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Self-consistent APW bandstructure of V_3Ga

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Abstract. Energy bands and densities of states have been calculated for V_3Ga using the self-consistent APW method. Relativistic effects and interstitial corrections to the muffin-tin approximation have been included. Calculations using the local density approximation (LDA) exchange of Hedin and Lundqvist, and an $\alpha = 2/3$, $\rho^{1/3}$, local exchange are compared. The general computational techniques used in this and other A15 material calculations in progress are discussed.

The A15 structure materials have generated a great deal of experimental and theoretical interest due to their unusual low-temperature properties which include high superconducting transition temperatures, elastic constant anomalies and structural phase transitions (see the following review articles: Testardi 1973, Weger and Goldberg 1973 and Izyumov and Kurmaev 1974). The nature of these anomalous properties have led many workers to ascribe them as originating in the electronic structure of the A15 compounds, a viewpoint to which we subscribe. Since the A15 crystal structure is quite complicated, electronic bandstructure calculations are difficult to perform, but such calculations have been done for several A15 compounds following different approaches. Mattheiss (1965) did early pioneering APW calculations for several A15 materials and he included corrections to the muffin-tin approximation in a subsequent work (Mattheiss 1975). Klein *et al* (1977) did the first self-consistent A15 calculation, using the APW method for V_3Si. Weger and Goldberg (1973) and Goldberg (1975 and references therein) used a tight-binding theory approach for A15 calculations. Recent work by Jarlborg and Arbman (1976) used the LMTO method. Here we will present results for V_3Ga (lattice constant 9·105 au); and in addition describe the methodology that we have used which is common to all of our anticipated A15 calculations. Further results on the other A15 materials and on the applications will be forthcoming in subsequent publications.

The basic bandstructure calculations follow the standard symmetrised APW procedures described by Mattheiss *et al* (1968). Some of the more important and unusual features of our bandstructure and density of states calculations will now be summarised:

(i) Self-consistency is achieved by iterating on the spherically averaged muffin-tin charge densities in the manner described by Papaconstantopoulos *et al* (1972) and Anderson *et al* (1973).

(ii) Corrections to the standard muffin-tin approximation were included self-consistently. These corrections involve including the spatial variation of the potential outside of the muffin-tin spheres (interstitial region) in the determination of the energy eigenvalues and wavefunctions. We follow Koelling *et al* (1970) in referring to this as the warped muffin-tin approximation. The approach that we have used is similar to the methods developed by Rudge (1969) and by Koelling *et al* (1970). In a given SC cycle, the APW wavefunctions in the interstitial region are used to determine the Fourier coefficients of the interstitial charge density. Using Poisson's equation, the Fourier coefficients of the Coulombic potential are readily determined (Rudge 1969). The exchange potential presents a special problem because it is a nonlinear function of the charge density. To deal with this we first determined the real space representation of the exchange potential from the charge density, and then found the Fourier coefficients using a least-squares fit (Koelling *et al* 1970). We checked these results by also determining the exchange potential Fourier coefficients from a form of the real space representation of the exchange potential linearised with respect to the charge density (see Rudge 1969). The results were virtually identical for V_3Ga. The interstitial Fourier potentials were then renormalised so as to have zero value inside the muffin-tin spheres and zero *average* value in the interstitial region (Rudge 1969). Finally the potential discontinuity at the muffin-tin sphere radii were eliminated (in the spherically averaged sense) by equating the value of the spherical muffin-tin potential and the value of the interstitial potential spherically averaged at the muffin-tin radii (remember that the interstitial potential is intrinsically nonspherically symmetric). Having thus determined the Fourier coefficients of the interstitial potential, they were then used to correct the eigenvalues and wavefunctions of the next SC cycle. The final interstitial charge density and potential coefficients were very well converged (e.g. better than 1 mRyd for the latter).

(iii) Relativistic effects, neglecting spin–orbit splitting (Boyer and Klein 1975 and Koelling and Harmon 1977) were included in our calculations.

(iv) The exchange potentials inside and outside the muffin-tins were calculated using the local density approximation (LDA) of Hedin and Lundqvist (1971). In addition, for V_3Ga a second calculation using a $\rho^{1/3}(r)$ local exchange with $\alpha = 2/3$ was performed to test how sensitive the bandstructure is to the exchange approximation.

