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Periodic table of 3d-metal dimers and their ions

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The ground states of the mixed 3d-metal dimers TiV, TiCr, TiMn, TiFe, TiCo, TiNi, TiCu, TiZn, VCr, VMn, VFe, VCo, VNi, VCu, VZn, CrMn, CrFe, CrCo, CrNi, CrCu, CrZn, MnFe, MnCo, MnNi, MnCu, MnZn, FeCo, FeNi, FeCu, FeZn, CoNi, CoCu, CoZn, NiCu, NiZn, and CuZn along with their singly negatively and positively charged ions are assigned based on the results of computations using density functional theory with generalized gradient approximation for the exchange-correlation functional. Except for TiCo and CrMn, our assignment agrees with experiment. Computed spectroscopic constants (r_e, ω_e, D_o) are in fair agreement with experiment. The ground-state spin multiplicities of all the ions are found to differ from the spin multiplicities of the corresponding neutral parents by ± 1 . Except for TiV, MnFe, and MnCu, the number of unpaired electrons, N , in a neutral ground-state dimer is either $N_1 + N_2$ or $|N_1 - N_2|$, where N_1 and N_2 are the numbers of unpaired 3d electrons in the $3d^n 4s^1$ occupation of the constituent atoms. Combining the present and previous results obtained at the same level of theory for homonuclear [Gutsev and Bauschlicher, *J. Phys. Chem. A* **107**, 4755 (2003)] 3d-metal and ScX ($X = \text{Ti-Zn}$) dimers [Gutsev, Bauschlicher, and Andrews, in *Theoretical Prospects of Negative Ions*, edited by J. Kalcher (Research Signpost, Trivandrum, 2002), pp. 43–60] allows one to construct “periodic” tables of all 3d-metal dimers along with their singly charged ions. © 2004 American Institute of Physics. [DOI: 10.1063/1.1788656]

I. INTRODUCTION

Contrary to the homonuclear 3d-metal dimers, which were the subject of numerous experimental^{1,2} and theoretical^{3–7} studies, heteronuclear 3d-metal dimers received considerably less attention. By 1985, the ground states of only 16 mixed dimers have tentatively been assigned⁶ on the basis of measurements of species trapped in inert matrices. Subsequent experimental studies were performed for ScCr (electron spin resonance [ESR], $X^6\Sigma$),⁷ ScNi [ESR, $X^2\Sigma$,^{8,9} and resonant two-photon ionization spectroscopy [R2PI], $X^2\Sigma^+$, $\Delta G''_{1/2} = 334.4 \text{ cm}^{-1}$ (Ref. 10)], TiV [ESR, $^4\Sigma$,¹¹ R2PI, $D_o^0 = 2.068 \pm 0.001 \text{ eV}$ (Ref. 12)], TiCo [ESR, $X^2\Sigma^+$,⁸ R2PI, $D_o^0 = 2.401 \pm 0.001 \text{ eV}$,¹² $X^2\Sigma^+$ (Ref. 13)], VCr (R2PI, $^2\Delta_{5/2}$, $r_o = 1.7260 \pm 0.0011 \text{ \AA}$),¹⁴ VFe and VCo (resonance Raman spectroscopy $\omega_e = 433$ and 461 cm^{-1} , respectively),¹⁵ VNi [ESR, $^4\Sigma$,¹¹ R2PI, $D_o^0 = 2.100 \pm 0.001 \text{ eV}$ (Ref. 12)], CrMn (ESR, $X^4\Sigma$),¹⁶ CrFe (RRS, $\omega_e = 166.6 \pm 0.8 \text{ cm}^{-1}$),¹⁷ NiCu (R2PI, $X^2\Delta_{5/2}$, $r_e = 2.233 \pm 0.006 \text{ \AA}$, $\omega_e = 273.01 \pm 1.15 \text{ cm}^{-1}$, $D_o = 2.05 \pm 0.10 \text{ eV}$).^{19–21} Photoelectron detachment spectra were obtained for NiCu[−] (Ref. 21) and MnCu[−] (Ref. 22). Dissociation energies of the MFe⁺ dimers ($M = \text{Sc, Ti, V, Cr, Co, Ni, and Cu}$) were obtained²³ using photodissociation.

Theoretical studies have been performed for a number of heteronuclear dimers using various *ab initio* and DFT techniques. ScNi was computed at both multireference configuration interaction (MRCI)²⁴ and local spin density approximation (LSDA) (Ref. 25) levels. Their results are in reasonable agreement with those from subsequent density functional theory with generalized gradient approximation (DFT-GGA) calculations,²⁶ except for D_o , where the MRCI values is half that of the DFT-GGA while the LSDA result is three times larger than the DFT-GGA value. TiV was computed at both LSDA (Ref. 27) and complete active space self-consistent field²⁸ (CASSCF) levels. The difference in the computed bond lengths is 0.09 \AA , while the computed dissociation energies differ by as much as 5 eV. VCr (Ref. 29) and VNi (Ref. 27) were computed at the LSDA level. TiFe,³⁰ CrMn,³¹ CrFe,³⁰ FeNi,³⁰ and NiCu (Refs. 32 and 33) were computed at different DFT-GGA levels but the ground states have not been assigned. Shim has computed FeNi (Ref. 34) and NiCu (Ref. 35) at the single-reference CI level and obtained the ground states $^5\Pi$ and $^2\Delta$, respectively.

The results of our computations of the homonuclear 3d-metal dimers and their ions performed at different DFT-GGA levels are found to be in good agreement with experimental data, which strongly suggests that the same level of theory can be applied to mixed 3d-dimers and their singly charged ions. The computed results could serve as a useful

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guide for future experimental studies, especially for those dimers for which no other data is available.

The aim of this work is to tentatively assign ground states, where the assignment is not yet established, of all the mixed $3d$ -metal dimers and their singly charged anions and cations, as well as to compute their spectroscopic constants: equilibrium bond lengths (r_e), harmonic vibrational frequencies (ω_e), dissociation energies (D_o). For the neutral dimers, the permanent dipole moments (μ), electron affinities (EA), and ionization energies (IE) are also reported. We should note that for some systems the states are close in energy and not all states are equally well described by a single configuration, and therefore, some of our tentative assignments of the ground state may be incorrect. However, this level of theory is the only one currently available that allows us to study all of these systems in a reasonable time and begin to establish the trends that exist for this class of compounds.

II. COMPUTATIONAL DETAILS

Different GGA functionals such as BLYP (Becke's exchange³⁶ and Lee-Yang-Parr's correlation³⁷), BP86 (Becke's exchange³⁶ and Perdew's correlation³⁸), BPW91 (Becke's exchange³⁶ and Perdew-Wang's correlation³⁹), BPBE (Becke's exchange³⁶ and Perdew-Burke-Ernzerhof's correlation⁴⁰), PBEPBE (or PBE*2) (Perdew-Burke-Ernzerhof's exchange and correlation), and PW91PW91 (or PW91*2) (Perdew-Wang's exchange and correlation) provided rather similar results for the homonuclear $3d$ dimers. Therefore, we choose to apply the BPW91 method in computations of the heteronuclear $3d$ dimers keeping in mind that vibrational frequencies computed with this approach are shown⁴¹ to be less sensitive to the integration grid.

The GAUSSIAN 98 program⁴² was used for all of the DFT calculations. We used the basis set denoted as 6-311+G* in the GAUSSIAN program, namely, $(15s11p6d1f)/[10s7p4d1f]$ ⁴³⁻⁴⁵ and the standard integration grid⁴² (FINE, pruned [99,302]). After the bond length of a dimer was optimized, the harmonic frequency calculation was performed using analytical second derivatives. Spatial symmetries of the wave functions corresponding to the optimized states were assigned using Slater determinants based on Kohn-Sham orbitals as is done in a conventional unrestricted-Hartree-Fock scheme. Correspondingly, the spin multiplicities are the differences between the numbers of majority (spin-up) and minority (spin-down) electrons plus one. Spin-unrestricted calculations were performed for all the states including the singlet states.

The optimizations are performed for each possible spin multiplicity until further increasing the spin multiplicity would result in a state whose total energy is above the energy of the lowest asymptote. Assignment of states whose spin-orbitals were not resolved by symmetry (Π , Φ , and occasionally Δ) was based on the analysis of the content of valence molecular orbitals in terms of atomic contributions and the results of the natural bond order (NBO) analysis.^{46,47}

Chart 1

| Atom | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|--------------------|------|------|------|------|------|------|------|-------|------|------|
| Δ_{sd} , eV | 1.43 | 0.81 | 0.25 | ... | 2.15 | 0.87 | 0.42 | -0.03 | ... | ... |
| IE, eV | 6.56 | 6.83 | 6.74 | 6.77 | 7.44 | 7.90 | 7.86 | 7.64 | 7.73 | 9.39 |
| EA, eV | 0.18 | 0.08 | 0.52 | 0.67 | ... | 0.16 | 0.66 | 1.16 | 1.23 | ... |

The electron affinities and ionization energies reported in this work are adiabatic values, that is, each state is at its equilibrium bond length

$$EA = E_{\text{tot}}(AB) - E_{\text{tot}}(AB^-) + 1/2\omega_e(AB) - 1/2\omega_e(AB^-),$$

$$IE = E_{\text{tot}}(AB^+) - E_{\text{tot}}(AB) + 1/2\omega_e(AB^+) - 1/2\omega_e(AB).$$

Dissociation energies are obtained as the differences in total energies of a dimer and its constituents

$$D_o = E_{\text{tot}}(AB) - E_{\text{tot}}(A) - E_{\text{tot}}(B) + 1/2\omega_e.$$

In our atomic computations, symmetry and equivalence restrictions are not imposed, and the solutions are in general a mixture of $3d^n4s^2$ and $3d^{n+1}4s^1$ occupations.⁴⁸

III. RESULTS AND DISCUSSIONS

The number of open-shell electrons (N) in the ground states of the mixed ScX ($X = \text{Ti-Zn}$) dimers are related^{26,49} to the numbers of unpaired $3d$ electrons in the $3d^24s^1$ and $3d^m4s^1$ occupations of Sc and X, two and N_x , respectively, according to a simple rule: N is either $2 + N_x$ or $|2 - N_x|$. The ions ScX^- and ScX^+ were found⁴⁹ to have the ground-state spin multiplicities that are larger or smaller by one (a “ ± 1 rule”) than the corresponding neutrals. These two empirical rules will serve as a useful guide when searching for the unknown ground states of the mixed $3d$ -metal dimers and their ions.

The NBO analysis,^{46,47} which describes chemical bonding in terms of localized (Lewis) orbitals, turns out to be very helpful⁵⁰ in describing the bonding trends of the homonuclear $3d$ -dimers and their ions. For these species, there are sets of six possible bonding orbitals: $4s + 4s$, $3d_\sigma + 3d_\sigma$, two $3d_\pi + 3d_\pi$, two $3d_\delta + 3d_\delta$ and the corresponding antibonding orbitals (neglecting small contributions from $4p$ and higher angular momentum atomic orbitals). Because the two atoms are different, the bonding and antibonding orbitals are asymmetric in the mixed dimers. However, for simplicity, we do not note the polarization unless the orbitals are very asymmetric. An occupied bonding-antibonding pair in a given spin representation corresponds to two localized atomic spin orbitals (LSO).

Since there is only one $4s + 4s$ bonding orbital (BO) in each spin representation, it is expected that atoms with a $3d^n4s^2$ ground state occupation will promote an electron to reach the $3d^{n+1}4s^1$ occupation in most cases. The experimental $3d^n4s^2 \rightarrow 3d^{n+1}4s^1$ promotion energies Δ_{sd} are summarized in Chart 1 together with ionization energies and electron affinities.²⁰ There is no promotion energy for Cr, Cu, and Zn, since they possess $3d^54s^1$, $3d^{10}4s^1$, and $3d^{10}4s^2$ ground-state electronic configurations, respectively.

