count for DMR in zero magnetic field also explain the absence of DMR in a strong magnetic field, under the conditions established in these experiments. This provides strong evidence that the anisotropy and energy dependence of electron-phonon scattering is the principal cause of DMR in aluminum, at least at low impurity concentrations.

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[1] In those regimes where Matthiessen's rule is apparently obeyed, e.g., alloys at high temperatures, it is only approximately obeyed and then only over a small temperature range.

[2] J. Bass, Adv. Phys. 21, 431 (1972).

[3] J. S. Langer, Phys. Rev. 127, 5 (1962).

[4] A. B. Bhatia and O. P. Gupta, Phys. Lett. A29, 358 (1969); Yu. Kagan and A. P. Zhernov, Zh. Eksp. Teor. Fiz. 60, 1832 (1971) [Sov. Phys. JETP 33, 990 (1971)].

[5] See, for example, Kagan and Zhernov, Ref. 4, and references therein.

[6] See, for example, Yu. Kagan and V. N. Flerov, Zh. Eksp. Teor. Fiz. 66, 1374 (1974) [Sov. Phys. JETP 39, 673 (1974)]; J. W. Ekin and A. Bringer, Phys. Rev. B 7, 4468 (1973); W. E. Lawrence and J. W. Wilkins, Phys. Rev. B 6, 4466 (1972); Y. Bergman, M. Kaveh, and N. Wiser, Phys. Rev. Lett. 32, 606 (1974); W. D. Jumper and W. E. Lawrence, Phys. Rev. 16, 3314 (1977), and references listed in M. R. Cimberle, G. Bobel, and C. Rizzuto, Adv. Phys. 23, 639 (1974), and Ref. 2.

[7] Cimberle, Bobel, and Rizzuto, Ref. 6.

[8] D. K. Wagner, Phys. Rev. B 5, 336 (1972), and Ph.D. thesis, Cornell University, 1971 (unpublished).

[9] I. M. Lifshitz, M. Ya Azbel, and M. I. Kaganov, Zh. Eksp. Teor. Fiz. 31, 63 (1956) [Sov. Phys. JETP 4, 41 (1957)].

[10] P. T. Coleridge and P. M. Holtham, J. Phys. F 7, 1891 (1977).

[11] R. J. Douglas and W. R. Datars, Can. J. Phys. 51, 1770 (1973).

[12] F. R. Fickett, Cryogenics 11, 349 (1971).

[13] T. Amundsen and P. Jerstad, J. Low Temp. Phys. 15, 4596 (1974).

[14] W. Kesternick and C. Papostaikoudis, J. Phys. F 7, 837 (1977).

[15] The design is similar to that of P. M. Martin, J. B. Sampsell, and J. C. Garland, Phys. Rev. B 15, 5598 (1977).

[16] A. Matthiessen and C. Vogt, Ann. Phys. (Leipzig) 122, 19 (1864).

[17] V. N. Morgun, V. I. Khotkevich, N. N. Chebotaev, and V. A. Bondar, Fiz. Nizk. Temp. 2, 130 (1976) [Sov. J. Low Temp. Phys. 2, 634 (1977)]; M. I. Kaganov, A. M. Kadigrohov, and A. A. Slutskin, Zh. Eksp. Teor. Fiz. 53, 1135 (1967) [Sov. Phys. JETP 26, 670 (1968)].

Microscopic Basis of Miedema's Empirical Theory of Transition-Metal Compound Formation

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The success of Miedema's empirical theory of transition-metal compound formation has given credence to the physical picture used in its construction. Self-consistently calculated electron densities, state densities, and heats of formation reveal this picture to be inappropriate. Miedema's success is shown to result from the implicit incorporation of a dominant chemical trend, which is well described by Pettifor's d-bond model.

The success of an empirical theory due to Miedema and co-workers[1] has generated interest in the microscopic mechanisms responsible for intermetallic compound formation. The theory asserts that a large body of experimental data reflects the interplay of *just two* constituent properties, a rather ill-defined "electronegativity", $\varphi(z)$, and the electron density, $\rho(z)$, at the boundary separating atomic cells in the constituent (z is the atomic number). The heat of compound formation $\Delta H(z_a, z_b)$ (the total energy of the compound less those of the constituents) is, according to Miedema, simply[2]

$$\Delta H(z_a, z_b) = [\rho(z_a) - \rho(z_b)]^2 - [\varphi(z_a) - \varphi(z_b)]^2. \quad (1)$$

We consider here the microscopic significance of the parameters $\rho(z)$ and $\varphi(z)$; and their relevance to the heat of formation.

