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Electronic structure of $MnSi_{0.7}Al_{1.3}$ and related transition metal alloys with the $TiSi_2$ structure

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Abstract

The densities of states of some ternary alloys ($NbSi_{1.4}Al_{0.6}$, $MoAl_{1.3}Si_{0.7}$, $MoGa_{1.4}Ge_{0.6}$, $MnAl_{1.3}Si_{0.7}$) with the $TiSi_2$ structure have been obtained with the tight binding-linear muffin tin orbital (TB-LMTO)-average *T* matrix approximation (ATA) method and have been found to be similar to those of the chimney-ladder structures, previously computed with the same method. This is in agreement with the similar behaviour of their valence electron concentration. $MnAl_{1.3}Si_{0.7}$ has been found found to be magnetic and a more elaborate KKR-CPA calculation predicts a magnetic moment of 0, 4 μ_B for Mn in this alloy.

Keywords: Manganese aluminium silicon compounds; Band structure calculations; Magnetic properties

1. Introduction

Jeitschko and Parthé have shown in 1967 [1] that some transition metal alloys with the $TiSi_2$ structure ($NbSi_{1.4}Al_{0.6}$, $MoAl_{1.3}Si_{0.7}$, $MoGa_{1.4}Ge_{0.6}$, $MnAl_{1.3}Si_{0.7}$) shared the basic property of the much more complicated 'chimney-ladder' compounds. The chimney ladder have a large unit cell which can be regarded as a piling up along the *c*-axis of a large number of $TiSi_2$-like subcells where the silicon atom sites vary slightly from one subcell to the next. But for both the alloys and the chimney ladder compounds, the VEC (valence electron concentration per transition metal atom) follows roughly the same curve as a function of the column number of the transition element.

For the $TiSi_2$ alloys we have performed tight binding-linear muffin tin orbital (TB-LMTO) band structure calculations similar to those previously performed for the 'chimney-ladder' structures [2,3]. These calculations indeed show striking similarities between the density of states for the alloys and the chimney-ladder compounds with a transition element in column five to seven, giving indications of a similar origin for their stability. In the case of $MnAl_{1.3}Si_{0.7}$, where a high density of states is found at the Fermi level, a fully selfconsistent spin polarised Korringa Kohn Rostoker-coherent potential approximation (KKR-CPA) has been performed, which confirms the results of the TB-LMTO calculation and predicts a magnetic moment of 0.4 μ_B per Mn atom.

2. Computational methods and results

The calculations have been performed using the TB-LMTO parameters tabulated by Andersen [4,5] and the recursion procedure in real space [6] to obtain the densities of states in a continuous fraction form. The atomic sphere radius have been chosen so as to obtain a local neutrality in each sphere. This rather simple method gives reasonable results for $TiSi_2$, $RuAl_2$ and Ru_2Si_3 where a comparison with other calculations [7,8,11] is possible. There are no adjustable parameters. To treat the disorder on the non transition element sites, we have used an a weighted mean of the TB-LMTO potential elements for the two atoms. The partial Green functions for Si and Al were then obtained by replacing the first level of the continuous fraction for the mean atom by that of the real ones. This corresponds to the average *T* matrix approximation (ATA), which should be satisfactory here due to the similarity of Al and Si.

The alloys band structures are found to interpolate between the band structure of $TiSi_2$ and that of $RuAl_2$, $NbSi_{1.4}Al_{0.6}$ (VEC=12.33) beeing close to $TiSi_2$ (VEC=12) and $MnAl_{1.3}Si_{0.7}$ (VEC=13.67) close to $RuAl_2$