While the lowest spin-orbit component of the Ni atom arises from the $3d^8 4s^2$ occupation, $3d^9 4s^1$ occupation is somewhat lower than its $3d^8 4s^2$ occupation if one uses the weighted average of the spin-orbit components. Despite the large promotion energy, we find that Sc in the ScX dimers has a $3d^2 4s^1$ occupation. For the MnX species promotion occurs for all species except MnFe and MnCu, as discussed below.

A. Electronic structure and bonding of the neutral dimers and its ions

We are using the NBO results to describe the changes occurring when moving along rows in the neutral (Table I), negatively charged (Table II), and positively charged (Table III) species. For each dimer, we discuss first the electronic structure of the neutral and then we describe the changes invoked by attachment and detachment of an electron. For convenience, we will position the lighter atom to be the first in a dimer chemical symbol. Since the electronic structure and chemical bonding of the homonuclear and mixed ScX dimers were discussed elsewhere,^{26,49} we begin with TiV.

TiV. If the “spin multiplicity rule” is valid, then the ground state of TiV has to have a spin multiplicity of two or eight. However, the lowest energy state found is $^4\Sigma^-$ [Ti($3d^{3.0} 4s^{0.90}$), V($3d^{4.2} 4s^{0.90}$)] in agreement with experiment¹¹ and results of the LSDA and CASSCF calculations.^{27,28} Our BPW91 set of spectroscopic constants presented in Table I ($r_e = 1.78 \text{ \AA}$, $\omega_e = 562 \text{ cm}^{-1}$, $D_o = 2.78 \text{ eV}$) has to be compared with the LSDA ($r_e = 1.76 \text{ \AA}$, ω_e is not given, $D_o = 5.88 \text{ eV}$) (Ref. 27) and CASSCF ($r_e = 1.86 \text{ \AA}$, $\omega_e = 495 \text{ cm}^{-1}$, $D_o = 0.80 \text{ eV}$) (Ref. 28) results along with the experimental¹² D_o of $2.068 \pm 0.001 \text{ eV}$. The BPW91 D_o value is in reasonable agreement with the experiment considering that the D_o values obtained using the BPW91 approach, as well as other pure DFT methods, are usually larger than experiment by up to 1 eV (Refs. 49 and 50) for the neutral dimers. However, the BPW91 D_o values of the dimer ions are expected to be in better agreement with experiment because the atomic DFT calculations reproduce^{48,51} $3d^m 4s^2$ (anions) and $3d^1$ (cation) electronic configurations with less admixtures than in the neutral atoms.

The lowest doublet state of TiV is a $^2\Gamma$ state, which has five BO ($4s+4s$, $3d_\sigma+3d_\sigma$, two $3d_\pi+3d_\pi$, $3d_\delta+3d_\delta$) in the α -spin representations and four β -BOs ($3d_\sigma 4s+3d_\sigma 4s$, two $3d_\pi+3d_\pi$, $3d_\delta+3d_\delta$). The ground $^4\Sigma^-$ state has six α -BOs [$4s+4s$, $3d_\sigma+3d_\sigma$, two $3d_\pi+3d_\pi$, two $3d_\delta+3d_\delta$] and three β -BOs ($4s+4s$, two $3d_\pi+3d_\pi$) and is below the $^2\Gamma$ state by 0.29 eV. Since both states have nine bonding orbitals, the ground state is probably $^4\Sigma^-$ due to its larger d - d exchange energy.

The ground state of TiV⁻ arises from adding an electron to the β -($3d_\sigma+3d_\sigma$) BO, while the ground state of TiV⁺ is formed by detachment of an electron from the α -($4s+4s$) BO. Both ions have $^3\Sigma^-$ ground states and, thus, their spin multiplicities obey the ± 1 rule. The bond length elongates by 0.03 Å in the anion and decreases by 0.08 Å in the cation as compared to the bond length in the neutral parent, see Tables II and III.

TiCr. The ground state found is $^3\Sigma^-$ [Ti($3d^{2.73} 4s^{1.02}$),

Cr($3d^{5.24} 4s^{0.99}$)] where an additional, with respect to TiV, electron fills into the β σ -BO similar to the formation of the ground state in the TiV⁻ anion. The ground $^4\Sigma^-$ state [Ti($3d^{2.71} 4s^{1.54}$), Cr($3d^{5.24} 4s^{1.38}$)] of the TiCr⁻ anion attaches an extra electron to the antibonding α -($4s-4s$) MO, which results in formation of a $4s$ -LSO at each atomic site. A $^2\Delta$ state [Ti($3d^{3.13} 4s^{1.05}$), Cr($3d^{5.59} 4s^{1.10}$)], where the extra electron fills into a β δ -BO, is above by 0.13 eV. Comparing the atomic occupations of both states suggests that the $^4\Sigma^-$ state, which has two less BOs, is below the $^2\Delta$ state because it has a smaller promotion energy. The ground $^4\Sigma^-$ state of TiCr⁺, with three β -BOs ($3d_\sigma 4s+3d_\sigma 4s$ and two $3d_\pi+3d_\pi$), is formed after detachment of an electron from the β -($4s+4s$) BO.

TiMn. An additional electron, with respect to TiCr, fills the β δ -BO and the ground state is $^2\Delta$ [Ti($3d^{2.72} 4s^{0.95}$), Mn($3d^{6.26} 4s^{1.06}$)]. This is accompanied by the breaking of both α δ -BOs and formation of two Mn α δ -LSOs. The TiMn⁻ and TiMn⁺ ions possess $^3\Delta$ ground states. To form the anion, an extra electron fills into an α -($4s-4s$) MO that breaks the $4s+4s$ bond and adds two $4s$ LSOs, while an electron detaches from the β -($4s+4s$) BO to form the ground state of the cation.

TiFe. Twelve valence electrons fill into all available bonding orbitals, and the ground state of the dimer is $^1\Sigma^+$ [Ti($3d^{2.58} 4s^{0.97}$), Fe($3d^{7.42} 4s^{1.03}$)]. The corresponding α - and β -BOs are equivalent, and TiFe may be considered as having a classic sextuple bond. This dimer is found to be the most stable among all mixed and homonuclear dimers, see Table 1 and Table 3 of Ref. 50. Both TiFe⁻ and TiFe⁺ have $^2\Sigma^+$ ground states and 11 BOs each.

TiCo. The lowest energy state found is $^2\Delta$ [Ti($3d^{2.68} 4s^{0.91}$), Co($3d^{8.33} 4s^{1.08}$)], while experiment favors $^2\Sigma$ (ESR)¹⁰ and $^2\Sigma^+$ (R2PI) (Ref. 13) states. The $^2\Delta$ state has five α -BO ($4s+4s$, $3d_\sigma+3d_\sigma$, two $3d_\pi+3d_\pi$, $3d_\delta+3d_\delta$), two α -LSOs (Ti $3d_\delta$ and Co $3d_\delta$), four β -BOs [$4s+4s$, $3d_\sigma+3d_\sigma$, two $3d_\pi+3d_\pi$], and two β - $3d_\delta$ LSOs of Co. A $^2\Pi$ state is obtained by replacement of an α -($3d_\pi+3d_\pi$) BO by the second $3d_\delta+3d_\delta$ BO which, in turn, results in the change of symmetry of both α -LSOs which become $3d_\pi$ LSOs. The BPW91 level places the $^2\Pi$ state above the $^2\Delta$ state by 0.61 eV. Applying the B3LYP approach, we obtained a $^2\Sigma^+$ state which is higher than a $^2\Delta$ state by 0.77 eV, while the $^2\Pi$ state is higher than $^2\Sigma^+$ state by 0.07 eV. The $^2\Sigma^+$ state [Ti($3d^{2.39} 4s^{1.24}$), Co($3d^{8.11} 4s^{1.23}$)] has the same α -bonding pattern while it has only one β -($4s+4s$) bond and five Co $3d$ -electrons are inert and occupy the half shell.

Our attempts to obtain a $^2\Sigma^+$ state at the BPW91, BLYP, and BP86 levels using the B3LYP $^2\Sigma^+$ orbitals as a guess failed: all optimizations arrived at the $^2\Delta$ state. A CCSD(T) run failed to converge due to a large amplitude exceeding 1.0 which indicates that this state is multiconfigurational. Density functional theory with the exact exchange correlation functional should reproduce⁵² the lowest energy state of each particular symmetry. However, approximate functionals, such as BPW91, may not achieve sufficient accuracy in correctly predicting the ground state, and TiCo is such a case. In order to clarify the reasons for the BPW91 failure, we per-

TABLE I. Computed spectroscopic constants for the neutral dimers.^a

| | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|----|--|---------------|---------------|---------------|---------------|----------------|-------------------|---------------|---------------|---------------|
| | Ground state symmetry | | | | | | | | | |
| Sc | $5\Sigma_u^-$ | $6\Sigma_g^+$ | $7\Sigma_g^+$ | $4\Sigma_g^-$ | $3\Sigma_g^-$ | 2Δ | $1\Sigma_g^+$ | $2\Sigma_g^+$ | 3Δ | $4\Sigma_g^-$ |
| Ti | | $3\Delta_g$ | $4\Sigma_g^-$ | $3\Sigma_g^-$ | 2Δ | $1\Sigma_g^+$ | $2\Sigma_g^+$ | 3Δ | 4Φ | 5Δ |
| V | | | $3\Sigma_g^-$ | 2Δ | $1\Sigma_g^+$ | 2Δ | $3\Sigma_g^-$ | $4\Sigma_g^-$ | 5Δ | 6Δ |
| Cr | | | | $1\Sigma_g^+$ | $2\Sigma_g^+$ | 3Π | 4Δ | $5\Sigma_g^+$ | $6\Sigma_g^+$ | $7\Sigma_g^+$ |
| Mn | | | | | $1^1\Pi_u$ | $10\Sigma_g^-$ | 7Δ | $6\Sigma_g^+$ | $7\Sigma_g^+$ | $6\Sigma_g^+$ |
| Fe | | | | | | $7\Delta_u$ | $6\Sigma_g^+$ | 5Δ | 4Π | 5Π |
| Co | | | | | | | $5\Delta_g$ | 4Δ | 3Δ | 4Δ |
| Ni | | | | | | | | $3\Sigma_g^-$ | 2Δ | 3Δ |
| Cu | | | | | | | | | $1\Sigma_g^+$ | $2\Sigma_g^+$ |
| Zn | | | | | | | | | | $1\Sigma_g^+$ |
| | Bond length in Å | | | | | | | | | |
| Sc | 2.63 | 2.29 | 2.51 | 1.99 | 1.94 | 1.85 | 1.80 | 2.05 | 2.54 | 2.71 |
| Ti | | 1.89 | 1.78 | 1.79 | 1.76 | 1.67 | 1.88 ^b | 2.06 | 2.45 | 2.74 |
| V | | | 1.74 | 1.72 | 1.69 | 1.74 | 1.81 | 2.11 | 2.42 | 2.71 |
| Cr | | | | 1.75 | 2.46 | 2.37 | 2.34 | 2.25 | 2.42 | 2.75 |
| Mn | | | | | 2.62 | 2.42 | 2.09 | 2.09 | 2.37 | 2.99 |
| Fe | | | | | | 2.01 | 1.96 | 2.07 | 2.31 | 2.53 |
| Co | | | | | | | 1.98 | 2.10 | 2.26 | 2.44 |
| Ni | | | | | | | | 2.11 | 2.25 | 2.39 |
| Cu | | | | | | | | | 2.25 | 2.40 |
| Zn | | | | | | | | | | 3.27 |
| | Harmonic frequency in cm^{-1} | | | | | | | | | |
| Sc | 241 | 272 | 246 | 262 | 382 | 474 | 513 | 353 | 216 | 173 |
| Ti | | 463 | 562 | 559 | 454 | 681 | 340 ^b | 327 | 219 | 146 |
| V | | | 652 | 481 | 432 | 363 | 404 | 287 | 220 | 143 |
| Cr | | | | 283 | 164 | 177 | 195 | 209 | 217 | 126 |
| Mn | | | | | 202 | 243 | 348 | 339 | 231 | 85 |
| Fe | | | | | | 397 | 407 | 350 | 242 | 159 |
| Co | | | | | | | 382 | 338 | 254 | 176 |
| Ni | | | | | | | | 325 | 266 | 202 |
| Cu | | | | | | | | | 256 | 190 |
| Zn | | | | | | | | | | 35 |
| | Dissociation energy in eV | | | | | | | | | |
| Sc | 1.51 | 2.22 | 2.57 | 1.05 | 1.98 | 3.19 | 2.63 | 3.26 | 1.85 | 0.15 |
| Ti | | 2.54 | 2.78 | 1.82 | 2.76 | 4.10 | 1.88 ^b | 2.93 | 1.80 | 0.44 |
| V | | | 2.80 | 1.84 | 2.88 | 2.86 | 2.38 | 2.44 | 1.62 | 0.40 |
| Cr | | | | 1.05 | 0.93 | 1.17 | 1.34 | 1.48 | 1.36 | 0.28 |
| Mn | | | | | 1.15 | 1.57 | 1.91 | 2.41 | 1.56 | 0.16 |
| Fe | | | | | | 2.18 | 2.42 | 2.51 | 1.56 | 0.38 |
| Co | | | | | | | 2.24 | 2.36 | 1.80 | 0.60 |
| Ni | | | | | | | | 2.50 | 1.95 | 0.65 |
| Cu | | | | | | | | | 1.94 | 0.61 |
| Zn | | | | | | | | | | 0.02 |