Our analysis is based on the direct, internally consistent calculation of *both* the heat of formation and all the microscopic quantities (electron densities, chemical potentials, etc.) on which it is expected to depend. The relevant virtues of our method of analysis are: (a) Calculated heats of formation agree well with available measurements.[3] (b) The efficiency of our augmented-spherical-wave (ASW) method[3] makes possible the study of chemical trends by permitting the calculation of $\Delta H(z_a, z_b)$ for entire classes of compounds. (The ASW method is the only available source of theoretical total energies for transition-metal compounds.) (c) The fact that heats of formation are an order of magnitude smaller than cohesive energies makes it particularly important that our analytical procedure depends in no way on the system to which it is applied. (The only inputs are constituent atomic numbers and a crystal structure; equilibrium volumes are given by total-energy minimization.)

We restrict the present discussion to the class of compounds for which Miedema's formula is appropriate in its simplest form,[1] that is, to compounds involving only transition metals. Previous efforts to establish a microscopic picture of bonding in these systems consist of three principal components: (1) *Miedema's picture,* based on Eq. (1) and the interpretation of the parameters $\varphi(z)$ and $\rho(z)$ that enter it, (2) the *chemical-potential model,*[4] based on the equilibration of constituent chemical potentials by means of charge transfer, and (3) the *d-bond model,*[5] based exclusively on bonding among the localized *d* electrons.

The evidence supporting *Miedema's picture* is (a) his ability to predict almost unerringly the sign (and often the magnitude) of the heat of formation; (b) the fact that $\rho(z)$ deduced by Miedema from compressiblity data and adjusted to improve the predictions of Eq. (1) correlates well with the boundary electron densities given by first-principles calculations[6]; (c) the existence of the interfacial electron-density rearrangements emphasized by Miedema is unambiguously confirmed by the present calculations for compounds.

The plausibility of the *chemical-potential* model stems from the point-by-point justification it provides for both the form of Eq. (1) and for its ingredients $\rho(z)$ and $\varphi(z)$. This model applies rigorously only to compounds formed from constituents possessing the same boundary density (footnote 7 of Ref. 4). This apparent limitation is exploited by considering the formation process to consist of two steps, the first of which eliminates the density mismatch by compressing the constituent possessing the smaller boundary density and vice versa; the second step is described by the chemical-potential model *per se*. The strain energy required by the preparation (compression/expansion) step neatly accounts for the positive term in Eq. (1); the fact that bonding in the chemical-potential model is due to charge transfer induced by the chemical-potential difference between the constituents accounts for the negative term. This model thus identifies $\varphi(z)$ as the chemical potential of the prepared constituents. The strong correlation[4] between calculated values for the latter and Miedema's $\varphi(z)$ supports this interpretation. However, since the model provides no means of calculating charge transfer in the compound, which the model requires, it has not previously been extensively or stringently tested.

Supporting the *d-bond model*, proposed by Pettifor,[5] is the fact that it (a) provides the correct interpretation of elemental transition-metal cohesion; and (b) convincingly accounts for the single chemical trend which dominates bonding in these systems (see below). The source of bonding in this model is not charge transfer among states near E_F, as in the chemical-potential model, but rather pervasive changes in the valence band, driven by the nondegeneracy of the constituent *d* levels. The source of resistance to bonding is yet more controversial; the *d*-bond model completely ignores the *s* and *p* electrons responsible for the interfacial density rearrangements to which resistance to bonding is ascribed by both Miedema and the chemical-potential model. The paradoxical nature of the controversy is heightened by the fact that our calculations confirm the existence of these rearrangements, which consist of a dipole layer formed by the spillout of (*s* and *p*) electrons from the constituent having the larger boundary density. One would expect the electrostatic potential of such a dipole layer to strongly affect the energy separation of the constituent *d* levels. Since the *d*-bond model depends critically on this separation, how can the neglect of

s and p electrons be justified?

