Submitted to Journal de Physique for publication in the 1972 issue devoted to the conference "Perspectives for Computation of Electronic Structure in Ordered and Disordered Solids."

Preprint

Three Aspects of the Computation of Electronic Structures of Metals at the University of Florida: Isomorphic Phase Transition and Cohesive Energy in Cs; Vanadium Non-Magnetic to Magnetic Transition with Lattice Size; and Soft X-Ray Emission Spectra of TiC and NbC. *†

by

James B. Conklin, Jr., Frank W. Averill, and Thomas M. Hattox

Quantum Theory Project,

Department of Physics and Astronomy, University of Florida, Gainesville, Florida 32601, U.S.A.

ABSTRACT

Self-consistent APW calculations have been performed to provide electron eigenvalues and wave functions for several systems, within the X α approximation for the exchange and within the muffin-tin approximation for generating and utilizing the effective one-electron potential. This information has been used to calculate cohesive energies for metallic cesium and vanadium and to calculate the isomorphic phase transition of cesium. The formal magnetization of vanadium as a function of its lattice parameter has been examined and a magnetic transition found. Momentum matrix elements for titanium carbide and niobium carbide have been estimated to provide an approximate expression for the energy dependence of the soft x-ray valenceband emission in terms of partial densities of states, allowing interpretation of the experimental data in terms of the calculated electronic properties.

> *Supported in part by the National Science Foundation.
> *Based in part on dissertations presented by F. W. Averill and T. M. Hattox to the Department of Physics and Astronomy, University of Florida, in partial fulfillment of the requirements for the Ph.D. degree.

INTRODUCTION

It has been suggested that analysis of wave functions will be an important aspect of the study of electronic states in the next decade. In this paper are presented results of the following calculations, which illustrate several aspects of such analysis, for crystalline solids: the cohesive energy, pressure, and enthalpy of cesium metal as a function of unit cell volume, to show computationally the isomorphic phase transition of cesium (Cs); magnetization and cohesive energy of vanadium (V) as a function of lattice parameter, to exhibit the nature of the formal transition from non-magnetic to magnetic behavior as the lattice is expanded; estimation of momentum matrix elements and interpretation of the spectral lineshapes of soft x-ray emission from the valence bands of titanium carbide (TiC) and niobium carbide (NbC). All of the energy-band calculations reported are self-consistent and are based on the $X\alpha$ exchange approximation [1], with no explicit inclusion of correlation effects.

The calculations have been done by the APW (Augmented Plane Wave) method of Slater [2], within the muffin-tin approximation [2] for the one-electron effective potential and for handling the charge density during the generation of that potential in the selfconsistency iterations. (This approximation should be excellent for fcc Cs, with its close-packed structure and metallic valence charge distribution, and adequate for bcc Cs and V, and for TiC and NbC.) Brillouin zone sampling has been done at the equivalent of 256 equally spaced points in the full zone for the fcc Bravais lattices (128 for the bcc structures); for the V calculation, additional interpolation of the bands has been performed to obtain more accurate weighting factors for the contributions of the computed k-points in the charge-density calculation [3] and to estimate electronic densities of states. A grid of the equivalent of only 32 equally-spaced points is used for states well below the valence bands when only a

4

few percent of their charge is outside the APW spheres [4]. Wave functions and energies of true core levels are computed in atomic fashion, but in the crystal potential. The cohesive energy is calculated as the difference between the X α total energy per unit cell of the crystal [5] and the X α total energy of the isolated atom (-15,107.7719 Ry for Cs, -1885.867 Ry for the ⁶D multiplet of V in the 3d⁴ 4s¹ configuration, and -1885.743 Ry for the ⁴F multiplet of the V 3d³ 4s² configuration), with the same value of α used for both the crystal and the atomic calculations. (Numerical techniques used for the crystal and the atom are made as nearly identical as possible, to allow maximum cancellation of numerical errors.)