^aExperiment—ScCr: $X^6\Sigma$ (see Ref. 7).ScNi: $X^2\Sigma$ (see Ref. 9); $X^2\Sigma^+$, $\Delta G''_{1/2} = 334.4 \text{ cm}^{-1}$ (see Ref. 10).TiV: $X^4\Sigma$ (see Ref. 11).TiV: $D_0^0 = 2.068 \pm 0.001 \text{ eV}$ (see Ref. 12).TiCo: 2Σ (see Refs. 56 and 9).TiCo: $D_0^0 = 2.401 \pm 0.001 \text{ eV}$ (see Ref. 12).TiCo: $2\Sigma^+$, $r_0'' = 1.8508 \pm 0.0004 \text{ Å}$ (see Ref. 13).VCr: $2\Delta_{5/2}$, $r_0 = 1.7260 \pm 0.0011 \text{ Å}$, (see Ref. 14).VMn: 1Σ (as cited in Ref. 15).VFe: $\omega_e = 433 \text{ cm}^{-1}$ (see Ref. 15).VCo: $\omega_e = 461 \text{ cm}^{-1}$ (see Ref. 15).VNi: $X^4\Sigma$ (see Ref. 11).VNi: $D_0^0 = 2.100 \pm 0.001 \text{ eV}$ (see Ref. 12).CrMn: $X^4\Sigma$ (see Ref. 16).CrFe: $\omega_e = 166.6 \pm 0.8 \text{ cm}^{-1}$ (see Ref. 17).CrCu: $X^6\Sigma$ (see Ref. 56).CrCu: $X^4\Sigma$ (see Ref. 57).CrCu: $D_0 = 1.56 \pm 0.26 \text{ eV}$ (see Ref. 62).CrZn: $X^7\Sigma$ (see Ref. 62).MnCu: $X^7\Sigma^+$, $\omega_e = 213 \pm 2.0 \text{ cm}^{-1}$, $D_0 \approx 1.5 \text{ eV}$ (see Ref. 22).FeCo: $X^6\Sigma$ (see Ref. 59).FeNi: $\omega_e = 320.0 \text{ cm}^{-1}$ (see Ref. 60).CoCu: $D_0 = 1.65 \pm 0.21 \text{ eV}$ (see Ref. 62).CoCu: $\omega_e = 270.0 \text{ cm}^{-1}$, $D_0 = 1.65 \text{ eV}$ (see Ref. 61).NiCu: $X^2\Delta_{5/2}$, $r_e = 2.233 \pm 0.006 \text{ Å}$, $\omega_e = 273.01 \pm 1.15 \text{ cm}^{-1}$, $D_0 = 2.05 \pm 0.10 \text{ eV}$ (see Ref. 18) $R_0 = 2.2346(5) \text{ Å}$ (see Refs. 19 and 20).NiCu: $D_0 = 2.06 \pm 0.21 \text{ eV}$ (see Ref. 62).CuZn: $X^2\Sigma^+$ (see Ref. 63).^bThe results of IC-MRCI calculations. The lowest BPW91 state is 2Δ ($r_e = 1.79 \text{ Å}$, $\omega_e = 493 \text{ cm}^{-1}$, $D_0 = 3.39 \text{ eV}$).

TABLE II. Spectroscopic constants of the ground-state dimer anions.

| | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|----|---|-------------|---------------|-------------|-------------------|-------------|-------------|---------------|-------------------|-------------------|
| | Ground state symmetry | | | | | | | | | |
| Sc | $4\Sigma_u^-$ | $7\Sigma^+$ | 6Π | $5\Sigma^+$ | $4\Sigma^-$ | 3Δ | $2\Sigma^+$ | $1\Sigma^+$ | 2Δ | $3\Sigma^-$ |
| Ti | | $4\Delta_u$ | $5\Sigma^-$ | $4\Sigma^-$ | 3Δ | $2\Sigma^+$ | 3Δ | 2Δ | 3Φ | 4Δ |
| V | | | $4\Sigma_u^-$ | $1\Sigma^+$ | $2\Sigma^+$ | 3Δ | $4\Sigma^-$ | 5Π | $6\Sigma^+$ | 5Δ |
| Cr | | | | $2\Sigma^+$ | $1\Sigma^+$ | 2Δ | 5Δ | $6\Sigma^+$ | $7\Sigma^+$ | $6\Sigma^+$ |
| Mn | | | | | $10\Sigma_g^-$ | $9\Sigma^-$ | 8Δ | $7\Sigma^+$ | $6\Sigma^+$ | $5\Sigma^+$ |
| Fe | | | | | | $8\Delta_g$ | $7\Sigma^+$ | 6Δ | 5Δ | 4Π |
| Co | | | | | | | $6\Delta_u$ | 5Δ | 4Δ | 3Δ |
| Ni | | | | | | | | $4\Sigma_u^-$ | $3\Delta^b$ | 2Δ |
| Cu | | | | | | | | | $2\Sigma^+$ | $1\Sigma^+$ |
| Zn | | | | | | | | | | $2\Sigma_g^+$ |
| | Bond length in Å | | | | | | | | | |
| Sc | 2.73 | 2.27 | 2.19 | 2.04 | 2.00 | 1.79 | 1.82 | 2.09 | 2.68 | 2.79 |
| Ti | | 1.93 | 1.81 | 1.81 | 1.76 | 1.68 | 1.81 | 2.11 | 2.55 | 2.81 |
| V | | | 1.76 | 1.63 | 1.69 | 1.79 | 1.84 | 2.17 | 2.54 | 2.78 |
| Cr | | | | 1.74 | 2.51 | 2.43 | 2.40 | 2.28 | 2.54 | 2.83 |
| Mn | | | | | 2.39 | 2.19 | 2.16 | 2.14 | 2.51 | 2.86 |
| Fe | | | | | | 2.07 | 2.04 | 2.12 | 2.45 | 2.67 |
| Co | | | | | | | 2.03 | 2.16 | 2.36 | 2.59 |
| Ni | | | | | | | | 2.17 | 2.36 ^b | 2.54 |
| Cu | | | | | | | | | 2.36 | 2.57 |
| Zn | | | | | | | | | | 3.06 |
| | Vibrational frequency in cm^{-1} | | | | | | | | | |
| Sc | 218 | 296 | 238 | 223 | 279 | 534 | 472 | 321 | 169 | 151 |
| Ti | | 429 | 504 | 524 | 448 | 648 | 458 | 299 | 179 | 130 |
| V | | | 615 | 616 | 420 | 334 | 279 | 236 | 171 | 129 |
| Cr | | | | 305 | 155 | 160 | 165 | 185 | 169 | 111 |
| Mn | | | | | 247 | 305 | 308 | 310 | 171 ^a | 106 |
| Fe | | | | | | 350 | 323 | 316 | 185 | 132 |
| Co | | | | | | | 347 | 291 | 198 | 140 |
| Ni | | | | | | | | 280 | 211 ^b | 147 |
| Cu | | | | | | | | | 208 | 133 |
| Zn | | | | | | | | | | 76 |
| | Dissociation energy, eV^c | | | | | | | | | |
| Sc | 2.18 | 2.24 | 2.14 | 1.43 | 2.30 | 3.08 | 3.52 | 3.03 | 1.53 | 0.84 |
| Ti | | 2.80 | 3.00 | 1.91 | 2.81 | 4.01 | 3.09 | 2.61 | 1.36 | 0.67 |
| V | | | 3.01 | 2.12 | 3.00 | 2.82 | 2.13 | 2.18 | 1.33 | 0.62 |
| Cr | | | | 0.77 | 1.33 | 1.18 | 1.26 | 1.34 | 1.12 | 0.48 |
| Mn | | | | | 1.69 ^b | 1.68 | 1.94 | 2.26 | 1.34 ^a | 0.76 ^d |
| Fe | | | | | | 2.53 | 2.46 | 2.39 | 1.53 | 0.69 |
| Co | | | | | | | 2.25 | 2.29 | 1.55 | 0.67 |
| Ni | | | | | | | | 2.40 | 1.72 ^b | 0.75 |
| Cu | | | | | | | | | 1.69 | 0.64 |
| Zn | | | | | | | | | | Unst ^e |

^aExperiment: $X^6\Sigma$, $\omega_e = 147 \pm 4 \text{ cm}^{-1}$, $D_0 = 1.3^{+0.5}_{-0.2} \text{ eV}$ (see Ref. 22).

^bExperiment: $X^3\Delta$, $r_e = 2.36 \pm 0.01 \text{ \AA}$, $\omega_e = 235 \pm 25 \text{ cm}^{-1}$, $D_0 = 1.70 \pm 0.02 \text{ eV}$ (see Ref. 21).

^cComputed with respect to the lowest asymptote.

^d $M_2^- \rightarrow 2M + e$.

^eUnstable towards autodetachment by 0.17 eV.

formed calculations on TiCo using the CASSCF based internally contracted⁵³ multireference configuration interaction calculation (IC-MRCI). The $[7s6p4d3f2g]$ averaged atomic natural orbital basis set⁵⁴ is used. The initial active space consisted of the $3d$ and $4s$ orbitals, but the occupation of the first σ orbital was so close to two that it was made inactive, leading to an 11 electrons in 11 orbitals CASSCF calculations. Separate CASSCF optimizations are performed for each state. All 13 valence electrons are correlated in the IC-MRCI calculation, with all of the configurations in the CASSCF calculations as reference configurations. The mul-

tireference analog of the Davidson correction is used, and denoted as “+ Q .”

This approach results in a $2\Sigma^+$ ground state with $r_e = 1.876 \text{ \AA}$, $\omega_e = 340 \text{ cm}^{-1}$ and $D_0 = 1.82 \text{ eV}$. The 2Δ state is 2541 cm^{-1} (0.315 eV) higher and its spectroscopic constants are $r_e = 1.822 \text{ \AA}$ and $\omega_e = 457 \text{ cm}^{-1}$. The ground-state wave function is almost equal parts of $(12\sigma^2 13\sigma^1 5\pi^4 1\delta^4)$ and $(12\sigma^2 13\sigma^1 5\pi^4 1\delta^3 2\delta^1)$ and, therefore, it is not too surprising that DFT methods cannot describe the $2\Sigma^+$ state as well as the 2Δ state.

