

Phase stabilities of the Co_3Ti and Ni_3V alloys

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A linear muffin-tin orbitals (LMTO) total-energy calculation has been carried out on the ordered Co_3Ti and Ni_3V compounds in order to evaluate the relative stability of the $L1_2$ and DO_{22} crystal structures in the A_3B -type transition metal alloys. The correct structure was obtained for both the Co_3Ti (which occurs as the $L1_2$) and the Ni_3V (which occurs as the DO_{22}). The calculated structural preferences were further analyzed in terms of the density of states, which indicates that the DO_{22} structure tends to exist when the concentration of valence electrons per atom exceeds 8.65.

I. INTRODUCTION

Ordered alloys $(\text{Fe,Co,Ni})_3X$ ($X=\text{V}$, or V plus a small fraction of Ti) have recently been found rather attractive as potential new structural materials for mechanical applications.¹ Unlike conventional disordered alloys, the yield strength of these ordered alloys increases with temperature, peaking around the ordering transition temperature. Because of the unusual behavior of the yield strength with temperature, the ordered $(\text{Fe,Co,Ni})_3X$ alloys have been found to be much stronger than conventional disordered alloys in evaluated temperature environments. Therefore such alloys are promising as potential structural materials in the future.

Since structural materials also require sufficient ductility, one of the important problems in designing technologically useful ordered alloys is the control of their crystal structure. Alloys having the $L1_2$ structure [Fig. 1(a)] have been found to be surprisingly ductile, and are therefore of special interest for possible applications. By contrast, alloys having the DO_{22} structure [Fig. 1(b)], are generally found to be rather brittle, mainly due to the lack of a sufficient number of slip systems; and they are therefore less promising structural materials.

The problem of the relative stability between the $L1_2$ and the DO_{22} structures in alloys has been considered previously by a number of researchers. In an empirical approach, Sinha has attempted to correlate the occurrence of the $L1_2$ and DO_{22} structures observed in quasibinary A_3B -type transition metal alloys with the valence electron per atom ratio (e/a) of these alloys.² Here, the valence number was defined as all electrons outside the argon core. Sinha claimed that the DO_{22} structure tends to exist at higher values of e/a (> 8.65), while the $L1_2$ structure tends to exist at lower values of e/a (< 8.65). In a theoretical approach, Stocks *et al.* and Xu *et al.* have recently demonstrated that the correct crystal structures for the Ni_3Al and Ni_3V alloys can be predicted

from a first-principles calculation utilizing the linear muffin-tin orbitals (LMTO) method.^{3,4}

In this work, we report an attempt to study this problem in more detail. In particular, we attempted to understand from the electronic structure calculation, the experimentally observed structural correlation with e/a , and we also attempted to discover if the LMTO total-energy method could also be applied to a more general case of A_3B -type alloys of our interest. In order to see if any bias may exist in the LMTO calculation towards favoring either the $L1_2$ or the DO_{22} structures, we selected two similar alloys: Co_3Ti , which is known experimentally to be stable as $L1_2$, and Ni_3V , which is known experimentally to be stable as DO_{22} . The total energy (E_{tot}) for the two structural modifications was calculated for each of these two selected alloys. In each case, the stable crystal

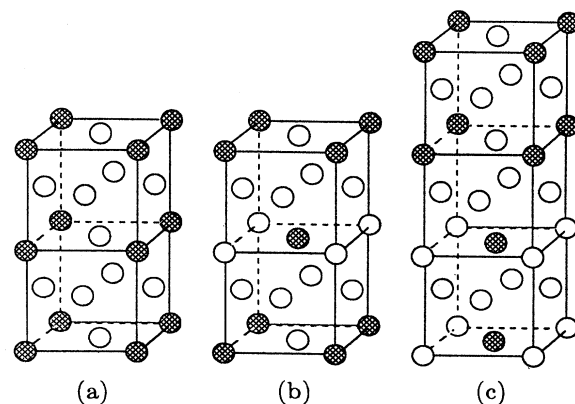


FIG. 1. The unit cell of (a) the $L1_2$ structure (two unit cells), and (b) the DO_{22} structure. The Co and Ni atoms occupy the positions marked by open circles, and the Ti and V atoms occupy the positions marked by hatched circles. (c) The cubic cell in the middle shows the $\{001\}$ -type antiphase boundary commonly occurring in the $L1_2$ structures.

structure was found to coincide with a slightly lower value of E_{tot} .