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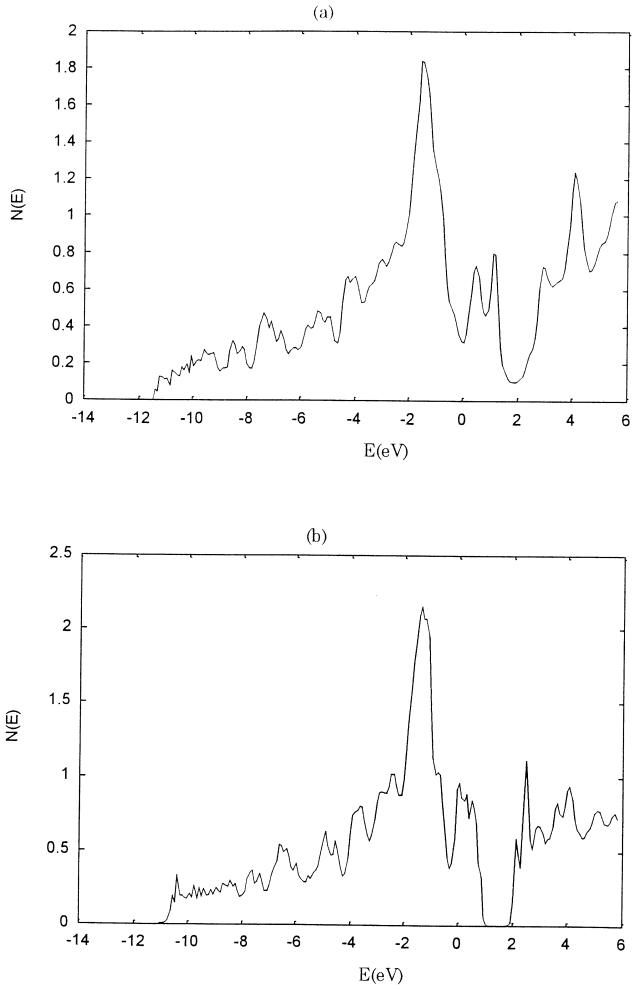

Fig. 1. Total density of states for (a) $NbSi_{1.4}Al_{0.6}$ and (b) $MoAl_{1.3}Si_{0.7}$ ($E_F=0$).

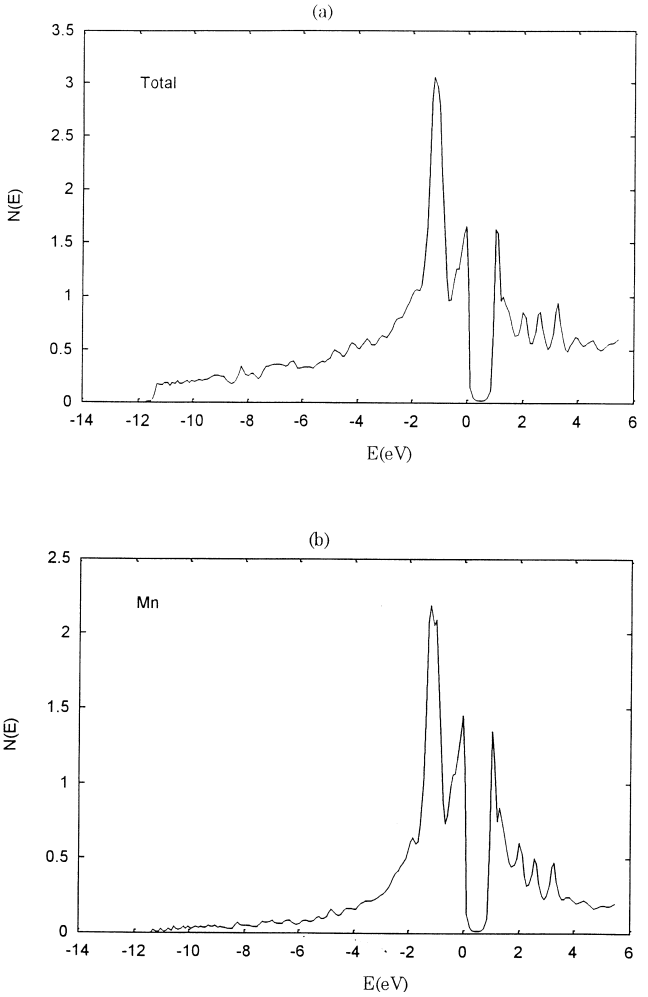

Fig. 2. Total density of states for $MnAl_{1.3}Si_{0.7}$ (a) and partial density of states for Mn (b).

