VANADIUM

The existence of a stable magnetic moment in an itinerant-electron ferromagnet requires a high density of states around the Fermi energy of the non-magnetic energy bands, a condition which is obtained when there are partially filled atomic states having relatively small interatomic overlap in the crystal, as in the 3d states of iron, nickel, and cobalt [18]. Thus, if the lattice of a non-magnetic transition metal with partially filled atomic 3d level were expanded, the decrease in overlap of the d-states and the concomitant increase in the density of states might cause the material to become magnetic. The spin-polarized Xα method has been shown by Connolly [19] and others to be capable of explaining the behavior of the magnetic transition metals. It has therefore been employed in an effort to determine the nature of the magnetic transition which would occur in V if its lattice could be expanded substantially beyond the equilibrium size. The magnetic moment has been calculated as the difference between the number of majority-spin and minority-spin electrons per unit cell, with an assumed ferromagnetic arrangement of the moments; it is shown as a function of lattice parameter in Fig. 4. In order to obtain this result, the self-consistency iterations were initiated with a net magnetic moment (net spin density) at each lattice constant and were continued until the net magnetic moment, as well as the individual eigenvalues and other indicators of self-consistency, had stabilized. The calculation correctly predicts the lack of permanent magnetic moment

for V at its equilibrium lattice constant, indicated by a_o in Fig. 4. The dependence of total energy on magnetization near the transition is apparently extremely small, as might be expected. This is evidenced computationally by very slow convergence of the net magnetic moment from lattice constants of about 6.3 to about 7.3 atomic units (a.u.), which makes it impractical to compute the precise nature of the magnetization curve in this region. However, it seems clear that the curve must be bracketed, in the spin-polarized Xα model, by the solid and dashed segments of Fig. 4. The transition is clearly rather abrupt, even with the uncertainty in the region of initial rise. In addition, the two calculated points shown for a lattice constant of 7.0 a.u. represent two distinct self-consistent solutions, arising, respectively, from large and small initial magnetic moment for the self-consistency iterations. (At no other lattice constant for which calculations were performed is there any evidence that the final configuration depends on the assumed initial configuration.) This result appears to indicate the presence of a double minimum in the energy versus magnetization curve, for lattice constants near 7 a.u. The magnetization curve is drawn through the point $\mu \approx 2.2$ electrons/atom for 7.0 a.u. because that point corresponds to the configuration of lower total energy.

The cohesive energy of V was calculated, relative to the isolated atom in the $3d^4 4s^1$ configuration (the spin-polarized Xα atomic ground state and thus the APW separated-atom limit). It is plotted as a function of the lattice parameter, in Fig. 5. The experimental equilibrium cohesive energy [12] is indicated as the error bar in Fig. 5, for comparison, as is the experimentally observed