Above is the puzzle presented to us by previous work; a summary of our resolution of that puzzle is: (1) The information contained in $\Delta H(z_a,z_b)$ (particularly its sign) is far less than had been thought and can be reproduced within a particular transition series with far fewer parameters than used by Miedema. There is no reason, therefore, to accept the importance (for the heat of formation) ascribed to $\rho(z)$ and $\varphi(z)$ by Miedema. (2) The chemical-potential model is simply inappropriate for these systems.[7] (3) The d-bond model is correct. In particular, its neglect of s and p electrons is both justifiable and understandable. The balance of this report is a summary of the evidence supporting these conclusions; a more detailed description will be published separately.

With the informational content of $\Delta H(z_a,z_b)$ (in particular, its sign) in mind, consider the 28 binary combinations of the eight $4d$ transition metals Y through Pd. (Our experience with transition-metal cohesion[6] indicates that the unimportance of both relativistic and magnetic effects in these systems makes them the "hydrogen atom" of this context.) The construction that reveals the informational content of this array is the quantity $\Delta H(z_a,z_b)/(\Delta z)^2$ $(\Delta z \equiv z_a - z_b)$ plotted as a function of $\bar{z}$ $[\equiv (z_a+z_b)/2]$. The motivation for this construction is the form of the Taylor-series expansion of $\Delta H(z_a,z_b)$ in powers of Δz:

$$\Delta H(z_a,z_b) = \Delta H_2(\bar{z})(\Delta z)^2 + \Delta H_4(\bar{z})(\Delta z)^4 + \dots \quad (2)$$

This form is dictated by the definition of ΔH [i.e., $\Delta H(z_a,z_b) \equiv \Delta H(z_b,z_a)$ and $\Delta H(z,z) \equiv 0$]; physical considerations affect only the rate of convergence (discussed below). Equation (2) shows that, to the extent that the quadratic term dominates the series, the entire set of 28 heats of formation is described by the single $\Delta H_2(\bar{z})$. Figure 1 shows the extent to which this is the case. Plotted in Fig. 1 are the (normalized) heats of formation given by Miedema's formula and those given by our calculations for two crystal structures.[8] The dependence of $\Delta H(z_a,z_b)/(\Delta z)^2$ both on crystal structure and on Δz will be discussed below. More important to the present discussion is the overall similarity of the curves in Fig. 1, the fact that compounds for which $\bar{z}$ is near the middle of the transition series form ($\Delta H < 0$), while those for which $\bar{z}$ is near either end of the series do not. Bearing in mind that Miedema is primarily concerned with the sign of the heat of formation (deducible from phase diagrams), we note that the curves in Fig. 1 corresponding to different values of Δz pass through zero at approximately common values of $\bar{z}$. This means that the sign of all 28 heats of formation is described by just