(VEC=14). Fig. 1a shows the total density of states for $NbSi_{1.4}Al_{0.6}$. The density of states is similar to that of $TiSi_2$. The low energy part is dominated by the s states of the non-transition elements. Between −4.5 eV and the Fermi level at 0 eV, there is a strong hybridisation between the d orbitals of Nb and the sp orbitals of Si and Al. The Fermi level is found in a minimum of density of states which separate this strong hybridisation region from weakly bonding states dominated by the d orbitals of Nb, which extend between 0 and 2 eV. There is a second minimum at 2 eV (VEC=14) which also exists in $TiSi_2$ but is deeper for the alloy. Fig. 1b shows the total density of states for $MoAl_{1.3}Si_{0.7}$ (VEC=12.66). This density of states is similar to the previous one, but the higher Fermi level is in the weakly bonding region. The minimum at a VEC=14 has evolved into a gap. Fig. 2a shows the total density of states for $MnAl_{1.3}Si_{0.7}$ (VEC=13.67). This density is closer to the density of $RuAl_2$ than to the density of $TiSi_2$. The width of the d partial density of states (Fig. 2b) is smaller than in the previous cases, since the d element belong to the 3d series. Fig. 3a and b show the partial density of states for Si and Al. Together with Fig. 2b these curves clearly show the sp(Al,Si)–d(Mn) hybridisation in the −4 eV to −0.5 eV region, and the weakly bonding states between −0.5 eV and +0.3 eV. The Fermi level is again in this region, close to the top of the valence band and corresponds to a high density of states. At low energy, the density of states is dominated by the s orbitals of Al and Si (the lower energy Si s orbitals contributing more than the Al s orbitals).

Since the structure of the alloys is much simpler than that of the 'chimney-ladder' themselves, we have been able to perform a more elaborate calculation for the interesting case of $MnAl_{1.3}Si_{0.7}$ where, as stated above, the density of states at the Fermi level is found to be rather high. (The Stoner criterion is satisfied using a Stoner constant of 0.9 eV for Mn). We then performed a fully selfconsistent spin polarised KKR-CPA method [9,10]. This calculation uses a k space procedure to obtain the densities of states and leads to more precise value for $N(E_F)$ than the real space method that we used in connection with the TB-LMTO calculations. The total density of states obtained with this