II. METHOD

The electronic structure and the E_{tot} results presented below were obtained by the semirelativistic linear muffin-tin orbitals (LMTO) method in the atomic-sphere approximation (ASA) (Ref. 5). The von Barth-Hedin exchange-correlation potential was used.⁶ Since Co and Ti, and Ni and V, involved in the two alloys have very similar atomic radii, we assumed that each atom, regardless of the difference in atomic species, occupied the same volume in the unit cell and hence that the Wigner-Seitz radius of these atoms could be assumed to be identical. In order to determine the number of k points required in an irreducible wedge of the first Brillouin zone (IBZ) that would be sufficient to bring about satisfactory convergence of E_{tot} , we have calculated the E_{tot} of the Co_3Ti compound in the $L1_2$ structure for three different cases: (1) 35 k points in the cubic IBZ, (2) 84 k points in the cubic IBZ, and (3) 84 k points in the tetragonal IBZ. In the third case, E_{tot} was calculated in a double cubic unit cell or a tetragonal unit cell. Figure 2 shows the obtained E_{tot} for the above three cases at several different lattice spacings close to the experimental value. We note that the calculated E_{tot} 's are almost the same for the second and third cases, even though the density of k points for the two cases differs substantially (a factor of 2.5), and even though a different kind of IBZ has been used. This indicates that the density of 84 k points in the tetragonal IBZ is already sufficiently high for the convergence of E_{tot} . We consequently used this density of k points

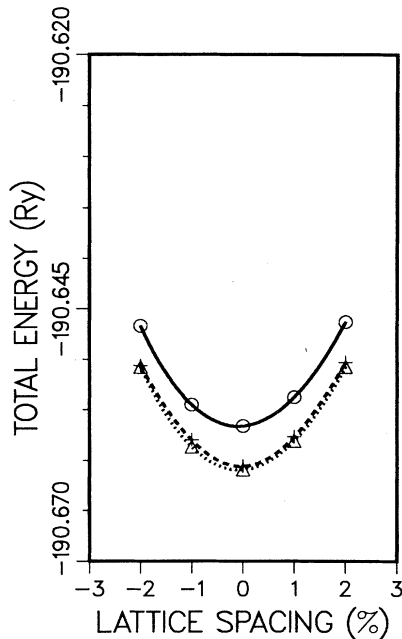


FIG. 2. Convergence of the total energy per formula of the Co_3Ti compound in the $L1_2$ structure for three different densities of k points in the Brillouin zone: 35 k points in the cubic IBZ (solid line), 84 k points in the cubic IBZ (dashed line), and 84 k points in the tetragonal IBZ (dotted line).

throughout our subsequent calculations. The density of states (DOS) shown in this paper was calculated at 0.5-mRy unit energy intervals. We found that such fine intervals were necessary in order to reveal the band-filling contribution to the resultant structural stability.

III. RESULTS AND DISCUSSION

Figure 3 shows the calculated E_{tot} 's at five different lattice spacing values close to the experimental values. The lattice parameter is taken to be $a = 3.612 \text{ \AA}$ for the cubic Co_3Ti , and $a = 3.522 \text{ \AA}$ and $c = 7.184 \text{ \AA}$ for the tetragonal Ni_3V (Ref. 2). Solid curves in Fig. 3 were obtained by utilizing the Lagrange's interpolation formula. For the $D0_{22}$ structure, the small deviation (about 2%) of the experimental c/a ratio from the ideal value was ignored. We note that the predicted lattice spacings, which correspond to the minimum of E_{tot} 's, are within one percent deviation from the measured value for both alloys. Furthermore, the present calculation yielded the correct prediction of the stable crystal structure for both the Co_3Ti (which exists as the $L1_2$), and the Ni_3V (which exists as the $D0_{22}$). The total-energy difference between the $L1_2$ and $D0_{22}$ structures was -17.2 mRy per formula for the Co_3Ti compound and $+27.9 \text{ mRy}$ per formula unit for the Ni_3V compound. The Ni_3V results were later found to be very close to that obtained by Xu *et al.* using the same method.⁴ The bulk modulus, which can be calculated from the second derivative of the E_{tot} with respect to the lattice spacing charge, was found to be 2.65 Mbar for the Co_3Ti and 2.59 Mbar for the Ni_3V .

Since the Co_3Ti and Ni_3V compounds are considered to be rather closely related in the sense that Co and Ni, and Ti and V are, respectively, nearest neighbors in the Periodic Table, it is of interest to compare the detailed electronic structures for these two alloys in order to discover reasons behind the obtained structural preferences. For this purpose, we have subsequently calculated the DOS trend for both alloys, as shown in Fig. 4.