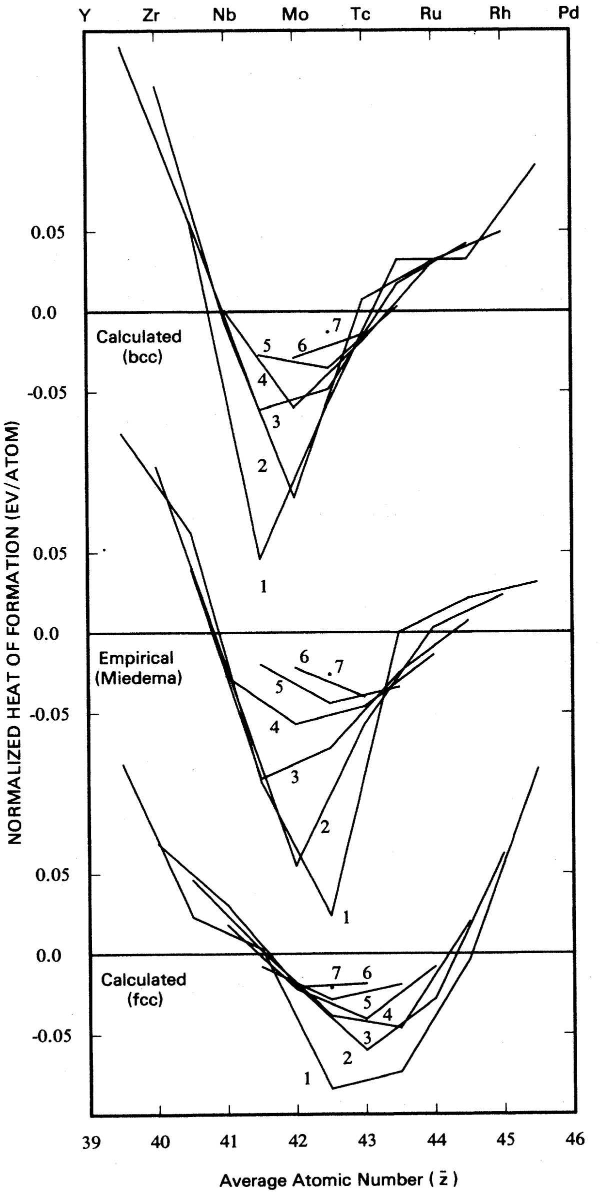

FIG. 1. Normalized heats of formation $\Delta H(z_a, z_b)/(\Delta z)^2$ vs the average atomic number $\bar{z}$. z_a and z_b are the constituent atomic numbers; Δz is their difference. Integers indicate the common value of Δz of points connected by lines. Miedema's results are tabulated in Ref. 1. Theoretical values were calculated using the parameter-free ASW method (Ref. 3). For the compounds, the labels fcc and bcc indicate the CuAu and CsCl structures, respectively (see Ref. 8). Available experimental data: RhPd, $\Delta H = +0.104$ eV/atom [Ref. 9(a)]; ZrRu, $\Delta G/(\Delta z)^2 = -0.058$ eV/atom [Ref. 9(b)]; NbMo, $\Delta H = -0.097$ eV/atom [Ref. 9(c)].

two numbers $\bar{z}_1$ and $\bar{z}_2$, the two nodes of $\Delta H_2(\bar{z})$. To see how these two numbers are incorporated in Miedema's formula, we expand Eq. (1) in powers of Δz, obtaining for the important quantity $\Delta H_2(\bar{z})$

$$\Delta H_2(\bar{z}) = [\rho'(\bar{z})]^2 - [\varphi'(\bar{z})]^2, \qquad (3)$$

where the prime indicates differentiation with respect to z. Thus, the requirement that $\Delta H_2(\bar{z})$ vanish for $\bar{z} = \bar{z}_1$ and $\bar{z}_2$ translates into the requirement that

$$|\varphi'(z)| = |\rho'(z)|; \quad z = \bar{z}_1, \bar{z}_2. \qquad (4)$$

This observation greatly reduces the importance of Miedema's interpretation of $\varphi(z)$ and $\rho(z)$, because we see that *any two properties of the constituents, regardless of their relevance to the formation process, will, in conjunction with Eq. (1), equally well describe the sign of the heat of formation for this series, as long as they satisfy the two conditions of Eq. (4).* Let us emphasize at this point that our purpose here is not to criticize either the use or the utility of Miedema's formula, but rather to decouple its empirical success from the physical picture used to describe it.

Consider now our second conclusion that the chemical-potential model is inappropriate for transition-metal compounds. Our confidence in this categorical conclusion stems from the fact that the model is based on a single, mathematically precise assumption which we can test with our calculations. The physical content of the assumption is that the local chemical potential inside each constituent atomic cell is unaffected by the compound-formation process, except for rigid electrostatic shifts due to charge transfer. This assumption leads, without further approximation, to a simple expression for the nonelectrostatic portion of the heat of formation, called the electrochemical energy in Ref. 4. We find this quantity to have the wrong sign[10] in most of the systems we have studied and to have a magnitude which is frequently incorrect by an amount greater than ΔH itself. This unambiguous failure, together with the success of the d-bond model (which is based on precisely the *inter*atomic wave-mechanical interactions ignored by the chemical-potential model), would seem to preclude any Thomas-Fermi-like (non-wave-mechanical kinetic energy) theory of transition-metal compound formation.

Our third principal conclusion is that Pettifor's d-bond model is fundamentally correct. We have used our calculations to check in detail the numerous and seemingly drastic assumptions on which the model is based (constant state densities, single d band in the compound, neglect of two-electron terms, and neglect of s and p electrons). We find, in particular, that the s and p electrons transfer in whichever direction is required for the elimination of the boundary-density mismatch, but that this transfer has little effect on the d levels. The d-electron transfer is quite independent and is governed by the d-level separation much as described by Pettifor.[11] The neglect of the s and p electrons is therefore justifiable, but why? The answer lies in a systematic cancellation of interatomic and intraatomic Coulomb electrostatic effects. The important observation is that the *inter*atomic (Madelung) effect can be represented as due to charge transferred to the region just inside the surface of the atomic cell where it cancels the *intra*atomic effect of the interfacial dipole layer.