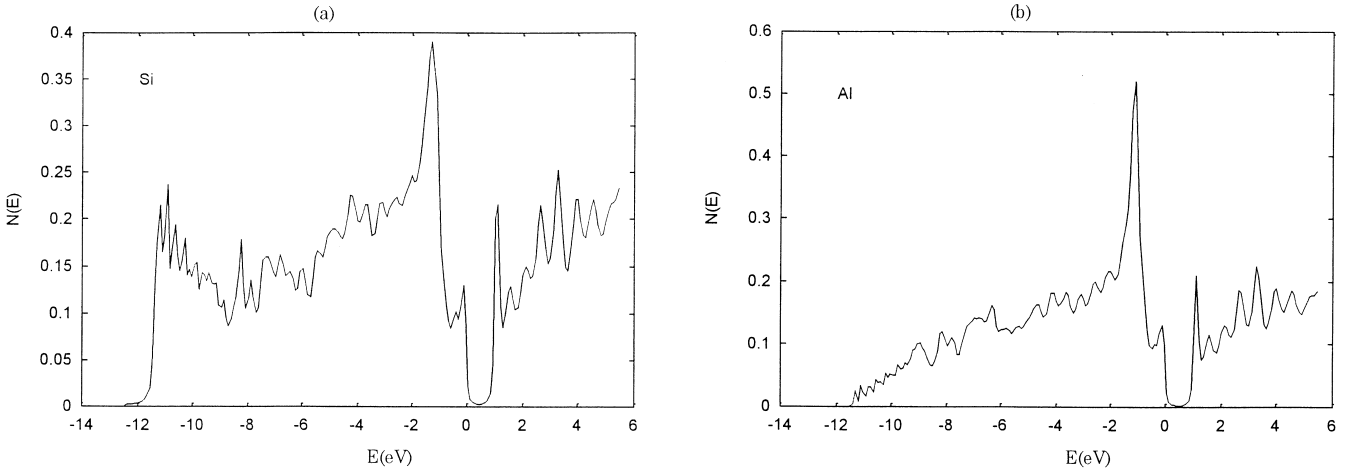

Fig. 3. Partial density of states (a) for Si and (b) for Al in $MnAl_{1.3}Si_{0.7}$.

KKR-CPA method (Fig. 4) confirms the gross features of the TB-LMTO results, in particular the weak bonding states at the top of the valence band. It also predicts a magnetic moment of 0.4 μ_B per Mn atom. An experimental investigation of this alloy is in progress. In preliminary measurements no magnetic transition was found (the sample was paramagnetic), but this sample included several grains with compositions differing slightly from $MnAl_{1.3}Si_{0.7}$. Since the Fermi level is in a region where the density of state varies strongly, this is not conclusive.

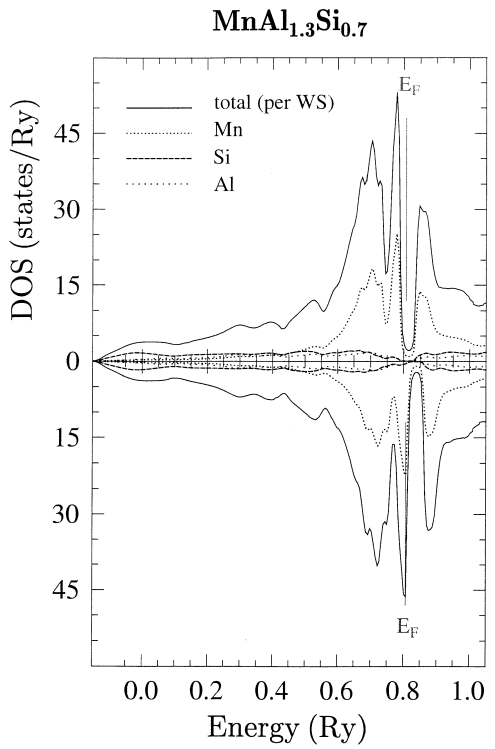

Fig. 4. Spin polarised KKR-CPA densities of states for $MnAl_{1.3}Si_{0.7}$. The total density of states is for the Wigner–Seitz cell (WS) and includes the contribution of the interstitial region between the muffin-tin spheres.

3. Conclusions

The alloys all show a gap (or a deep minimum in the case of $NbSi_{1.4}Al_{0.6}$) at an energy corresponding to a VEC

