher Γ_{12} and Γ_{25}' , which reflect the antibonding states are strongly characterized by the Ti atom contribution. Comparing our DOS graphs with those of TiFe which were published previously¹⁴ we find strong similarities; with the qualitative difference being the position of the Fermi level E_F . For TiFe E_F falls at the minimum of the DOS separating the bonding from the antibonding states. However, here for TiNi, E_F has moved up into the middle of the antibonding states. A comparison of the energy bands of TiFe and TiNi shows two changes of the ordering of levels at X (X_2 and X_2' , X_5 and X_4'). These interchanges of the levels at X and the different position of E_F result in different Fermi surface profiles as discussed in Section IV.

Having calculated the DOS at E_F for TiNi we can compare with the DOS deduced from specific heat and susceptibility experiments. Specific heat measurements¹⁵ give a value for the bare DOS equal to 1.08 states/eV-atom. On the other hand, susceptibility measurements⁴ give a value of 1.73 states/eV-atom. Our calculated value is 1.62 states/eV-atom. However, a serious comparison between theory and experiment cannot be made because the calculations were performed in the cubic phase while the measurements were done in the low temperature martensitic phase.

IV Fermi Surface

The shape of the Fermi surface (FS) is shown in Fig. 2 as the intersections of the surface with the principal planes of the Brillouin zone (BZ). This figure is to be imagined as folded along the

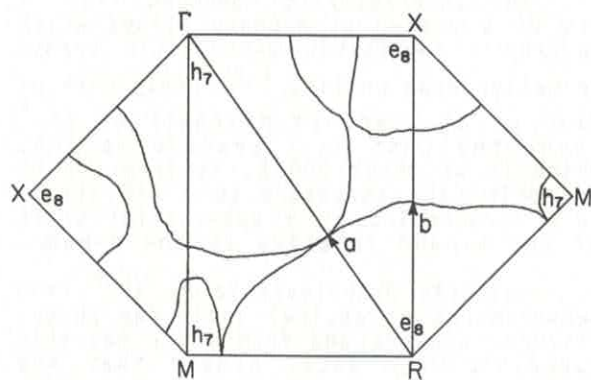


Fig. 2 Fermi surface cross-sections for TiNi. The arrows at a and b indicate the nesting vectors.

lines shown to form a tetrahedron; 48 such tetrahedra would fill the cubic BZ. Figure 2 resulted from a grid of 969 k-points in the $1/48^{\text{th}}$ of the BZ. The energy eigenvalues were found from our APW results by the interpolation procedure of Boyer¹² as it was done for the DOS.

From Fig. 2 we see that the largest surface is the electron surface derived from the 8th band at the BZ cube corners R. This surface, which approximates an octahedron, has a volume 0.19 the total BZ volume. Corners and faces are rounded and the flat faces bow slightly outward towards their degenerate contact with the central hole surface along Γ -R. Perpendicular to $\langle 111 \rangle$ directions in an

extended zone, the nearly flat octahedron faces form a pattern of parallel planes. Similarly, perpendicular to $\langle 110 \rangle$ directions, the octahedron edges form a pattern of broad parallel ridges running in $\langle 110 \rangle$ directions. From Fig. 2, the distance R-a, 0.38 of R- Γ , is one-half the vector spanning opposite parallel faces. Similarly, the distance R-b, 0.48 of R-X, is one-half the vector spanning opposite parallel ridges of the octahedra.

In NbC and TaC, parallel Fermi surface areas (nesting) have been related to anomalous features of the phonon dispersion curves.^{16,17} In TiNi, neutron diffraction⁶ and ultrasonic attenuation experiments¹⁸ also show anomalies in longitudinal waves in a $\langle 111 \rangle$ direction and in transverse wave in a $\langle 110 \rangle$ direction with particle motion perpendicular in a $\langle 110 \rangle$ direction. Furthermore, in the intermediate transformation stage incommensurate superlattices appear in $\langle 111 \rangle$ and $\langle 110 \rangle$ directions, longitudinally and transversely polarized respectively. This behavior correlates very well qualitatively with the features of our calculated FS. Nearly parallel surfaces hold the possibility of a charge density wave and this interaction has been proposed by Salamon et al.⁶ as the driving force of the martensitic transformation in TiNi. Recently Bruinsma¹⁹ used our band structure results to calculate the phonon dispersion curves in TiNi. His results indicate the importance of the electron-phonon matrix elements and that nesting alone is not sufficient to provide a quantitative understanding of the experimental situation.