The values of α used throughout the unit cell for Cs and V and in the APW spheres for Ti and C in TiC are those for which the statistical (X α) total energy for the isolated atom equals the expectation value of the Hartree-Fock total energy operator with

respect to the X α one-electron orbitals [6]. The prescription gives α to be 0.69941 for Cs, 0.715 for V, 0.7165 for Ti, and 0.7581 for C. $\alpha = 2/3$ was used between (outside) the spheres for TiC. For NbC, $\alpha = 1$ was used everywhere, as originally suggested by Slater [7]. The results presented for TiC and NbC should be insensitive to the choice of α , as shown [4] for TiC. The same is true for the cohesive energies, as long as the α -variation is not too great and the same value of α is used in the respective APW spheres as for the isolated atoms (to allow proper cancellation of terms arising from the core electrons). The magnetization curve calculated for V may show somewhat more dependence on α , though this has not been computationally verified; the form of the curve is expected to be insensitive to α , however.

5

CESIUM

Cesium metal undergoes a phase transition from bcc to fcc structure at 23 kbar. At 42 kbar it experiences another phase transition, often called isomorphic, in which its unit cell volume decreases by about 9% without change of crystal structure [8]. Sternheimer [9], in 1949, concluded that the isomorphic transition is due to the crossing of the previously unoccupied 5d bands through the partially occupied 6s band as the lattice constant is decreased. More recent calculations by Yamashita and Asano [10] and by Kmetko [11] have shown that the cesium d-bands are broader than those obtained by Sternheimer, indicating that his explanation may be an oversimplification. These calculations have also shown some very interesting topological changes in the Fermi surface which are computed to occur in the range of unit-cell volume across which the phase change occurs. However, they have not included the estimates of cohesive energy, pressure, and enthalpy necessary to determine if the computed electronic properties do, in fact, give rise to a phase transition. Since the Fermiology of Cs has not been experimentally studied at the very high pressures at which the transition takes place, there has been no conclusive evidence that the calculated effects actually correspond

to the observed phase transition. The work reported here provides that evidence by demonstrating that the computed electronic energies and wave functions actually do lead to an isomorphic phase transition at unit cell volumes very near those experimentally associated with the isomorphic phase transition of Cs.

The energy bands found for Cs resemble so closely those reported by Yamashita and Asano [10] that it is unnecessary to present them here. The cohesive energy per atom calculated from these bands and from the corresponding wave functions is shown in Fig. 1a as a function of the volume per primitive unit cell (per atom) for both the fcc and the bcc structures. The calculated equilibrium cohesive energy for the bcc phase (-0.061 Ry/atom) is in good agreement with the experimental value of -0.062 Ry/atom reported by Gschneider [12], and the calculated equilibrium unit-cell volume, 780 cubic atomic units (Bohr radii), agrees well with the 745 cubic atomic units determined experimentally by Barrett [13]. The computed energy curves predict the fcc phase to be the O K equilibrium phase, in contradiction to the experimental results. However, the computed energy difference between the fcc and bcc phases at the equilibrium volume is small and may well be due to use of the muffin-tin approximation. (Since the same (fcc) phase prevails on both sides of the high-pressure isomorphic transition, the errors due to this approximation should be nearly identical for the two phases involved and should thus be unimportant in the investigation of that transition.)

It is significant that the $X\alpha$ calculations do so well for the cohesive energy, because the model does not include any explicit estimate of the correlation energy. Slater [1] has suggested that the local $(X\alpha)$ exchange approximation itself includes certain features of correlation. For example, it leads to the correct separated-atom limit for the one-electron eigenvalues and the total energy, and it treats excited one-electron states in a more desirable fashion than is done with the virtual states in the Hartree-Fock method. (For instance, the undesirable and non-physical vanishing of the free-electron-gas density of states at the Fermi energy, which is obtained in the Hartree-Fock approximations, is eliminated by the local, averaged exchange of the Xa method.) It may thus be that the $X\alpha$ approximation includes certain of those features of the correlation correction which are most crucial to binding, even though it does not explicitly include any correlation term. (For accurate cohesive energies, it is only necessary to duplicate the variation of the correlation energy as the atoms coalesce into the solid or molecule, not to

obtain the total correlation correction.)