(v) The deep core states were redetermined in each SC cycle in an atomic-like fashion (soft core approximation). For V_3Ga these were the states: $(1s^2 2s^2 2p^6)$ for V and $(1s^2 2s^2 2p^6 3s^2 3p^6)$ for Ga, all with energies less than -5 Ryd. The relatively low-lying semi-core states were treated as bands, but since the bandwidths were $\gtrsim 70$ mRyd, it was accurate enough to iterate these states on a mesh of four k points in the irreducible Brillouin zone (BZ), corresponding to eight points in the full BZ. For V_3Ga these were the states: $(3s^2 3p^6)$ for V and $(3d^{10})$ for Ga. The remaining valence states were iterated on a mesh of ten k points, corresponding to 64 points in the full BZ. These were the V $(3d^3 4s^2)$ and Ga $(4s^2 4p^1)$ states in V_3Ga. Self-consistency was achieved generally in seven to eight cycles (seven for V_3Ga), whence the maximum eigenvalue change in two successive cycles was ~ 1 mRyd.

(vi) For the purposes of the density of states (DOS) determination, a final APW run was done on a mesh of 35 k points (512 points in the full BZ). These first principles APW energies were then interpolated onto a mesh of 165 k points (4096 points in the full BZ) using a newly developed fitting technique (Boyer 1977). This method fits the 35 k point mesh energies with a Fourier series in k space, and makes explicit

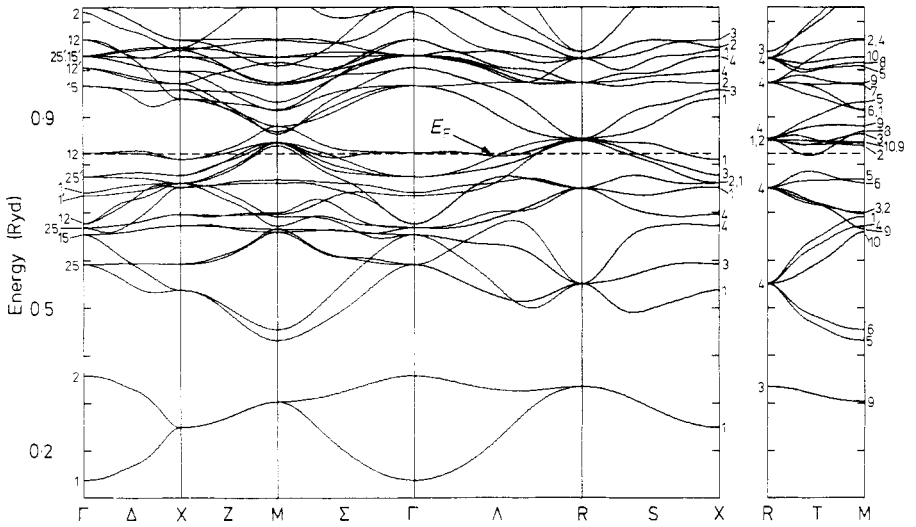

Figure 1. Energy bands along several symmetry directions for V_3Ga. The APW calculation is self-consistent, has warped muffin-tin corrections and uses the local density exchange approximation.

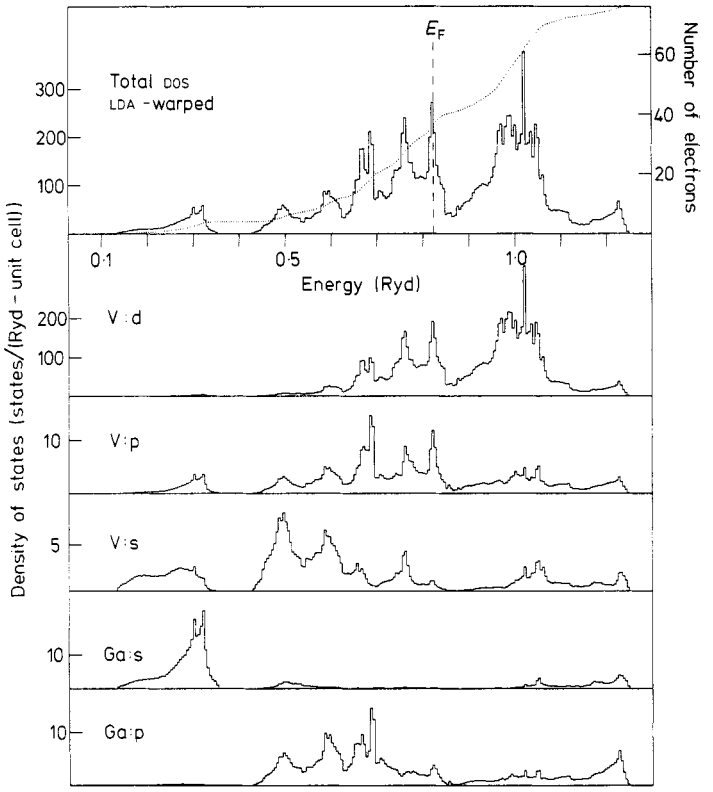

Figure 2. Total and site-angular-momentum decomposed densities of states for V_3Ga from a self-consistent warped muffin-tin APW calculation with the local density exchange approximation.