Attachment of an electron to the α - and β -($4s-4s$)

TABLE III. Spectroscopic constants for the ground-states of the dimer cations.

| | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|----|---|-------------|---------------|-------------|-------------|-------------|-------------|-------------|---------------|---------------|
| | Ground state symmetry | | | | | | | | | |
| Sc | $4\Sigma_g^-$ | 5Δ | $6\Sigma^+$ | $5\Sigma^+$ | $4\Sigma^-$ | 3Δ | $2\Sigma^+$ | $1\Sigma^+$ | 2Δ | $3\Sigma^-$ |
| Ti | | $2\Delta_g$ | $3\Sigma^-$ | $4\Sigma^-$ | 3Δ | $2\Sigma^+$ | $1\Sigma^+$ | 2Δ | 3Φ | 4Δ |
| V | | | $4\Sigma_g^-$ | $1\Sigma^+$ | $2\Sigma^+$ | $1\Sigma^+$ | 2Δ | $3\Sigma^-$ | 4Δ | 5Δ |
| Cr | | | | $2\Sigma^+$ | $1\Sigma^+$ | 2Δ | $3\Sigma^-$ | 6Π | $7\Sigma^+$ | $6\Sigma^+$ |
| Mn | | | | | $10\Pi_u$ | $9\Sigma^-$ | 8Δ | 7Δ | $6\Sigma^+$ | $7\Sigma^+$ |
| Fe | | | | | | $8\Delta_u$ | 7Δ | $6\Sigma^+$ | 5Δ | 4Π |
| Co | | | | | | | $6\Gamma_g$ | 5Φ | 4Φ | 3Δ |
| Ni | | | | | | | | $4\Delta_g$ | 3Δ | 2Δ |
| Cu | | | | | | | | | $2\Sigma_g^+$ | $1\Sigma^+$ |
| Zn | | | | | | | | | | $2\Sigma_u^+$ |
| | Bond length in Å | | | | | | | | | |
| Sc | 2.57 | 2.50 | 2.44 | 2.69 | 2.39 | 1.85 | 1.77 | 2.00 | 2.44 | 2.64 |
| Ti | | 1.78 | 1.70 | 1.74 | 1.69 | 1.64 | 1.76 | 1.99 | 2.37 | 2.65 |
| V | | | 1.70 | 1.56 | 1.64 | 1.89 | 1.97 | 2.05 | 2.35 | 2.62 |
| Cr | | | | 1.67 | 2.41 | 2.34 | 2.36 | 2.37 | 2.61 | 2.60 |
| Mn | | | | | 2.50 | 2.32 | 2.30 | 2.27 | 2.34 | 2.80 |
| Fe | | | | | | 2.17 | 2.11 | 2.06 | 2.31 | 2.43 |
| Co | | | | | | | 2.09 | 2.23 | 2.29 | 2.36 |
| Ni | | | | | | | | 2.28 | 2.36 | 2.33 |
| Cu | | | | | | | | | 2.40 | 2.33 |
| Zn | | | | | | | | | | 2.60 |
| | Vibrational frequency in cm^{-1} | | | | | | | | | |
| Sc | 269 | 274 | 271 | 182 | 199 | 474 | 520 | 390 | 248 | 192 |
| Ti | | 723 | 799 | 656 | 608 | 693 | 541 | 367 | 252 | 180 |
| V | | | 715 | 967 | 519 | 239 | 250 | 287 | 247 | 172 |
| Cr | | | | 413 | 187 | 201 | 203 | 185 | 148 | 172 |
| Mn | | | | | 246 | 275 | 261 | 262 | 235 | 136 |
| Fe | | | | | | 319 | 283 | 327 | 236 | 205 |
| Co | | | | | | | 342 | 272 | 240 | 222 |
| Ni | | | | | | | | 262 | 211 | 229 |
| Cu | | | | | | | | | 201 | 221 |
| Zn | | | | | | | | | | 151 |
| | Dissociation energy in $\text{eV}^{\text{a,b}}$ | | | | | | | | | |
| Sc | 2.54 | 2.62 | 2.47 | 1.44 | 2.40 | 2.96 | 3.48 | 3.78 | 2.17 | 0.58 |
| Ti | | 3.09 | 3.19 | 2.08 | 2.68 | 3.83 | 3.61 | 3.18 | 1.92 | 0.93 |
| V | | | 3.51 | 2.21 | 2.88 | 3.33 | 2.81 | 2.40 | 1.76 | 1.11 |
| Cr | | | | 1.30 | 2.38 | 2.27 | 1.85 | 1.64 | 1.36 | 1.14 |
| Mn | | | | | 1.91 | 2.40 | 2.52 | 2.55 | 2.25 | 0.93 |
| Fe | | | | | | 3.35 | 3.27 | 3.27 | 2.61 | 1.56 |
| Co | | | | | | | 2.97 | 2.85 | 2.26 | 1.78 |
| Ni | | | | | | | | 2.87 | 2.28 | 1.94 |
| Cu | | | | | | | | | 2.02 | 1.95 |
| Zn | | | | | | | | | | 1.73 |

^aComputed with respect to the lowest asymptote.^bExperiment: (Ref. 23).ScFe⁺ (2.12±0.22); TiFe⁺ (2.60±0.26).VFe⁺ (3.25±0.22); CrFe⁺ (2.17±0.30).FeCo⁺ (2.69±0.22); FeNi⁺ (2.78±0.22); FeCu⁺ (2.30±0.30).

MOs of the 2Δ state leads to formation of 1Δ and 3Δ states, respectively, with the 3Δ state being lower by 0.06 eV. Detachment of an electron from an α -LSO leaves 12 valence electrons and the ground $1\Sigma^+$ state of TiCo⁺ possesses the same bonding pattern as isoelectronic VFe.

TiNi. The lowest state found is 3Δ [Ti($3d^{2.49}4s^{1.12}$), Ni($3d^{9.11}4s^{1.25}$)]. It has three BOs ($3d_{\sigma}4s + 3d_{\sigma}4s$ and two $3d_{\pi} + 3d_{\pi}$) and two Ti ($3d_{\sigma}4s$ and $3d_{\delta}$) and three Ni ($3d_{\sigma}4s$ and two $3d_{\delta}$) LSOs in the α -spin representation, along with one β -($4s + 4s$) BO and five Ni electrons in the β - $3d$ half shell. To form the lowest 2Δ state of the anion, an

extra electron adds to the Ti β - $4s$ LSO, which transforms the slightly asymmetric neutral β -($4s + 4s$) BO into a strongly asymmetric β -(12% $3d_{\sigma}$ Ti + 88% $3d_{\sigma}$ Ni) BO in the anion, and the pure Ni β $3d_{\sigma}$ LSO turns into a 76% $4s + 24\%$ $3d_{\sigma}$ LSO. Detachment of an electron from the α - $3d_{\sigma}4s$ LSO of Ti results in a rather drastic change in the bonding patterns of the cation: a $3d_{\sigma}$ BO adds in the α -spin representation along with two 12% $3d_{\pi}$ Ti + 88% $3d_{\pi}$ Ni BOs in the β -spin representation. The TiNi⁺ cation has a 2Δ ground state.

TiCu. Only the 4s electrons participate in the bonding, thus, making the ground-state symmetry defined by the most energetically favorable distribution of three 3d valence electrons of Ti over five possible α -3d LSOs. In the lowest energy state found, three LSOs $3d_{\sigma}4s$, $3d_{\pi}$, and $3d_{\delta}$ are occupied. While this calculation corresponds to a mixture of $^4\Pi$ and $^4\Phi$, we assign the ground state $[\text{Ti}(3d^{2.69}4s^{1.00}), \text{Cu}(3d^{9.88}4s^{1.39})]$ as $^4\Phi$ having assumed that the Hund's rule of the largest angular momentum holds for the dimer. The state has a hybrid α - $(3d_{\sigma}4s+4s)$ BO, a β - $(4s+4s)$ BO, and ten Cu electrons occupy the 3d shell. A symmetry-resolved $^4\Delta$ state $[\text{Ti}(3d^{3.13}4s^{0.60}), \text{Cu}(3d^{9.91}4s^{1.33})]$, which has a $3d_{\delta}$ and two $3d_{\pi}$ LSOs of Ti is above by 0.33 eV. The attachment of an electron to the antibonding β - $(4s-4s)$ orbital yields the ground $^3\Phi$ state TiCu^- while detachment of an electron from the α - $3d_{\sigma}4s$ LSO yields the ground $^3\Phi$ state of TiCu^+ .

TiZn. The lowest state is $^5\Delta$ $[\text{Ti}(3d^{3.00}4s^{1.04}), \text{Zn}(3d^{10.00}4s^{1.84}p^{0.07})]$, and its spatial symmetry is defined by distribution of four Ti α -LSOs $[4s, \text{two } 3d_{\pi}, 3d_{\delta}]$. A weak bonding is provided by a strongly asymmetric β - $(4s+4s)$ BO, whose contribution from Ti is only 10%. In the anion, an extra electron adds to an antibonding β - $(4s-4s)$ MO that eliminates the single bond and creates two 4s-LSOs. To form the lowest cation state, an electron detaches from the Ti α -4s LSO, which leads to formation of an asymmetric α - $(3d_{\sigma}4s \text{ Ti} + 4s \text{ Zn})$ BO, while the β -spin representation is presented by six LSOs $[4s, 3d_{\sigma}, \text{two } 3d_{\pi}, \text{two } 3d_{\delta}]$ of Zn. Both ions have a $^4\Delta$ ground state.

VCr. In agreement with experiment¹⁴ and the results of CASSCF-PT2 calculations⁵⁵ the lowest state found for VCr is $^2\Delta$ $[\text{V}(3d^{3.88}4s^{1.01}), \text{Cr}(3d^{5.11}4s^{1.00})]$. The computed bond length of 1.724 Å is in excellent agreement with the experimental value¹⁴ of 1.7260 ± 0.0011 Å. Eleven valence electrons all occupy bonding orbitals. The $^2\Delta$ state is antiferromagnetic with the local magnetic moments of $-1.7\mu_B$ and $2.7\mu_B$ at V and Cr, respectively. The antiferromagnetic character arises from the spin polarization of the 3d bonding orbitals; the α orbitals are polarized to one atom while the β orbitals are polarized toward the other atom. Similar bonding patterns were found for the Cr_2 dimer.⁵⁰ Such an asymmetry of the bonding orbitals appears to be a reason for a low dissociation energy, see Table IV, despite the large number of the occupied BOs. Attachment of an extra electron to the vacant β - $(3d_{\delta}+3d_{\delta})$ BO results in a nonmagnetic $^1\Sigma^+$ state with six equivalent bonds in each spin representation, similar to that in isoelectronic TiFe, while attachment to an antibonding α - $(4s-4s)$ MO results in an antiferromagnetic $[-0.7\mu_B, 2.7\mu_B]$ $^3\Delta$ state which is above the $^1\Sigma^+$ state by 0.17 eV. For the cation, the nonmagnetic ground $^1\Sigma^+$ state is formed by the detachment of an electron from the α - $(4s+4s)$ BO, while detachment from the β - $(4s+4s)$ BO results in an antiferromagnetic $[-0.4\mu_B, 2.4\mu_B]$ $^3\Delta$ state which is above the ground state by 0.10 eV.