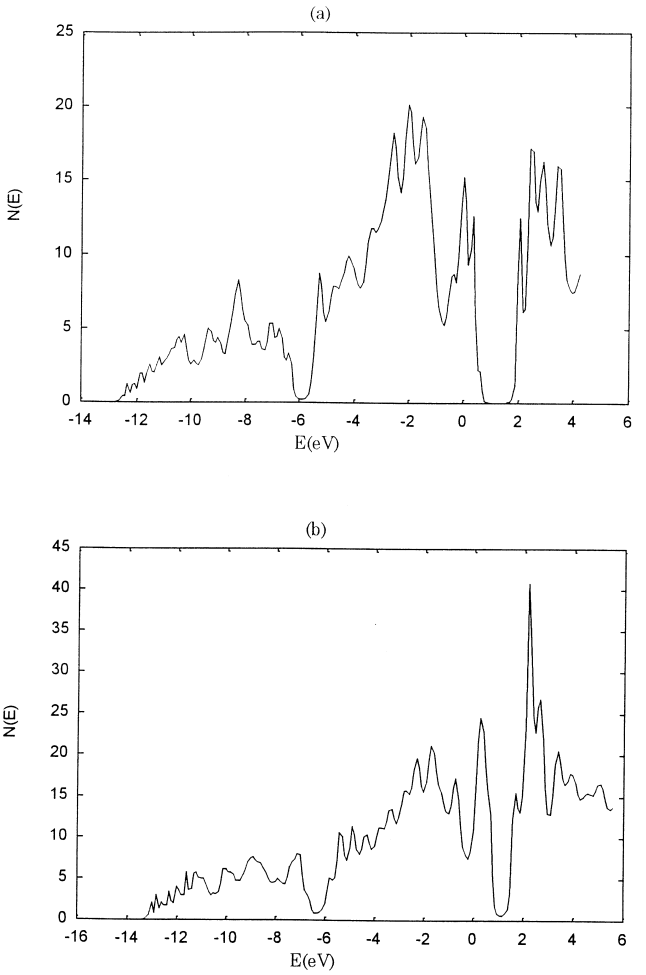

Fig. 5. Total density of states for the chimney ladder compounds (a) $Mo_{13}Ge_{23}$ (b) $V_{17}Ge_{31}$.

of 14. In the energy range between a VEC of ~12.3 and a VEC of 14 there are weakly bonding states, mostly derived from the transition metal d states. For all the alloys, the Fermi level is located in these weakly bonding states. This is very similar to what has been found [2,3] for the 'chimney-ladder' compounds with a transition element in column five to seven of the periodic table (VEC $\leq$ 14). Fig. 5 shows for comparison the density of states obtained with the same TB-LMTO method for the chimney-ladder $Mo_{13}Ge_{23}$ (VEC = 13.08) and $V_{17}Ge_{31}$ (VEC = 12.29). This confirms that the stability of both series is due to the filling of the bonding states associated with the sp–d gap (or deep minimum) at the VEC of 14. The partial unfilling of the weakly bonding states just below the gap does not suppress the stability of both series.

Further experimental work, on better samples is needed to see whether or not $MnAl_{1.3}Si_{0.7}$ is magnetic, as predicted by both calculations.

References

[1] W. Jeitschko, E. Parthé, Acta Cryst. 22 (1967) 417.
[2] H. Kenzari, Thése INPL Nancy (1998) and to be published.
[3] P. Pécheur, G. Toussaint, H. Kenzari, B. Malaman, R. Welter, J. Alloys Comp. 262–263 (1997) 363–365.
[4] O.K. Andersen, O. Jepsen, D. Glötzel, in: F. Bassani, F. Fumi, M.P. Tosi (Eds.), Highlights of Condensed Matter Theory, North Holland, New York, 1985, p. 59.
[5] A. Kümm, Ph.D. Thesis, Stuttgart, Germany, 1992.
[6] R. Haydock, in: H. Ehrenreich, F. Seitz, D. Turnbull (Eds.), Solid State Physics, Vol. 35, Academic Press, New York, 1980, p. 216.
[7] D. Nguyen Manh, G. Trambly de Laissardiere, J.P. Jullien, D. Mayou, F. Cyrot-Lackmann, Solid State Commun. 82 (1992) 329.
[8] W. Wolf, G. Bihlmayer, S. Blügel, Phys. Rev. B 55 (1997) 6918.
[9] S. Kaprzyk, Acta Phys. Pol. A 91 (1997) 135.
[10] A. Bansil, S. Kaprzyk, P.E. Mijnarends, J. Tobola, Phys. Rev. B 60 (1999) 13396.
[11] L.F. Mattheiss, J.C. Hensel, Phys. Rev. B 39 (1989) 7754.