The central hole surface at Γ , originating from the 7th band, is nearly as large as the surface at R, having a volume 0.17 that of the BZ. It is of convoluted shape, depressed in $\langle 100 \rangle$ directions and extended in $\langle 111 \rangle$ directions where it makes contact with the electron surfaces at R, while in $\langle 110 \rangle$ directions it is, according to our model, barely pinched off from small hole sur-

faces at M. There are three such surfaces at M, each with approximately 0.003 of the BZ volume. The electron surface at X, derived from the 8th band, is round like a pillbox with smoothed edges and dished-in top and bottom surfaces. There are three such surfaces each with 0.038 of the BZ volume.

Within the accuracy of the calculation, the energy band along Γ -M could be entirely above the Fermi level. This would fuse the surfaces at M and Γ permitting open orbits for holes. While this detail would influence the high field magnetoresistance, it probably is unrelated to the martensitic transformation. On the other hand, the existence of octahedra at R is a persistent feature of a range of Ti(Ni, Co, Fe) alloys. In TiFe, for example, these octahedra become vestigial since the 12' band at R lies at the Fermi energy within the accuracy of the calculations. Extrapolation from experiments on other alloys²⁰ suggest a martensitic transformation for TiFe might begin at 2 K. However, no evidence for it is seen in the FS as observed through the de Haas-van Alphen effect at 1.4 K.¹⁴

V Conclusions

In view of our band structure calculations, the explanation of the electronic properties changes during the martensitic transformation given by Mitchell, et al.⁴, namely, a proposed shift of the s-band of about 10 eV due to a temperature dependent potential, seems unlikely and probably an order of magnitude wrong. The same conclusion was reached by Lee and Withers²¹, who searched for such a change in the intermediate transformation stage using SXAPS. The explanation based on a charge density wave⁶ is consistent with our calculated FS and is certainly more plausible.

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References

1. "Proceedings of the International Conference on Martensitic Transformations, ICOMAT 1979", Cambridge, MA, 24-29 June 1979.
2. H. Warlimont and L. Delaey, Prog. in Mat. Sci., 18, 1 (1974).
3. F.E. Wang, B.F. DeSavage, W.J. Buehler, and W.R. Höslner, J. Appl. Phys. 39, 2166 (1968).
4. M.A. Mitchell, F.E. Wang, and J.R. Cullen, J. of Appl. Phys. 45, N8, 3337 (1974).

5. S.A. Shabalovskaja, A.I. Lotkov, and I.I. Sasovskaja, Solid State Commun. 32, 735 (1979).
6. M.B. Salamon, M.E. Meichle, C.M. Wayman, C.M. Hwang, and S.M. Shapiro, AIP Conf. Proc. 53, 223 (1979); Michael E. Meichle, Thesis, Department of Physics, University of Illinois, 1981; S.K. Satija, S.M. Shapiro, and M.B. Salamon, Bull. Am. Phys. Soc., 26, 381 (1981); M.E. Meichle, M.B. Salamon, and C.M. Wayman, *ibid.*
7. M.J. Kelly and W.M. Stobbs, Phys. Rev. Lett. 45, 922 (1980).
8. D.A. Papaconstantopoulos and D.J. Nagel, International J. of Quantum Chem. S5, 515 (1971).
9. D.A. Papaconstantopoulos, J.W. McCaffrey, and D.J. Nagel, J. of Physics F3, L26 (1973).
10. K. Schwarz, Phys. Rev. B5, 2466 (1972).
11. F. Herman and S. Skillman "Atomic Structure Calculations", Prentice Hall (1963).
12. L.L. Boyer, Phys. Rev. B19, 2824 (1979).
13. G. Lehmann and M. Taut, Physica Status Solidi (b)54, 469 (1972).
14. D.A. Papaconstantopoulos, Phys. Rev. B11, 4801 (1975); G.N. Kamm, Phys. Rev. B12, 3013 (1975).
15. D. Abbe, R. Caudron, and P. Costa, p 469, *ibid* Reference 1.
16. B.M. Klein, L.L. Boyer, and D.A. Papaconstantopoulos, Solid State Commun. 20, 937 (1976).
17. W. Weber, Institute of Physics Conference Series No. 55, 495 (1980).
18. O. Mercier, K.N. Melton, G. Gremaud, and J. Hägi, J. Appl. Phys. 51, 1833 (1980).
19. R. Bruinsma, to be published.
20. F. Wang, J. of Appl. Phys. 38, 822 (1967).
21. R.N. Lee and R. Withers, J. of Appl. Phys. 49, 5488 (1978).