VMn. This dimer has 12 valence electron and its ground state is $^1\Sigma^+$ $[\text{V}(3d^{3.88}4s^{1.01}), \text{Mn}(3d^{5.11}4s^{1.00})]$ in agreement with experiment.¹⁵ Contrary to the nonmagnetic ground $^1\Sigma^+$ states of isoelectronic TiFe and VFe^+ , the $\text{VMn}^1\Sigma^+$ state is antiferromagnetic $[2.5\mu_B, -2.5\mu_B]$. There are six α -BOs,

four β -BOs, and two Mn β - $3d_{\delta}$ LSOs. A nonmagnetic $^1\Sigma^+$ $[\text{V}(3d^{3.76}4s^{1.01}), \text{Mn}(3d^{6.24}4s^{1.00})]$ state with six equivalent bonds in each spin representation possesses a shorter bond length of 1.61 Å and is 0.13 eV higher in energy. Two possible descriptions for the $^1\Sigma^+$ state is similar to that in the isoelectronic Cr_2 dimer.⁵⁰ Attachment of an extra electron to the α - $(4s-4s)$ MOs of these two $^1\Sigma^+$ states results into two $^2\Sigma^+$ states of VMn^- . The lowest state is antiferromagnetic $[2.6\mu_B, -1.6\mu_B]$ and is given in Table II, while the other state is ferromagnetic $[0.45\mu_B, 0.55\mu_B]$ with a shorter bond length of 1.62 Å, a larger vibrational frequency of 739 cm^{-1} , and it is above the ground state by 0.09 eV. The VMn^+ cation possesses a similar pair of $^2\Sigma^+$ states formed by removal of an electron from the β - $(4s+4s)$ BO of the two neutral $^1\Sigma^+$ states. The antiferromagnetic $[2.1\mu_B, -1.1\mu_B]$ state, given in Table III, is lower than the ferromagnetic state $[(0.3\mu_B, 0.7\mu_B), r_e = 1.59 \text{ Å}, \omega_e = 815 \text{ cm}^{-1}]$ by 0.09 eV.

VFe. The ground state of this dimer is $^2\Delta$ $[\text{V}(3d^{3.82}4s^{0.92}), \text{Fe}(3d^{7.19}4s^{1.07})]$, since the 13th valence electron must occupy an antibonding orbital ($3d_{\delta}$ - $3d_{\delta}$ is the lowest one). This state is antiferromagnetic (see Table IV); there are five α -BOs ($4s+4s, 3d_{\sigma}+3d_{\sigma}, \text{two } 3d_{\pi}+3d_{\pi}, 3d_{\delta}+3d_{\delta}$) and an α - $3d_{\delta}$ LSO at each site, along with four β -BOs $[4s+4s, 3d_{\sigma}+3d_{\sigma}, \text{two } 3d_{\pi}+3d_{\pi}]$ and two Fe β - $3d_{\delta}$ LSOs. The computed vibrational frequency of 363 cm^{-1} is smaller than the experimental value¹⁵ of 433 cm^{-1} . The ground $^3\Delta$ state of VFe^- is formed by the attachment of an electron to the β - $(4s-4s)$ antibonding orbital. This state is only 0.06 eV below the $^1\Delta$ state which is formed by the attachment of an electron to the α - $(4s-4s)$ antibonding orbital. The ground $^1\Sigma^+$ state of VFe^+ is antiferromagnetic $[-3.2\mu_B, 3.2\mu_B]$ and is formed by detachment of an electron from the antibonding α - $(3d_{\delta}-3d_{\delta})$ MO, while a nonmagnetic $^1\Sigma^+$ state is 0.46 eV higher in energy.

VCo. The 14th valence electron fills the second antibonding α - $(3d_{\delta}-3d_{\delta})$ orbital, which leads to formation of the second α - $3d_{\delta}$ LSO pair, and the ground state is $^3\Sigma^-$ $[\text{V}(3d^{3.80}4s^{0.91}), \text{Co}(3d^{8.22}4s^{1.07})]$. There are four α -BOs ($4s+4s, \text{two } 3d_{\pi}+3d_{\pi}, 3d_{\sigma}+3d_{\sigma}$) and two α - $3d_{\delta}$ LSOs at each site, while the β -spin representation contains the same bonding set and two Co $3d_{\delta}$ LSOs. Replacement of the α - $(3d_{\sigma}+3d_{\sigma})$ BO by an α - $(3d_{\delta}+3d_{\delta})$ BO results in a $^3\Delta$ $[\text{V}(3d^{3.78}4s^{0.96}), \text{Co}(3d^{7.94}4s^{1.30})]$ state which has completely different bonding patterns in the β -spin representation (a single $4s+4s$ BO and a half filled 3d shell of Co) and a pair of V and Co α - $3d_{\delta}$ LSOs are replaced by the pair of α - $3d_{\sigma}4s$ LSOs. This state $[(3.9\mu_B, -1.9\mu_B), r_e = 2.05 \text{ Å}, \omega_e = 239 \text{ cm}^{-1}]$ is above the $^3\Sigma^-$ state by only 0.04 eV. The experimental frequency¹⁵ of 461 cm^{-1} is more consistent with the value of 404 cm^{-1} computed for the $^3\Sigma^-$ state. Here, one observes a close competition between delocalization and localization of 3d states of "magnetic" Co. Attachment of an extra electron to the antibonding α - $(4s-4s)$ MO in the ground $^3\Sigma^-$ state of VCo results into the lowest $^4\Sigma^-$ state of the anion whose bonding patterns are the same as in the neutral parent state, except the α - $(4s+4s)$ BO is replaced by the pair of 4s

TABLE IV. Electron affinities (eV), ionization energies (eV), dipole moments (D), and magnetic moments at atoms (Bohr magneton).

| | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---------------------------------|---------|---------|---------|----------|----------|----------|----------|----------|-------------------|---------|
| Electron affinity | | | | | | | | | | |
| Sc | 0.86 | 0.88 | 0.74 | 0.67 | 0.52 | 0.51 | 0.52 | 0.80 | 0.83 | 0.89 |
| Ti | | 0.67 | 0.64 | 0.52 | 0.49 | 0.52 | 0.60 | 0.71 | 0.71 | 0.66 |
| V | | | 0.55 | 0.65 | 0.48 | 0.56 | 0.65 | 0.77 | 0.86 | 0.60 |
| Cr | | | | 0.43 | 0.68 | 0.63 | 0.82 | 0.89 | 0.91 | 0.48 |
| Mn | | | | | 0.59 | 0.73 | 0.93 | 0.88 | 0.93 ^a | 0.60 |
| Fe | | | | | | 0.94 | 0.95 | 0.91 | 1.12 | 0.91 |
| Co | | | | | | | 0.91 | 0.95 | 0.91 ^b | 0.97 |
| Ni | | | | | | | | 0.93 | 0.92 | 1.13 |
| Cu | | | | | | | | | 0.90 | 1.18 |
| Zn | | | | | | | | | | 0.< |
| Ionization energy | | | | | | | | | | |
| Sc | 5.13 | 5.33 | 5.46 | 5.78 | 5.74 | 6.36 | 6.56 | 5.65 | 5.85 | 5.73 |
| Ti | | 5.91 | 6.07 | 6.21 | 6.54 | 6.74 | 6.25 | 6.22 | 6.34 | 5.98 |
| V | | | 6.21 | 6.54 | 6.91 | 6.46 | 6.48 | 6.96 | 6.78 | 6.19 |
| Cr | | | | 7.03 | 5.61 | 6.20 | 6.79 | 7.11 | 7.30 | 6.43 |
| Mn | | | | | 6.24 | 6.22 | 6.45 | 6.93 | 6.38 | 6.28 |
| Fe | | | | | | 6.68 | 6.98 | 7.08 | 6.78 | 6.66 |
| Co | | | | | | | 7.14 | 7.37 | 7.40 | 6.68 |
| Ni | | | | | | | | 7.66 | 7.70 | 6.74 |
| Cu | | | | | | | | | 8.05 | 6.79 |
| Zn | | | | | | | | | | 7.63 |
| Dipole moment | | | | | | | | | | |
| Sc | 0.0 | +0.57 | -0.13 | -1.58 | -1.74 | -2.33 | -2.65 | -1.71 | -2.09 | -1.37 |
| Ti | | 0.0 | -0.66 | -0.57 | -1.23 | -1.61 | -2.05 | -2.11 | -2.25 | -0.51 |
| V | | | 0.0 | -0.26 | -0.92 | -1.38 | -1.77 | -2.23 | -1.95 | -0.72 |
| Cr | | | | 0.0 | -0.90 | -0.95 | -1.04 | -1.53 | -1.87 | -0.27 |
| Mn | | | | | 0.0 | +0.23 | -0.93 | -1.17 | -1.24 | -0.52 |
| Fe | | | | | | 0.0 | -0.34 | -0.71 | -0.75 | +0.20 |
| Co | | | | | | | 0.0 | -0.23 | -0.63 | +0.20 |
| Ni | | | | | | | | 0.0 | -0.14 | +0.29 |
| Cu | | | | | | | | | 0.0 | +0.46 |
| Zn | | | | | | | | | | 0.0 |
| Magnetic moments on each center | | | | | | | | | | |
| Sc | 2.0,2.0 | 1.5,3.5 | 1.5,4.5 | -0.7,3.7 | -1.2,3.2 | -0.7,1.7 | 0.0,0.0 | 0.8,0.2 | 1.9,0.1 | 2.7,0.3 |
| Ti | | 1.0,1.0 | 0.8,2.2 | -0.5,2.5 | -1.4,2.8 | 0.0,0.0 | 1.4,-0.4 | 2.3,-0.3 | 3.1,-0.1 | 3.8,0.2 |
| V | | | 1.0,1.0 | -1.7,2.7 | 2.5,-2.5 | 2.8,-1.8 | 2.9,-0.9 | 3.9,-0.9 | 4.3,-0.3 | 4.7,0.3 |
| Cr | | | | 3.6,-3.6 | 5.6,-4.6 | 5.4,-3.4 | 5.3,-2.3 | 5.1,-1.1 | 5.3,-0.3 | 5.8,0.2 |
| Mn | | | | | 5.0,5.0 | 3.8,5.2 | 1.6,4.4 | 4.6,0.4 | 5.6,0.4 | 4.9,0.1 |
| Fe | | | | | | 3.0,3.0 | 3.2,1.8 | 3.4,0.6 | 3.2,-0.2 | 3.8,0.2 |
| Co | | | | | | | 2.0,2.0 | 2.2,0.8 | 2.2,-0.2 | 2.7,0.3 |
| Ni | | | | | | | | 1.0,1.0 | 1.0,0.0 | 1.7,0.3 |
| Cu | | | | | | | | | 0.0,0.0 | 0.7,0.3 |
| Zn | | | | | | | | | | 0.0,0.0 |

^aExperiment: 1.075 ± 0.003 eV (see Ref. 22).^bExperiment: 0.889 ± 0.010 eV (see Ref. 21).

LSOs. Attachment to the α -($4s-4s$) antibonding orbital of the $^3\Delta$ state results into a $^4\Delta$ state ($[4.7\mu_B, -1.7\mu_B]$, $r_e = 2.15 \text{ \AA}$, $\omega_e = 224 \text{ cm}^{-1}$), which is higher than the $^4\Sigma^-$ state by 0.12 eV. The lowest $^2\Delta$ state of VCo^+ is formed by detachment of an electron from an α - $3d_\sigma 4s$ LSO of the neutral $^3\Delta$ state, which results in the formation of an α -($3d_\sigma + 3d_\sigma$) BO. Detachment of an electron from the α -($4s + 4s$) BO of the $^3\Sigma^-$ state results in the $^4\Sigma^-$ state of VCo^+ , which is higher than the $^2\Delta$ by 0.59 eV.