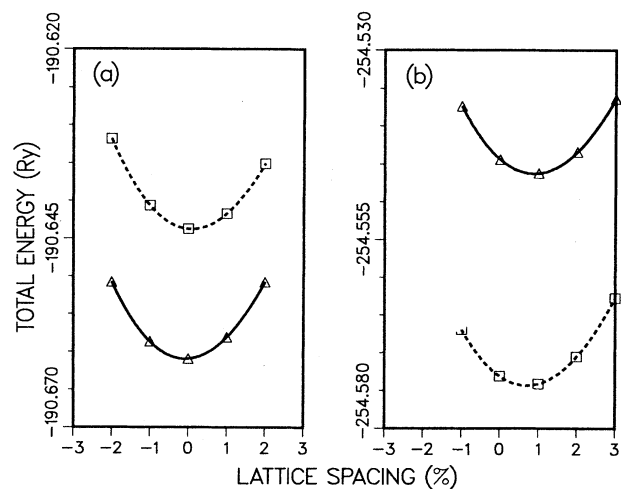


FIG. 3. The total energy per formula calculated for (a) the Co_3Ti alloy and (b) the Ni_3V alloy in both the $L1_2$ (solid line) and the $D0_{22}$ (dashed line) structures.

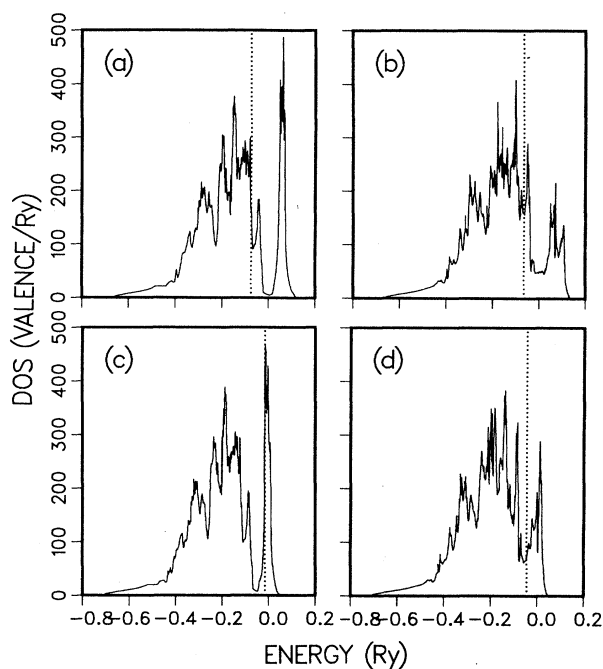


FIG. 4. The density of states of two formulas for (a) the Co_3Ti in the $L1_2$, (b) the Co_3Ti in the DO_{22} , (c) the Ni_3V in the $L1_2$, and (d) the Ni_3V in the DO_{22} . The vertical dashed lines indicate the Fermi energy levels.

The obtained DOS trend appears to be rather similar for both alloys in either the $L1_2$ or the DO_{22} structure. On the other hand, the difference in DOS trend between the $L1_2$ and DO_{22} structures is quite apparent and this consequently provides an energy difference, $\Delta E_{\text{band}} = E_{\text{band}}(DO_{22}) - E_{\text{band}}(L1_2)$, which represents the band-filling contribution to the total-energy difference. We have noted that there is a valley in the DOS trend of both the $L1_2$ and the DO_{22} , and that the valley associated with the $L1_2$ is deeper than that of the DO_{22} and almost forms a gap. When E_F of any alloy is above this valley, a portion of valence electrons has to be accommodated into higher energy states in the $L1_2$ structure than in the DO_{22} structure. Therefore, in this case, it seems that the $L1_2$ structure may be an energy-saving configuration, compared with the DO_{22} structure. In Fig. 5, we plot ΔE_{band} versus the number of valence electrons filling the bands. The main feature of each such plot turns out to be also similar for the two alloys. At the lower e/a end in this range, ΔE_{band} is always positive and increases with the number of valence electrons. This indicates that the filling of more valence electrons into the bands tends to further stabilize the $L1_2$ structure with respect to the DO_{22} structure. When e/a further increases, ΔE_{band} begins to decrease rapidly with valence and then becomes a negative value with a small e/a change. When this occurs, the band-filling contribution no longer tends to favor the $L1_2$, but now tends to favor the DO_{22} instead. The negative value of ΔE_{band} occurs near 69–70 valence electrons per tetragonal unit cell (containing eight