The pressure p on the solid at a given volume V per primitive unit cell can be calculated from the non-equilibrium virial theorem [14,15],

9

 $pV = (\langle U \rangle + 2 \langle T \rangle) / 3 , \qquad (1)$

which is satisfied identically in the X α approximation, for the statistical (X α) effective total potential energy $\langle U \rangle$ and kinetic energy $\langle T \rangle$ per primitive unit cell. Such a calculation has been performed, and the computed pressure is shown as a function of volume in Fig. 1b. As a check on the numerical accuracy of the calculation, the pressure has also been obtained from the relation

p = -dE/dV(2)

(where E is the total or cohesive energy per primitive unit cell), which is found to give results in good agreement with those shown. The bcc p-V curve is found by Averill [16] to be in good agreement with the compression measured by Swenson [17] at low temperatures.

It is in the pressure curve for fcc cesium that the first clear indication of the isomorphic phase transition appears: the curve dips, showing a clear minimum at a volume of about 350 cubic atomic units (c.a.u.) per atom. From the fcc cohesive energy and pressure curves, the enthalpy is obtained, as illustrated in Fig. 2. (The relevant computed points are numbered in Fig. 1a. 1b, and 2, to facilitate comparison. All points with a given number correspond to a single lattice volume and pressure.) In this curve, the transition appears as the intersection of the line from point 1 to point 2, with that from 4 to 5. As the metal is compressed at O K, it must move along the curves from point 1 to the point of this intersection on the enthalpy curve (about 26 kbar, which corresponds to $V \approx 410$ c.a.u.), at which point it jumps to the corresponding point on the curves. from point 4 to point 5 (26 kbar, and about 320 c.a.u.), following the curves to point 5. The 0 x computed isomorphic phase transition thus consists of a discontinuous volume change from approximately 410 c.a.u. to 320 c.a.u., at a pressure of roughly 26 kbar . There is no experimental data with which to compare these results at 0 K, but the volumes are in good agreement with the observed room temperature decrease from 362 c.a.u. to 329 c.a.u. [8]. The calculated pressure of 26 kbar (for 0 K) is not in such close agreement with the 42 kbar pressure observed for the transition at the higher temperatures. but the calculated pressure is subject to all the errors of the model (and is not a variational quantity like the total energy).

Furthermore, the computed and experimental results are only partially comparable because of the difference in the relevant temperatures. Thus, it seems reasonable to assume that the computed transition does, in fact, represent the observed isomorphic phase transition in cesium, thereby providing justification for the assumptions of Yamashita and Asano [10] and Kmetko [11].

11

The APW wave functions are expanded, in each sphere, in spherical harmonics, which allows the charge of each state to be broken down, inside the spheres, into components associated with each value of *l* in the spherical harmonic expansion [2]. The sums over all occupied valence states of these components is indicative of, though not identical to, the contributions of the corresponding atomic states to the occupied valence states in the crystal [4]. These sums together with the amount of valence charge outside the spheres, are plotted for Cs in Fig. 3 as a function of lattice volume per atom. The behavior of the d-like (l=2) part of the valence charge reveals an interesting extension of Sternheimer's [9] hypothesis regarding the nature of the isomorphic phase transition: even though the d-bands are broad, the transition appears to be intimately associated with a sharp increase in the d-like character of the fcc valence charge, as the lattice volume is decreased. This increase (at about 400 c.a.u.) is clearly associated with the dip in the pressure curve which occurs at the

same atomic volume. Furthermore, the structure (fcc or bcc) which has more d-like charge at any volume also has the lower computed pressure at that volume. Even the topological changes which occur in the Fermi surface can be closely correlated with the kinks in the curve of this d-like charge component [16]. Thus, Sternheimer's explanation appears to have a very great deal of truth, if slightly generalized to allow for broader d-bands.