VNi . The lowest state found is $^4\Sigma^-[\text{V}(3d^{3.80}4s^{0.93}), \text{Ni}(3d^{9.09}4s^{1.16})]$ which is in accord with the experimental assignment.¹¹ The bonding patterns of this state are similar to those of the $\text{VCo}^+ ^4\Delta$ state [α : three BO ($4s + 4s$, two $3d_\pi + 3d_\pi$), three V LSOs ($3d_\sigma 4s$, two

$3d_\delta$), and three Ni LSOs ($3d_\sigma$, two $3d_\delta$); β : one ($4s + 4s$) BO and a Ni half filled $3d$ shell]. That is, the localization of five Ni β - $3d$ electrons becomes favorable. As expected, our computed dissociation energy of 2.93 eV is higher than the experimental¹² $D_o^0 = 2.100 \pm 0.001$ eV. Attachment of an extra electron to the β -($4s-4s$) MO results in a $^3\Sigma^-$ state ($[3.0\mu_B, -1.0\mu_B]$, $r_e = 2.15 \text{ \AA}$, $\omega_e = 259 \text{ cm}^{-1}$) of the VNi^- anion, which retains three BOs ($3d_\sigma + 3d_\sigma$ and two $3d_\pi + 3d_\pi$) as well as six LSOs of its neutral parent in the α -spin representation, while the β -spin representation contains seven LSOs: one $4s$ of V and six of Ni. Attachment of an extra electron to the α -($4s-4s$) MO creates a pair of $4s$ LSOs and leads to two closely spaced

states ${}^5\Delta(3d_\sigma+3d_\sigma,3d_\delta+3d_\delta)$ and ${}^5\Pi(3d_\sigma+3d_\sigma,3d_\pi+3d_\pi)$. The ground state is ${}^5\Pi$; it is lower than the ${}^5\Delta$ and ${}^3\Sigma^-$ by 0.09 and 0.13 eV, respectively. Detachment of an electron from an α σ -LSO leads to the ${}^3\Sigma^-[\text{V}(3d^{3.47}4s^{0.67}),\text{Ni}(3d^{8.77}4s^{1.07})]$ ground state of the VNi^+ cation, which has one more α σ -BO than its neutral parent ${}^4\Sigma^-$ state.

VCu. The ground state of the dimer is ${}^5\Delta[\text{V}(3d^{3.85}4s^{0.89}),\text{Cu}(3d^{9.88}4s^{1.34})]$. There is a single $(3d_\sigma 4s+4s)$ -BO in each spin representation, $3d$ -electrons of Cu form a closed shell, and the ground state symmetry is defined by the occupation of four V LSOs ($3d_\sigma$, two $3d_\pi$, $3d_\delta$). Attachment of an extra electron to the vacant V α δ -LSO results in the ground ${}^6\Sigma^+$ state of VCu^- , while detachment from an α $3d_\sigma$ -LSO of V arrives at the ${}^4\Delta$ ground state of VCu^+ .

VZn. The lowest state found is ${}^6\Delta[\text{V}(3d^{3.98}4s^{1.04}),\text{Zn}(3d^{10.00}4s^{1.87})]$, which has five V α -LSOs (two $4s3d_\sigma$, two $3d_\pi$, $3d_\delta$), six Zn α -LSOs [$4s$, $3d_\sigma$, two $3d_\pi$, two $3d_\delta$], a single strongly asymmetric (10%V+90%Zn) β - $(4s+4s)$ -BO, and a Zn β - $3d$ half shell. The ground ${}^6\Delta$ state of VZn^- is formed after the attachment of an extra electron to an antibonding β σ -MO that breaks the bond and creates two β - $4s$ LSO along with a strongly asymmetric (90%V+10%Zn) α - $(4s+4s4p_\sigma)$ BO. Attachment of an extra electron to the second V α - $3d_\delta$ LSO results in a ${}^7\Sigma^+$ state of VZn^- , which is higher by 0.04 eV. Detachment of an electron from an α - $4s3d_\sigma$ LSO of V results in the ground ${}^5\Delta$ state of VZn^+ , which possesses a single α - $(24\%V4s+76\%Zn4s)$ BO.

CrMn. In agreement with previous theoretical work,³¹ the ground state found is ${}^2\Sigma^+[\text{Cr}(3d^{4.81}4s^{1.01}),\text{Mn}(3d^{5.40}4s^{1.72})]$, while the ESR measurements predict a ${}^4\Sigma$ state. Since both CrMn^- and CrMn^+ ions are found to possess ${}^1\Sigma^+$ ground states, we would like to see confirmation of the ESR assignment of neutral ground state and higher level calculations performed on CrMn . The ${}^2\Sigma^+$ state is antiferromagnetic with the $3d$ -half shells of Cr and Mn placed in the opposite spin representations. Promotion $4s \rightarrow 3d$ at Mn is costly (2.15 eV, see Chart 1); therefore, one $4s$ electron of Mn remains inactive and occupies an α - $4s$ LSO, while the second $4s$ electron of Mn together with a $4s$ electron of Cr occupy a single σ -BO in each spin representation which are asymmetric in the opposite directions, as it was the case for VCr and Cr_2 .⁵⁰ The lowest ferromagnetic ${}^{12}\Sigma^+$ state, which has all six α -LSOs filled at each site and a β - $(4s+4s)$ BO, is higher by 0.40 eV. Attachment of an extra electron to an antibonding β σ -MO of the ${}^2\Sigma^+$ state results in the ground ${}^1\Sigma^+$ state of CrMn^- with a single σ bond in the α -spin representation, while detachment of an electron from the Mn α $4s$ -LSO yields the ground ${}^1\Sigma^+$ state of CrMn^+ .

CrFe. Two lowest states are antiferromagnetic and have the spin multiplicity of three. Their α -spin representations contain a $(4s+4s)$ BO, a half filled Cr $3d$ -shell, and two Fe LSOs, while their β -spin representations contain a $(4s+4s)$ BO and a Fe $3d$ -half shell. Thus, the spatial symmetry of the states is defined by distribution of two Fe $3d$ -electrons over five LSOs. The ${}^3\Pi(3d_\sigma,3d_\pi)[\text{Cr}(3d^{4.89}4s^{0.80}),$

$\text{Fe}(3d^{6.90}4s^{1.25})]$ is below the ${}^3\Delta(3d_\sigma,3d_\delta)$ state $[\text{Cr}(3d^{4.86}4s^{0.95}),\text{Fe}(3d^{6.80}4s^{1.37})]$ by only 0.02 eV. Attachment of an extra electron to an antibonding $\beta(4s-4s)$ MO breaks the bond and creates two $4s$ LSOs, which results in the lowest doublet state of the CrFe^- , a ${}^2\Delta(3d_\sigma 4s,3d_\delta)$. Attachment to the vacant Fe α - $3d_\pi$ LSO results into a ${}^4\Sigma^-$ state which retains both bonding orbitals of the neutral and is above the ${}^2\Delta$ state by only 0.01 eV. The closeness in total energies of two states may be related to the lack of promotion of a Fe $4s$ electron in the ${}^2\Delta$ state. Because of near degeneracy in total energy of the CrFe and CrFe^- states, assignments of the ground states of these species require further investigations. Detachment of an extra electron from the α - $3d_\sigma$ of Fe in the ${}^3\Pi$ and ${}^3\Delta$ states of the neutral, leads to the ${}^2\Pi$ (0.0 eV) and ${}^2\Delta$ (+0.18 eV) states of CrFe^+ , respectively.

CrCo. The lowest state is ${}^4\Delta[\text{Cr}(3d^{4.93}4s^{0.86}),\text{Co}(3d^{8.04}4s^{1.11})]$, with single α and β σ -BOs. There is an α - $3d$ half-shell of Cr, a β - $3d$ half-shell of Co, and three $3d$ electrons of Co occupy the α -LSOs [two $3d_\pi$, $3d_\delta$]. Attachment of an extra electron to an antibonding β σ -MO results into a ${}^3\Delta$ state of CrCo^- , while attachment to a σ -LSO of Co results in its ground ${}^5\Delta$ state, which is lower than the ${}^3\Delta$ state by 0.38 eV. The ${}^5\Delta$ state retains both BOs of the neutral parent, while the ${}^3\Delta$ state loses the β -BO, analogously to that in CrFe^- . The larger energetic difference between the two states with respect to CrFe could be related with a smaller $4s \rightarrow 3d$ promotion energy of Co with respect to that of Fe, see Chart 1. Detachment of an electron from different Cr α -LSOs leads to several closely spaced states of CrCo^+ . Our tentative assignment of the cation ground state is ${}^3\Sigma^-$, where detachment from a Cr α - $3d_\pi$ LSO results in formation of an additional $(3d_\pi+3d_\pi)$ BO.

CrNi. The lowest state is ${}^5\Sigma^+[\text{Cr}(3d^{4.86}4s^{0.91}),\text{Ni}(3d^{9.15}4s^{1.05})]$, with two α σ -bonds and one β - $(4s+4s)$ bond. There are four α -LSOs [two $3d_\pi$, two $3d_\delta$] at each site and a β - $3d$ half shell of Ni. A ${}^5\Delta$ state, which has one α and one $\beta(4s+4s)$ BO and a completed Cr α - $3d$ half shell, is above by 0.07 eV. Attachment of an extra electron to an antibonding α σ -MOs of the ${}^5\Sigma^+$ and ${}^5\Delta$ states leads to the ground ${}^6\Sigma^+$ (0.0 eV) and first excited ${}^5\Delta$ (+0.10 eV) states of CrNi^- . There are at least five states of CrNi^+ (${}^4\Sigma^-$, ${}^6\Sigma^+$, ${}^6\Pi$, ${}^6\Delta$, and ${}^8\Delta$) separated by less than 0.2 eV. A tentative assignment of the ground state is ${}^6\Pi$, which corresponds to detachment of an electron from a Ni β - $3d_\pi$ LSO of the neutral ground state.

CrCu. The lowest state is ${}^6\Sigma^+[\text{Cr}(3d^{4.96}4s^{0.83}),\text{Cu}(3d^{9.94}4s^{1.24})]$, with two $(4s+4s)$ BOs. The experimental assignment is controversial with the ground state assigned as either ${}^6\Sigma$ (Ref. 56) or ${}^4\Sigma$.⁵⁷ Our computations show the lowest quartet state to be above the ${}^6\Sigma^+$ state by 1.52 eV. Attachment of an extra electron to an antibonding α σ -MO creates the full set of 12 α -LSOs and the ground ${}^7\Sigma^+$ state of the CrCu^- anion. Attachment to an antibonding β - $(4s-4s)$ MO results in seven β -LSOs and a ${}^5\Sigma^+$ state, which is above the ${}^7\Sigma^+$ state by 0.40 eV. Detachment of an electron from the α - and β -BOs results in the ${}^5\Sigma^+$ (0.0 eV) and ${}^7\Sigma^+$ (0.18 eV) states of the cation.

CrZn. In agreement with experiment,⁵⁸ the lowest state

is ${}^7\Sigma^+$. There is no occupied BO, and the dimer may be considered as a van der Waals dimer since the dissociation energy of 0.28 eV and the bond length of 2.71 Å are compatible with this type of atomic interactions. Attachment of an extra electron to the β -4s LSO of Cr results in the ${}^6\Sigma^+$ state of the CrZn^- anion, which is below the neutral parent state by 0.48 eV. Detachment of an electron from the α -4s LSO of Cr allows the formation of a $4s+4s$ α -bond in the ${}^6\Sigma^+$ state of CrZn^+ , which is substantially more stable than its neutral parent state.