Table 1. Total density of states, $n(E_F)$, and site-angular-momentum decomposed densities of states, $n_l(E_F)$, for V_3Ga for two different exchange potential approximations, both self-consistent warped muffin-tin calculations. All density of states units are states/Ryd-spin-unit cell. LDA is the local density approximation exchange (bands shown in figure 1); and $\alpha = 2/3$ is from a $\rho^{1/3}(r)$ local exchange calculation.

	$n(E_F)$	$n_s(E_F)$	$n_p(E_F)$	$n_d(E_F)$	$n_f(E_F)$
V		0·5576	5·435	87·63	0·4736
LDA	124·8				
Ga		0·1223	1·854	1·236	0·1412
V		0·5453	5·187	81·93	0·4582
$\alpha = 2/3$	117·2				
Ga		0·1134	1·723	1·184	0·1350

use of the energy band compatibility relations. Since band crossings are treated properly, spurious structure in the DOS is largely eliminated. The interpolated bands on the 165 k point mesh were then used as input to a modification of the QUAD program (Mueller *et al* 1971) to determine the DOS.

Figures 1 and 2 show the energy bands and DOS of V_3Ga with the LDA exchange approximation and the warped muffin-tin corrections. The Fermi level, E_F, falls in a region of high DOS of predominantly V–d character. The bands near E_F are very flat, especially in the k space regions around Γ, with the Γ_{12} state lying just above

Table 2. Energy eigenvalues (E) near and below the Fermi energy (E_F) at the points $\Gamma(000)\pi/a$ and $X(010)\pi/a$ for V_3Ga. The values in the table are: $\Delta E \equiv (E_F - E)$ for each calculation, in units of mRyd. LDA refers to a local density approximation exchange, and $\alpha = 2/3$ is for a local $\rho^{1/3}(r)$ exchange calculation. Warping refers to the inclusion of interstitial potential corrections as described in the text.

	LDA Warped	LDA Unwarped	$\alpha = 2/3$ Warped
Γ_1	686	656	692
	82	91	81
Γ_1'	88	78	88
Γ_{12}	146	139	149
	−3	−4	−4
Γ_{15}	169	157	172
Γ_2	465	456	470
Γ_{25}	232	204	237
	154	132	156
Γ_{25}'	49	35	50
X_1	574	549	580
	285	266	289
	71	77	70
	61	45	63
	11	9	11
X_2	62	50	63
X_3	230	204	235
	45	40	45
X_4	151	141	152
	126	91	131

E_F. The energy band dispersion along the Δ, Σ and Λ directions is very small, and is responsible for the peak in the DOS at E_F.

The histogram widths in figure 2 are 5 mRyd. In determining the DOS values at E_F we were concerned that the sharp structure shown in figure 2 would lead to interpolation errors. We therefore calculated five different DOS curves, shifted by 1 mRyd from each other (by shifting the histogram energy origin), determined E_F and the DOS values at E_F for the five runs, and formed the arithmetic average. The results are shown in table 1 for the LDA and $\alpha = 2/3$ exchanges. The average deviations of the DOS in this averaging procedure were a few percent in each case.

Table 2 gives values of the band energies at Γ and X, near and below E_F for three different SC calculations: LDA warped and unwarped, and $\alpha = 2/3$ warped. A comparison of the numbers in table 2 shows the effects of warping and different exchange potentials. The warping correction shifts eigenvalues by up to approximately 30 mRyd, although near E_F the shifts are a good deal smaller and are similar to what was found by Mattheiss (1975) in his non-SC calculations for several other A15 compounds. Comparing the LDA and $\alpha = 2/3$ results in table 2 we see that the differences are very much smaller, being only a few mRyd near E_F. There does not seem to be a very serious variation in the bandstructure with the exchange approximation.

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