13 VANADIUM

The existence of a stable magnetic moment in an itinerantelectron 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 XX 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 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 Xa 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 $3d^44s^1$ configuration (the spin-polarized X α 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

equilibrium lattice constant, a_0 , [20]. (The difference between the V total energy at its minimum and the spin-polarized X α energy of the 4F multiplet of the $3d^34s^2$ configuration of the isolated V atom [which corresponds to the experimental ground state of the atom] is -0.45 Ry/atom. Thus, this figure and the equilibrium cohesive energy calculated with reference to the $3d^44s^1$ configuration bracket the experimental value of the cohesive energy.) The X α approximation thus predicts for V, as for Cs, a cohesive energy, compressibility [3], and lattice constant in good agreement with experimenta.

The kink in the cohesive energy curve, near the transition point (a \approx 7 a.u.), is indicative of the possibility of a phase transition in which a discontinuous volume change is associated with the onset of magnetic polarization. Unfortunately, detailed examination of this transition will probably require more detailed knowledge of the cohesive energy as a function of lattice constant near the transition point than is reported here.

The densities of states are illustrated in Fig. 6 for two nonmagnetic lattice constants, to show the increasing density of states at the Fermi energy which eventually leads to the stability of the magnetic state as the lattice constant is further increased. Fig. 7 shows the spin-polarized densities of states for the majority (α) and minority (β) spins, for magnetic V at a lattice constant of 8.5 a.u., well beyond the transition point. Note that the Fermi energy has passed through a minimum in the majority-spin (α) density of states in order to make the transition from the non-magnetic to the magnetized state. This may be associated with the phase transition mentioned above in which a discontinuous change in lattice constant may occur at the onset of magnetic behavior. It is precisely in this region of the transition that the minimum in the majority-spin density of states must pass through the Fermi energy.

16

TiC and NbC

17

The soft x-ray emission spectra of several of the refractory metal carbides and related compounds have been studied extensively [21-26] and have received a wide variety of explanations and interpretations. The intent of the present section is to demonstrate that an approximate calculation of the lineshapes based on selfconsistent APW energy-band calculations for these materials can yield unnormalized curves in good agreement with the experimentally observed spectra.

The calculation involves several fundamental approximations which are relatively commonly used [21-28] but warrant further investigation: (1) The localized nature of the initial state is ignored. It is assumed that the energy dependence of the transition matrix element should be well approximated by that matrix element calculated between the crystalline core and valence-band wave functions. (2) The distortion of the valence wave functions, and the resulting energy shifts, which are caused by the absence of a core electron in the initial state, are ignored. It is assumed that the effect on the matrix elements will be small and that, although the effect on the total energy is significant, the effect on energy <u>differences</u> between transitions from different parts of the valence band is negligible. (3) The variation of the vector potential <u>A</u> over the dimensions of the core wave function is ignored in order to reduce the calculation of $\langle \underline{p}, \underline{A} \rangle$ to the calculation of $\langle \underline{p} \rangle$. This approximation is equivalent to ignoring the atomic form factors for these x-ray transitions and should certainly be adequate for the computation of the desired lineshape estimates.

With these approximations, the matrix element of \underline{p} . A between the initial and final states is reduced to the matrix element of \underline{p} between the one-electron core wave function and the valence wave function for a state at the desired initial energy. The expansion (inside sphere t),

$$\Psi_{j}(\underline{k},\underline{r}) = \sum_{l,m} C_{l,m}^{t}(j,\underline{k}) Y_{l}^{m}(\theta, \overline{\varphi}) R_{l}(\underline{E}_{j}(\underline{k}), r),$$

for an APW eigenfunction [2,4] of band j and wave vector k then allows the usual atomic selection rules to be utilized to reduce the summations over ℓ and m. (In the expansion, Y_{ℓ}^{m} is a spherical harmonic, R_{ℓ} a radial function.) Examination of the radial functions R_{ℓ} for the materials of interest shows that their energy dependence, over the range of valence-band energies, is negligible. Furthermore, for these materials, a single value of ℓ dominates for each x-ray transition. The fractional variation in the frequency of x-rays emitted by valence electrons, as they drop into a given core level, is also negligible. Thus, the energy dependence of the x-ray intensity density is well

approximated (in the model assumed) by

$$\lim_{\Delta E} (\Delta E)^{-1} \sum_{\substack{\text{states } j \\ \Delta E}} |c_{\ell,m}^{t}(j,k)|^{2} \text{ x constant}$$

$$= \sum_{\substack{\text{sheets } j \\ \text{of} \\ \text{Fermi} \\ \text{Surf.}}} \iint \frac{dS_{j}}{|\nabla_{k} E_{j}(k)|} |c_{\ell,m}^{t}(j,k)|^{2} \text{ x constant},$$

for a single polarization and direction of the emitted x-ray. In this expression,

l = 1 for K-emission (metal or non-metal)
2 for L-emission (metal)
1 for M-emission (metal),