MnFe. The ground state of this dimer is ${}^{10}\Sigma^-$ [$\text{Mn}(3d^{5.47}4s^{1.34}), \text{Fe}(3d^{6.64}4s^{1.43})$], with all 12 available LSOs occupied in the α -spin representation and three BO ($4s+4s$, two $3d_\pi+3d_\pi$) in the β -spin representation. This result is consistent with our assignment⁵⁰ of an ${}^{11}\Pi_u$ state as the ground state of Mn_2 , which has the same bonding patterns but one π -BO. The population analysis of the ${}^{10}\Sigma^-$ state shows $4s \rightarrow 3d$ transfer to be shared by both sites. Since both atoms have not been promoted to $3d^{n+1}4s^1$, we find a violation of the spin multiplicity rule according to which the ground-state spin multiplicity of MnFe should be 2 or 8. The ground ${}^9\Sigma^-$ state of MnFe^- is formed after attachment of an extra electron to the β -($3d_\sigma+3d_\sigma$) BO. Attachment to a Fe β - $3d_\delta$ LSO results in a ${}^9\Delta$ state, which is higher by 0.22 eV. Detachment of an electron from the α -($4s-4s$) MO creates the α -($4s+4s$) BO in the cation ground ${}^9\Sigma^-$ state.

MnCo. Co has a smaller $4s \rightarrow 3d$ promotion energy than Fe and two 4s electrons are promoted into the 3d manifold to allow the formation of an α -($4s+4s$) BO. Therefore, the ground ${}^7\Delta$ state [$\text{Mn}(3d^{5.77}4s^{1.03}), \text{Co}(3d^{8.124}4s^{1.02})$] possesses one α -($4s+4s$) BO, four β -BOs [$4s+4s$, two $3d_\pi+3d_\pi$, $3d_\sigma+3d_\sigma$], and a β - $3d_\delta$ LSO of Co. Attachment of an extra electron to an α -($4s-4s$) antibonding orbital eliminates the α -($4s+4s$) BO and creates a pair of 4s LSOs instead without affecting the β -bonding patterns of the neutral parent state. The resulting ground state of the anion is ${}^8\Delta$. Attachment of an extra electron to the β -($4s-4s$) antibonding orbital results in a ${}^6\Delta$ state, which is higher than the ${}^8\Delta$ state by 0.40 eV. The lowest ${}^8\Delta$ state of MnCo^+ is formed by the detachment of an electron from the β -($4s+4s$) BO.

MnNi. The ground ${}^6\Sigma^+$ state [$\text{Mn}(3d^{5.67}4s^{1.08}), \text{Ni}(3d^{9.28}4s^{0.91})$] has the same bonding patterns as the ground state of MnCo except the second β - $3d_\delta$ LSO is occupied. For the anion, attachment of an extra electron to an α -($4s-4s$) antibonding orbital leads to the ground ${}^7\Sigma^+$ state while a ${}^5\Sigma^+$ state formed by attachment to a β -($4s-4s$) antibonding orbital is above by 0.32 eV. Detachment of an electron from the β -($4s+4s$) BO lead to rather drastic changes: one $3d_\pi+3d_\pi$ breaks and Ni has three different type β -LSOs ($3d_\pi, 3d_\delta, 3d_\sigma$). The corresponding ground state of MnNi^+ is ${}^7\Delta$. Although isoelectronic MnCo has also the ground ${}^7\Delta$ state, it has the different bonding patterns.

MnCu. The lowest state of MnCu is ${}^7\Sigma^+$ [$\text{Mn}(3d^{5.23}4s^{1.30}), \text{Cu}(3d^{9.82}4s^{1.52})$], where 12 electrons fill all the available α -LSOs, five electrons occupy a Cu β -3d shell, and the dimer has only one bonding orbital β -($4s+4s$). The lowest excited state, whose spin multiplicity obeys

the spin multiplicity rule is ${}^5\Sigma^+$ [$\text{Mn}(3d^{5.44}4s^{1.45}), \text{Cu}(3d^{9.91}4s^{1.15})$], which is above the ground state by 0.34 eV in rather close agreement with the experimental value²² of 0.382 ± 0.002 eV derived from photoelectron spectra. As is seen from Table I, the computed spectroscopic constants of the ${}^7\Sigma^+$ state are in good agreement with the experimental values.²² The ground ${}^6\Sigma^+$ state of the anion forms when an extra electron attaches to the β -4s LSO of Mn which retains the β σ -BO but changes its character to $3d_\sigma+4s$. Our computed values of $\omega_e = 171 \text{ cm}^{-1}$ and $D_o = 1.34 \text{ eV}$ are in good agreement with the analogous experimental values²² of $147 \pm 4 \text{ cm}^{-1}$ and $1.3_{+0.5}^{-0.2} \text{ eV}$ (see Table II). Detachment of an electron from the α -($4s-4s$) antibonding orbital creates the second ($4s+4s$) BO and the ground state of MnCu^+ is ${}^6\Sigma^+$.

MnZn. The only bound state is ${}^6\Sigma^+$ where all 4s and 3d electrons occupy the LSOs and both spatial symmetry and spin multiplicity of the state are defined by the β -3d half shell of Zn. An extra electron may fill into higher ($4p_\pi+4p_\pi$) or ($4p_\sigma 5s+4p_\sigma 5s$) BOs that brings ${}^7\Pi$ and ${}^7\Sigma^+$ states of the anion, which are below the ${}^6\Sigma^+$ state by 0.09 and 0.17 eV, respectively. Attachment of an extra electron to the Mn β - $3d_\sigma$ LSO allows the formation of a hybridized β -($3d_\sigma 4s+3d_\sigma 4s$) BO and yields the ground ${}^5\Sigma^+$ state of MnZn^- . The lowest energy state of MnZn^+ is formed by detachment of an electron from a β -4s LSO that is accompanied by formation of a β -($3d_\sigma 4s+4s$) BO in the ground ${}^7\Sigma^+$ state of MnZn^+ .

FeCo. In agreement with experiment,⁵⁹ the lowest energy state is ${}^6\Sigma^+$ [$\text{Fe}(3d^{6.84}4s^{1.06}), \text{Co}(3d^{8.10}4s^{0.95})$] that has an α -($4s+4s$) BO, two α -3d half shells, and six rather symmetric β -BOs. The ground ${}^7\Sigma^+$ state of FeCo^- is formed by the extra electron attachment to the α -($4s-4s$) antibonding orbital that breaks the α -($4s+4s$) bond and creates two α -4s LSOs. Attachment to the β -($4s-4s$) antibonding orbital results in a ${}^5\Sigma^+$ state which is higher by 0.35 eV. The ground ${}^7\Delta$ state of the cation is formed after detachment of an electron from a β -($3d_\delta+3d_\delta$) BO.

FeNi. The ground state is ${}^5\Delta$ [$\text{Fe}(3d^{6.80}4s^{1.05}), \text{Ni}(3d^{9.17}4s^{0.94})$]. An extra electron, with respect to FeCo, fills into an antibonding β -($3d_\delta-3d_\delta$) MO that results in the breaking of both β -($3d_\delta+3d_\delta$) BOs and the formation of three $3d_\delta$ LSOs (one at Fe and two at Ni). Our computed vibrational frequency of 350 cm^{-1} is in good agreement with the experimental frequency⁶⁰ of 320.0 cm^{-1} . Attachment of an extra electron to the α - and β -($4s-4s$) MOs results into ${}^4\Delta$ and ${}^6\Delta$ states, respectively. The latter state is lower by 0.28 eV. Detachment of an electron from a β -3d LSO of Ni yields the same bonding pattern as in isoelectronic FeCo and the same ground ${}^6\Sigma^+$ state.

FeCu. Only the α - and β -($4s+4s$) BOs survive after adding an extra electron, with respect to FeNi, into the β -spin representation. Since the 3d shell of Cu as well as an α -3d half shell of Fe are occupied, the spatial symmetry of this dimer is defined by the possible occupation of Fe β -LSOs by two electrons. The ground state is ${}^4\Pi$ [$\text{Fe}(3d^{6.93}4s^{1.00}), \text{Cu}(3d^{9.93}4s^{1.10})$] and corresponds to a ($3d_\sigma, 3d_\pi$) occupation. Attachment of an electron to the α -($4s-4s$) antibonding orbital destroys the α -bond and the

lowest state of FeCu^- is $^5\Delta$ [a $\text{Fe}(3d_\sigma, 3d_\delta)$ occupation] followed by a $^5\Pi$ state [+0.09 eV, a $\text{Fe}(3d_\sigma, 3d_\pi)$ occupation], and a $^5\Sigma^-$ [+0.36 eV, a $\text{Fe}(3d_\pi, 3d_\pi)$ occupation]. Note that the anion ground state prefers the $\text{Fe}(3d_\sigma, 3d_\delta)$ occupation not the $(3d_\sigma, 3d_\pi)$ one which would correspond to a one-electron process. The FeCu^+ cation has a $^5\Delta$ ground state with a single β $3d_\delta$ LSO at Fe.

FeZn. The $4s \rightarrow 3d$ promotion at Fe is favorable since the energy spend for the promotion is regained due to formation of a β - $(4s+4s)$ BO in two closely spaced $^5\Sigma^-$ [$\text{Fe}(3d^{6.93}4s^{1.14})$, $\text{Zn}(3d^{10.00}4s^{1.77})$] and $^5\Pi$ [+0.02 eV, $\text{Fe}(3d^{6.90}4s^{1.18})$, $\text{Zn}(3d^{10.00}4s^{1.79})$] states with Fe β -LSOs occupations of $(3d_\pi, 3d_\pi)$ and $(3d_\sigma, 3d_\pi)$, respectively. Despite the formation of a bond, dissociation energy of FeZn is rather small apparently because of the energy spend for the promotion. Attachment of an extra electron to the β - $4s$ LSO of Zn in the $^5\Sigma^-$ and $^5\Pi$ states, results into formation of the $^4\Sigma^-$ (+0.04 eV) and $^4\Pi$ (0.0 eV) states of the FeZn^- anion. Detachment of an extra electron from an α - $4s$ LSO results in formation of an α - $(4s+4s)$ BO in the lowest $^4\Pi$ state of the cation. This state is followed by $^4\Sigma^-$ and $^4\Delta$ states, which are higher by 0.01 and 0.12 eV, respectively.

CoNi. The lowest state is $^4\Delta$ [$\text{Co}(3d^{7.82}4s^{1.12})$, $\text{Ni}(3d^{9.09}4s^{0.94})$], which has an α - $(4s+4s)$ BO, two α - $3d$ half shells, four β -BOs ($4s+4s$, two $3d_\pi+3d_\pi$, $3d_\delta+3d_\delta$) and each site hosts two β -LSOs ($3d_\delta, 3d_\sigma$). A $^4\Phi$ state, which has three β -BOs ($4s+4s, 3d_\pi+3d_\pi, 3d_\sigma+3d_\sigma$), two β -LSOs of $\text{Co}(3d_\pi, 3d_\delta)$ and three β -LSOs of $\text{Ni}(3d_\pi, \text{two } 3d_\delta)$, is only marginally higher by 0.02 eV. Attachment of an extra electron to the antibonding $4s-4s$ MOs of these two states results in several closely spaced states of CoNi^- : $^5\Delta$ (0.0 eV), $^5\Phi$ (+0.08 eV), $^5\Sigma^-$ (+0.55 eV), $^3\Delta$ (+0.27 eV), and $^3\Pi$ (+0.23 eV). Detachment of an electron from the β - $(3d_\delta+3d_\delta)$ BO of the $^4\Delta$ state results in a $^5\Delta$ state of CoNi^+ , whose LSOs are different from those of the $^4\Delta$ state: one Co ($3d_\delta$) and three Ni (two $3d_\delta$, $3d_\sigma$) β -LSOs. This state is 0.04 eV above the ground $^5\Phi$ state, which forms after detachment of an electron from a β - σ MO of the $^4\Phi$ state.