Both the crystal structure and the Δz dependence of $\Delta H(z_a, z_b)/(\Delta z)^2$ seen in Fig. 1 can be traced to the dependence of the total energy on geometry-related variations in the d-band state density—through the sum of single-particle energies. This sum is the only source of rapid variation in ΔH with atomic number; it therefore controls the convergence of the series in Eq. (2) and, therefore, the Δz dependence of the curves in Fig. 1. Compounds corresponding to small Δz probe the rapid variations of this sum, whereas those corresponding to larger Δz sample its overall parabolic dependence on the number of d electrons.[5,12] This sum is also responsible for the known[13] relative stability of the bcc and fcc structures in the first and second halves of each transition series, which, in turn, is responsible[14] for the explicit geometry dependence (bcc vs fcc) seen in Fig. 1.

We gratefully acknowledge helpful discussions with N. D. Lang, P. de Chatel, A. R. Miedema, and E. S. Machlin.

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[1] A. R. Miedema, Philips Tech. Rev. 36, 217 (1976); see also A. R. Miedema, R. Boom, and F. R. deBoer, J. Less-Common Met. 41, 283 (1975).

[2] For simplicity, we absorb the constants which usually appear in Miedema's formula (see Ref. 1) into the definitions of $\varphi(z)$ and $\rho(z)$.

[3] A. R. Williams, J. Kübler, and C. D. Gelatt, Jr., Phys. Rev. B 19, 6094 (1979).

[4] J. A. Alonso and L. A. Girifalco, Phys. Rev. B 19, 3889 (1979).

[5] D. G. Pettifor, Phys. Rev. Lett. 42, 846 (1979).

[6] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978). See, in particular, page 6.

[7] Our preliminary results for compounds composed of a transition metal and a nontransition metal suggest the importance of interatomic covalent interactions in these systems as well. It is likely that the model is appropriate for intermetallic compounds not involving transition metals. It is ironic that Miedema indicates that his analysis does not apply to such systems. (See caption to Table I in Ref. 1.)

[8] For curves labeled fcc (bcc), heats of formation are the total-energy difference between compounds in the CuAu (CsCl) structure and elements in the fcc (bcc) structure. The CuAu (CsCl) structure reduces to the fcc (bcc) structure, for identical constituents.

[9a] K. M. Myles, Trans. Metall. Soc. AIME 242, 1523 (1968).

[9b] L. Brewer and P. R. Wengert, Metall. Trans. 4, 83 (1973).

[9c] S. C. Singhal and W. L. Worrell, Metall. Trans. 4, 1125 (1973).

[10] We compare the electrochemical energy per atom $-\frac{1}{4}Q\Delta\mu$ to the heat of formation minus its electrostatic (Madelung) component. The relevant heat of formation is that relative to the prepared constituents. We have used the particular definitions of the charge transfer Q and the chemical-potential difference $\Delta\mu$ which arise in the model (see Ref. 4).

[11] D. G. Pettifor, Solid State Commun. 28, 621 (1978).

[12] The discussion of Eq. (2) suggests that the chemical trend exhibited by Fig. 1 is embodied in the coefficient $\Delta H_2(\bar{z})$ in the expansion $\Delta H(z_a, z_b) = \Sigma_n \Delta H_n(\bar{z}) f_n(\Delta z)$, where $f_n(x) = x^n$. The existence of geometry-derived rapid variations with Δz means that the coefficient of the most slowly varying member of a set of oscillatory functions [e.g., $f_n(x) = \cos(nx)$] would be somewhat more appropriate.

[13] D. G. Pettifor, J. Phys. C 3, 36 (1970); O. K. Andersen, J. Madsen, U. K. Poulsen, O. Jepsen, and J. Kollar, Physica 86-88B, 249 (1977).

[14] The second valence derivative of the geometry dependence of the d-bond energy (Ref. 13) explains the fcc-bcc difference in Fig. 1.