<u>m</u> is determined by the x-ray polarization (assumed to be circular or parallel to the z axis), and the expansion coefficients C_{fm}^{t} are those for the APW sphere t around the atom in which the transition occurs. For unpolarized x-rays averaged over all angles of emission, the expression becomes proportional to the "partial density of states,"

$$z_{\ell}^{t}(E) = \sum_{\text{Sheets}} \iint \frac{ds_{j}}{\left| \sum_{k} E_{j}(k) \right|} \sum_{m} \left| c_{\ell,m}^{t}(j,k) \right|^{2},$$

which is just the expression for density of states except that

the contribution of each state is weighted by the *l*-component of its charge in the sphere t of interest [4]. This information is readily available from a self-consistent APW calculation.

The experimental data are reproduced in Fig. 8 and 9. In Fig. 10 is shown the decomposition of the Ti-L_{II,III} emission from TiC, based on the assumption that the two components have the same shape and are separated in energy by the atomic $\text{Ti-L}_{\text{TT}},$ Ti-L_{III} splitting. The experimental spectra are compared to the computed spectra (arbitrary units for both, no broadening included in the computed curves) in Fig. 11-13 for TiC and in Fig. 14-16 for NbC. In all cases, the calculated Fermi energy has been made coincident with the experimentally determined Fermi energy. For TiC, the curves are also shown with a relative shift of 0.6 eV from this position (dashed curves in Fig. 11 and 13, dot-dash in Fig. 12) which gives even better agreement. The shift to the dashed curve for Nb- $M_{IV,V}$ is to correct for a calibration error in Holliday's data, which was reported by Ramqvist, et. al. [25]. The agreement in all curves is seen to be excellent, if allowance is made for the broadening in the experimental data, which is not included in the theoretical curves.

19

CONCLUSION

It has been demonstrated that analysis of the one-electron wave functions and energies calculated in the Xa approximation can provide a basis for understanding a number of the physical properties of crystalline solids, including cohesion, p-V relationships, and phase transitions. X-ray spectra and magnetic properties have also been studied in the context of this approximation, to demonstrate their relationship to the energy-band properties of materials. The extension and refinement of studies of this general nature forms one aspect of the "perspectives for calculation of electronic properties in ordered and disordered solids".

ACKNOWLEDGEMENT

22

The authors are pleased to acknowledge the many stimulating and helpful conversations with members of the Quantum Theory Project about numerous aspects of the research reported herein.

One of them (J.B.C., Jr.) wishes to thank D. Nagel, R. Manne, E. Källne, E. Noreland, and L. Hedin for several very useful discussions regarding the measurement and interpretation of soft X-ray spectra, and K. Schwarz for much of the numerical data upon which the X-ray emission calculations are based. One of them (F.W.A.) is grateful for the cooperation of J. Springer and the Naval Weapons Laboratory for making possible several runs on their CDC 6700 computer. The major part of the computation was performed on the facilities provided by the University of Florida Computing Center.

23

[11] Continued.

States", U.S.A. National Bureau of Standards Special Publication 323, 1970.