CoCu. Spatial symmetry of the ground $^3\Delta$ ($3d_\sigma, 3d_\delta$) state is defined by the most favorable distribution of β - $3d$ electrons over the five Co LSOs, i.e., an occupation of two $3d_\pi$ and one $3d_\delta$. (There is a $4s+4s$ BO in each spin representations, two α - and one β - $3d$ half shells.) Our computed vibrational frequency of 254 cm^{-1} and dissociation energy of 1.80 eV are in good agreement with the analogous experimental values of 270.0 cm^{-1} (Ref. 61) and 1.65 eV.⁶¹ Attachment of an extra electron to the antibonding α - and β - $(4s-4s)$ MOs leads to formation of the $^4\Delta$ (0.0 eV) and $^2\Delta$ (+0.12 eV) states of the CoCu^- , respectively. Detachment of an electron from a β - $3d_\pi$ LSO of Co leaves its two β -LSOs: $3d_\delta$ and $3d_\pi$, which determine the spatial symmetry of the CoCu^+ cation. This occupation is a mixture of $^4\Pi$ and $^4\Phi$, and we tentative assignment the ground state as $^4\Phi$.

CoZn. The lowest $^4\Delta$ state possesses a β - $(4s+4s)$ BO and its spatial symmetry is defined by three Co β -LSOs [$3d_\delta$, two $3d_\pi$]. Attachment of an extra electron to an antibonding β - $(4s-4s)$ MO creates two β - $4s$ LSOs, and the

anion ground state is $^3\Delta$. Detachment of an electron from an α - $4s$ LSO results in the additional α - $(4s+4s)$ BO and the ground $^3\Delta$ state of CoZn^+ .

NiCu. In agreement with experiment,¹⁸⁻²⁰ the ground state is $^2\Delta$. There are two $(4s+4s)$ BOs, three $3d$ -half shells, and four Ni β -LSOs (two $3d_\pi$, $3d_\delta$, $3d_\sigma$). Several spectroscopic constants of NiCu were measured: $r_e = 2.233 \pm 0.006 \text{ \AA}$, $\omega_e = 273.01 \pm 1.15 \text{ cm}^{-1}$, $D_o = 2.05 \pm 0.10 \text{ eV}$,¹⁸ $r_o = 2.2346(5) \text{ \AA}$,^{19,20} $D_o = 2.06 \pm 0.21 \text{ eV}$.⁶² These values are to be compared with our computed $r_e = 2.247 \text{ \AA}$, $\omega_e = 266.4 \text{ cm}^{-1}$, $D_o = 1.95 \text{ eV}$. Attachment of an extra electron to the α - $(4s-4s)$ MO breaks the α -bond and creates the ground $^3\Delta$ state of NiCu^- . Our computed values $r_e = 2.36 \text{ \AA}$, $\omega_e = 211 \text{ cm}^{-1}$, $D_o = 1.74$ of this state are in good agreement with the experimental values²¹ of $2.36 \pm 0.01 \text{ \AA}$, $235 \pm 25 \text{ cm}^{-1}$, and $1.70 \pm 0.02 \text{ eV}$. Detachment of an electron from the Ni β - $3d_\sigma$ LSO creates the lowest $^3\Delta$ state of the NiCu^+ cation.

NiZn. There are a number of closely spaced singlet and triplet states. The lowest is a $^3\Delta$ state with 12 α -LSOs, one β - $(4s+4s)$ BO, a β -half shell of Zn and four Ni LSOs ($3d_\sigma$, two $3d_\pi$, $3d_\delta$). Attachment of an extra electron to a β - $(4s-4s)$ MO forms the ground $^2\Delta$ state of NiZn^- with no bonds, while detachment from an α - $4s$ LSOs leads to formation of an additional α - $(4s+4s)$ BO and a rather stable ground $^2\Delta$ state of NiZn^+ .

CuZn. In agreement with experiment,⁶⁰ the ground state is $^2\Sigma^+$ with a single β - $(4s+4s)$ BO. All other electrons occupy two α - $4s$ LSOs and two $3d$ shells. Attachment of an extra electron to the β - $(4s-4s)$ MO creates the full set of 24 LSOs and the ground state is $^1\Sigma^+$. Detachment of an electron from an α - $4s$ LSO creates the α - $(4s+4s)$ BO and the ground $^1\Sigma^+$ state which is rather stable toward dissociation, see Table III.

B. Properties and thermodynamic stability

The $3d$ -metal mixed dimers show a large variation in bond lengths and vibrational frequencies, see Table I. TiFe, possessing the $^1\Sigma^+$ ground state with a sextuple bond, has the shortest bond length and, correspondingly, the largest vibrational frequency. Note that the dimers surrounding TiFe have also large binding energies. The dimers containing Cr and Mn possess the smallest dissociation energies. The Cr-containing dimers have large bond lengths similar to those of the Cu-containing dimers. The latter dimers, however, possess larger and rather uniform binding energies that may be related to the lower energy of the Cu $4s$ -state with respect to that of Cr. All Zn-containing dimers have large bond lengths and small dissociation energies, which is consistent with the conventional anticipation of Zn chemical inertness in such species.

Most of the dipole moments presented in Table IV carry negative signs which is related with our choice of the coordinate system: the lighter atom is placed in the origin and the heavier one is displaced in the positive direction of the z axis. The largest dipole moment of 2.65 D belongs to ScCo, that may be related to a half electron transfer from Sc to Co as shows the effective electronic configurations

Sc ($3d^{1.50}4s^{0.92}$) and Co ($3d^{8.50}4s^{1.07}$) in the $^1\Sigma^+$ ground state of ScCo.

The neutral mixed dimers in columns from Cr to Cu and in rows from Sc to Cr possess an antiferromagnetic coupling of excess spin densities at atomic sites except for ScCo and TiFe, which are nonmagnetic, along with ScNi and ScCu, which are ferromagnetic. FeCu and CoCu also have small excess spin densities at Cu sites, which are antiferromagnetically coupled to the spin densities at Fe and Co sites. An analysis of the bonding patterns and the content of bonding orbital in the dimers allows us to indicate at least three possible contributions to the antiferromagnetic coupling: (1) different numbers of localized spin orbitals at the dimer atoms, (2) spin polarization of bonding orbitals, and (3) nonequivalent contributions to the same-type bonding orbitals in the α - and β -spin representations. As an example, let us consider CrFe, where Fe has two α - $3d$ LSOs and a β - $3d$ half shell, which reduces the magnetic moment at Fe to -3 . The additional $-0.4\mu_B$ comes mainly from spin polarization of the two CrFe bonding orbitals, which are

$$\begin{aligned} \sigma\text{-}\alpha: & 67\% \text{ Cr}(76\% 4s + 23\% 3d_\sigma) \\ & + 33\% \text{ Fe}(67\% 4s + 32\% 3d_\sigma), \\ \sigma\text{-}\beta: & 20\% \text{ Cr}(79\% 4s + 20\% 3d_\sigma) \\ & + 80\% \text{ Fe}(94\% 4s + 6\% 3d_\sigma). \end{aligned}$$

Experimental dissociation energies are known for TiV:¹² 2.068 ± 0.001 eV, TiCo:¹² 2.401 ± 0.001 eV, VNi:¹² 2.100 ± 0.001 eV, CrCu:⁶² 1.56 ± 0.26 eV, MnCu:²² ≈ 1.5 eV, CoCu:⁶² 1.65 ± 0.21 eV, and NiCu:¹⁸ 2.05 ± 0.10 eV. These values are to be compared to our computed values of 2.78, 3.39, 2.44, 1.36, 1.56, 1.80, and 1.95 eV, respectively. As seen, the largest discrepancy of 1 eV is obtained for TiCo. Overall, agreement is reasonable, but the size of the overestimate does not appear to be systematic.

We are unaware of any experimental data for the electron detachment energies of the mixed dimers, while the electron attachment energies are known for MnCu (Ref. 22) and NiCu.²¹ Our computed values of 0.93 and 0.91 eV are in good agreement with the experimental values of 1.075 ± 0.003 and 0.889 ± 0.010 eV, respectively. Comparing Chart 1 and Table IV, one can notice that electron attachment energies of the dimers are larger than the attachment energies of at least one atom entering the corresponding dimer.

Hettich and Freiser²³ have measured the dissociation energies for a number of mixed iron-containing dimer cations: ScFe⁺ 2.12 ± 0.22 , TiFe⁺ 2.60 ± 0.26 , VFe⁺ 3.25 ± 0.22 , CrFe⁺ 2.17 ± 0.30 , FeCo⁺ 2.69 ± 0.22 , FeNi⁺ 2.78 ± 0.22 , and FeCu⁺ 2.30 ± 0.30 eV. These values are to be compared to our computed values of the lowest asymptotes of 2.96, 3.83, 3.33, 2.27, 3.27, 3.27, and 2.61 eV, respectively. As expected, the theory has a tendency to overestimating the cation dissociation energies, but there does not appear to be any pattern in the overestimation.

IV. SUMMARY

Several conclusions may be drawn from the results of our computations on the structure of mixed $3d$ -metal dimers:

(1) When moving along the rows and columns, the ground-state spin multiplicities of the neutral mixed dimers do change by ± 1 except when moving from ScV to ScCr, ScV to TiV, CrFe to MnFe, CrCo to MnCo, MnFe to MnCo, and MnCu to FeCu. Sc possesses a high $3d^1 4s^2 \rightarrow 3d^2 4s^1$ promotion energy of 1.43 eV. This is an apparent reason why the Sc atoms do not have a $3d^2 4s^1$ occupation in Sc₂, ScTi, and ScV and why these molecules have higher spin multiplicities than those species where the both atoms have only one $4s$ electron. The “irregular” behavior of Mn is related to the high $3d^5 4s^2 \rightarrow 3d^6 4s^1$ promotion energy of 2.15 eV that means that Mn, like Sc, is not always promoted to the $3d^{n+1} 4s^1$ occupation.

(2) The number of unpaired electrons in the neutral mixed dimers is related to the numbers of unpaired $3d$ -electrons in the $3d^n 4s^1$ occupations of the constituent atoms N_1 and N_2 , respectively, according to a simple rule: the number is either $N_1 + N_2$ or $|N_1 - N_2|$. Exceptions are TiV (the ground state has three unpaired electrons instead of one or seven defined by the above rule), MnFe (nine unpaired electrons instead of one or seven) and MnCu (six instead of four).

(3) All 12-valence electron dimers. (ScCo, TiFe, and VMn) possess $^1\Sigma^+$ ground states; however, their bonding patterns are rather different. ScCo has four symmetric equivalent bonding orbitals and two Co $3d_\delta$ LSOs in each spin representations, TiFe has six symmetric equivalent bonding orbitals and may be considered as possessing a classic sextuple bond, while VMn has six α -bonding orbitals, four β -bonding orbitals, spin-polarized with respect to the α -bonding orbitals, and two Mn β - $3d_\delta$ LSOs. The VMn ground state is antiferromagnetic similar to that of isoelectronic Cr₂. There is no other singlet ground state among the rest of the mixed dimers.

(4) Ground states of the neutral dimers encompassed between columns Cr to Ni and rows Sc to Mn are mainly antiferromagnetic. The antiferromagnetic contributions come from the following sources: the larger number of localized spin orbitals at one site, nonequivalent contributions to the same-type bonding orbitals in the α - and β -spin representations, and/or spin polarization of bonding orbitals.

(5) Attachment or detachment of an electron lead to the ion ground state whose number of unpaired electrons is different by ± 1 from the number of unpaired electrons in the corresponding neutral ground state. It appears, however, that some ion ground states are not related to the neutral ground state via a one-electron process.

(6) Generally, the results of our density functional theory calculations are in reasonably good agreement with experimental data and could be considered as a helpful guide for future experiments and advanced computations.

(7) We noted several cases where there are states very close in energy, so some experimental data could help determine the ground state in these cases.

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