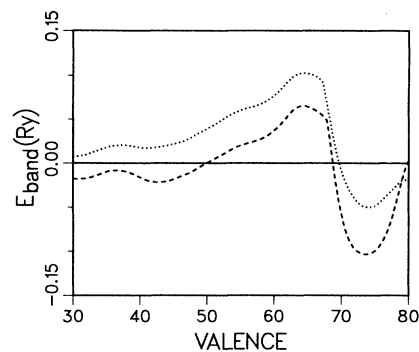


FIG. 5. The energy difference associated with band filling, $\Delta E_{\text{band}} = E_{\text{band}}(DO_{22}) - E_{\text{band}}(L1_2)$, as a function of the number of valence electrons in two formulas. The dashed line is for the Co_3Ti alloy, and the dotted line is for the Ni_3V alloy.

atoms), or 8.6–8.75 valence electrons per atom. This value coincides very well with Sinha's value of $e/a = 8.65$. Therefore, the present calculation explains on the basis of the electronic structure why the DO_{22} tends to occur with $e/a > 8.65$ while the $L1_2$ tends to occur with $e/a < 8.65$.

Since ΔE is only one of the several terms in the total-energy difference, it is necessary to consider how large a fraction of the total-energy difference comes from the band-filling contribution. For the Co_3Ti compound, we found that the energy difference arising from the band filling (-35.8 mRy per two formulas) is very close to the E_{tot} difference (-34.4 mRy per two formulas). Therefore, the relative stability between the $L1_2$ and the DO_{22} is mainly determined by the difference in their respective DOS trends. For the Ni_3V compound, however, we note that the band-filling contribution ($+10.0$ mRy per formula) is only a small fraction of the E_{tot} difference ($+55.8$ mRy per two formulas), and therefore the band filling is not the major factor in determining the structural stability. In fact, we found that the Madelung term changes significantly from the case of the Co_3Ti to the case of the Ni_3V , and therefore contributes an important part to the opposite structural preferences observed in the two alloys. This indicates need for caution when deriving

TABLE I. Some results of the present LMTO calculation. The experimental bulk modulus data of pure elements are taken from Ref. 7.

Alloys	Co_3Ti	Ni_3V
Crystal structure observed	$L1_2$	DO_{22}
Crystal structure calculated	$L1_2$	DO_{22}
ΔE_{tot} (mRy per formula)	-17.2	27.9
Antiphase boundary energy (mJ/m ²)	282	457
Deviation from experimental value of lattice spacing (%)	-0.1	0.7
Bulk modulus calculated from E_{tot} (Mbar)	2.65	2.59
Bulk modulus obtained from averaging pure element data (Mbar)	1.62	1.90

structural stabilities based solely on the DOS considerations.

The obtained results are summarized in Table I, including the energy of the $\{001\}$ -type antiphase boundary [Fig. 1(c)] which was estimated in each case from total-energy differences between the $L1_2$ and the DO_{22} . It appears that the calculated bulk moduli for both alloys are slightly larger than the compositional average obtained from experimental bulk moduli of the pure elements involved. Therefore slight hardening is indicated as a consequence of alloying.

In conclusion, the present LMTO total-energy calculation predicts correct structural preferences for the Co_3Ti and Ni_3V alloys. The fact that the opposite structural preferences can be obtained for the both alloys involving very similar elements, indicates that the LMTO total-energy method employed here is quite reliable in studying the relative phase stabilities in the A_3B -type transition metal alloys. Also, the present calculation shows that the

DO_{22} structure tends to be more stable than the $L1_2$ structure in the region of valence electrons per atom greater than 8.65. This is in good agreement with the earlier experimental observation.

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¹C. T. Liu, *Int. Metals Rev.* **29**, 168 (1984).

²A. K. Sinha, *Trans. AIME* **245**, 911 (1969).

³G. M. Stocks, D. M. Nicholson, F. J. Pinski, W. H. Bulter, P. Sterne, W. M. Temmerman, B. L. Gyorffy, D. D. Johnson, A. Gonis, X.-G. Zhang, and P. E. A. Turchi, in *High-Temperature Ordered Intermetallic Alloys II*, MRS Symp. Proc. No. 81, edited by N. S. Stoloff, C. C. Koch, C. T. Liu, O. Izumi (MRS, Pittsburgh, 1987), p. 15.

⁴J. H. Xu, T. Oguchi, and A. J. Freeman, *Phys. Rev. B* **35**, 6940 (1987).

⁵H. L. Skriver, *The LMTO Method*, Vol. 41 of *Topics in Solid State Sciences* (Springer-Verlag, New York, 1984).

⁶U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).

⁷G. E. Dieter, *Mechanical Metallurgy*, 2nd ed. (McGraw-Hill, Paris, 1981); W. Rostoker, *The Metallurgy of Vanadium* (Wiley, New York, 1958); Battelle Memorial Institute, Cobalt Monograph, Centre d'Information du Cobalt, Brussel, Belgium, 1960.