- [12] GSCHNEIDER (K.A., Jr.), "Solid State Physics" (Seitz and Turnbull, eds., Academic Press, Inc., New York), 1964, Vol. 16, 275.
- [13] BARRETT (C.S.), Acta Cryst., 1956, 9, 671.
- [14] ROSS (M.), Phys. Rev., 1969, 179, 612.
- [15] RUDGE (W.E.), Phys. Rev., 1969, 181, 1033.
- [16] AVERILL (F.W.), Ph. D. dissertation, Dept. of Physics and Astronomy, University of Florida, Gainesville, Florida, U.S.A., 1971.
- [17] SWENSON (C.A.), Phys. Rev., 1955, 99, 423.
- [18] SLATER (J.C.), Phys. Rev., 1936, 49, 537.
- [19] CONNOLLY (J.W.D.), Phys. Rev., 1967, 159, 415; Internat. J. Quantum Chem., 1967, S1, 615; ibid., 1968, S2, 257.
- [20] JAMES (W.J.) and STRAUMANIS (M.E.), Z. für Phys. Chem. Neue Folge, 1961, Bd 29, S134.

REFERENCES

- [1] SLATER (J.C.), Adv. Quantum Chem., 1971, 6, to be published.
- SLATER (J.C.), Phys. Rev., 1937, 51, 846.
 MATTHEISS (L.F.), WOOD (J.H.), and SWITENDICK (A.C.), "Methods of Computational Physics" (Adler, Fernbach, and Rotenberg, eds., Academic Press, Inc. New York), 1968, Vol. 8, 63.
- [3] HATTOX (T.M.), Ph. D. dissertation, Dept. of Physics and Astronomy, University of Florida, Gainesville, Florida, U.S.A., 1972.
- [4] SCHWARZ (K.) and CONKLIN (J.B., Jr.), to be published.
- [5] DeCICCO (P.D.), Phys. Rev., 1967, 153, 931, and Ph. D. dissertation, Dept. of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A., 1965. ROSS (M.) and JOHNSON (K.W.), Phys. Rev., 1970, B2, 4709.
- [6] SCHWARZ (K.), to be published.

BERRONDO (M.) and GOSCINSKI (O.), Phys. Rev., 1969, 184, 10. SLATER, (J.C.) and WOOD (J.H.), Internat. J. Quantum Chem., 1971, S4, 3.

- [7] SLATER (J.C.), Phys. Rev., 1951, 81, 385.
- [8] HALL (H.T.), MERRILL (L.), and BARNETT (J.D.), Science, 1964, 146, 1297.
- [9] STERNHEIMER (R.), Phys. Rev., 1949, 75, 888;
 ibid., 1959, 78, 235.
- [10] YAMASHITA (J.) and ASANO (S.), J. Phys. Soc. Japan, 1970, 29, 264.
- [11] KMETKO (E.A.), Proc. 3rd IMR Symposium, "Electronic Density of

- 24a
- [21] RAMQVIST (L.), EKSTIG (B.), KÄLLNE (E.), NORELAND (E.), and MANNE (R.), J. Chem. Phys. Solids, 1969, 30, 1849.
- [22] HOLLIDAY (J.E.), J. Appl. Phys., 1967, 38, 4720.
- [23] FISCHER (D.W.), J. Appl. Phys., 1970, 41, 3922; ibid., 3561; ibid., 1969, 40, 4151. FISCHER (D.W.) and BAUN (W.L.), J. Appl. Phys., 1968, 39, 4757.
- [24] MANNE (R.), private communication.
- [25] RAMQVIST (L.), EKSTIG (B.), KALLNE (E.), NORELAND (E.), and MANNE (R.), J. Phys. Chem. Solids, 1971, 32, 149. HOLLIDAY (J.E.), "The Electron Microprobe", (McKinley, Heinrich, and Wittry, eds., John Wiley) 1966, 3.
- [26] NEMNONOV (S.A.) and KOLOBOVA (K.M.), Fiz. Metal. Metalloved., 1966, 22, 680; transl. Physics Metals Metallogr., 1966, 22, 36.
- [27] PARRATT (L.G.), Rev. Mod. Phys., 1959, 31, 616. NAGEL (D.J.), "Advances in X-Ray Analysis" (Plenum Press), 1970, Vol. 13, 182.
- [28] MANNE (R.), J. Chem. Phys., 1970, 52, 5733.

FIGURE CAPTIONS

FIG. 1. (a) The cohesive energy of cesium metal as a function of primitive unit cell volume for the bcc and fcc lattices.

(b) The pressure required to compress cesium to the indicated unit cell volume, as determined from the non-equilibrium virial theorem.

In both (a) and (b) the circles and squares represent, respectively, the calculated values for the fcc and bcc structures. The dashed and solid curves are drawn to connect the calculated points.

- FIG. 2. The enthalpy calculated for fcc Cs for pressures near those of the computed isomorphic transition. The circles are the calculated points, which have simply been connected by straight line segments.
- FIG. 3. Components of the Cs valence charge inside the APW spheres corresponding to the L = 0, 1, and 2 spherical harmonics, and the component outside the spheres. The L = 2 (d-like) component is found to be closely related to the isomorphic transition, the compression, and the topological changes which occur in the Fermi surface.
- FIG. 4. Computed magnetic moment of vanadium metal as a function of its lattice parameter, showing the abrupt transition from non-magnetic to magnetic behavior. The dashed and solid curves bracket the behavior near the

26

transition point. Either of the two magnetic moments calculated for a = 7.0 a.u. is obtained, depending on the magnitude of the initial assumed magnetic moment in the self-consistency iterations.

- FIG. 5. Cohesive energy calculated for V, as a function of lattice parameter. The error bar indicates the experimental equilibrium lattice constant and cohesive energy, for comparison.
- FIG. 6. Non-magnetic densities of states, showing the increase in the density of states at the Fermi energy which eventually gives rise to magnetic behavior as the lattice parameter is increased further.
- FIG. 7. Magnetic densities of states for a = 8.5 a.u., for majority (α) and minority (β) spin, showing exchange shift between corresponding states with opposite spin, in the magnetic state.
- FIG. 8. Soft X-ray emission spectra from TiC: C K (solid curve), Ti - K (dotted), and Ti-L_{II,III} (dashed) spectra, as reported in references [22], [21], and [23], respectively.
- FIG. 9. Soft x-ray emission spectra from NbC: C K, Nb L_{III}, and Nb - M_{IV.V}, from reference [25].
- FIG. 10. Decomposition of the $\text{Ti}-L_{\text{II},\text{III}}$ emission spectrum from TiC into separate, proportional L_{II} and L_{III} components, separated by the energy splitting between the atomic L_{III} and L_{III} peaks.

- FIG. 11. Experimental C-K emission (smooth curves) from TiC, according to Holliday [22] as reported by Ramqvist et al. [21], and C - & = 1 partial density of states. Dashed curve corresponds to an 0.6 eV adjustment in relative Fermi energies.
- FIG. 12. Experimental Ti-K emission curves and calculated Ti-l = 1partial density-of-states histogram for TiC. Dotted curve is from Nemnonov and Kolobova [26]. Solid is uncorrected and dashed is corrected data from Ramqvist, et al. [21]. Dotdash curve is obtained from shifting dashed curve by 0.6 eV.
- FIG. 13. Ti L_{II} (from Fischer [23]) emission (smooth curves) and Ti- ℓ = 2 curves for TiC. Result of 0.6 eV shift is shown as dashed curve.
- FIG. 14. Comparison of C l = 1 partial density of states (histogram) for NbC with the C-K emission (smooth curve) reported by Ramqvist, et al. [25].
- FIG. 15. NbC Nb L_{III} emission, from Ramqvist, et al. [25], compared with the Nb- ℓ = 2 partial density of states.
- FIG. 16. Partial Nb $M_{IV,V}$ emission, from Holliday [25], and Nb - ℓ = 1 partial density of states. Dashed curve shows correction for apparent spectrometer callibration error, reported by Ramqvist et al. [25]. An additional peak in the spectrum has now been observed [24], in good agreement with the partial-density-of-states peak at about -11 eV. Separation of the two Nb-M peaks shown is also the energy

difference between the M_{IV} and the M_V transition, which renders the interpretation of this curve less certain than is the case for the others shown.







FIG. 1. Cs cohesive energy and pressure.



FIG. 3. Cs charge components.

.









FIG. 12. Ti-K emission from TiC.









FIG. 16. Nb-M $_{\rm IV,V}$ emission from NbC.