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Bonding and physical properties of Hume-Rothery compounds with the $PtHg_4$ structure

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We present a detailed experimental and theoretical study concerning bonding and structural stability of intermetallic electron compounds with the $PtHg_4$ structure. Due to the simplicity of the structure these compounds represent an excellent prototype system for a more general insight into bonding and stability of the large family of d-sp bonded Hume-Rothery compounds. In particular, the representatives $CrGa_4$ and $MnGa_4$ were synthesised and their resistivity, magnetic susceptibility, and bulk modulus measured. We find that both compounds are metallic conductors but show a remarkable large difference in their temperature independent magnetic susceptibilities. The value of the Pauli paramagnetic susceptibility of $MnGa_4$ is about 5×10^{-9} m^3/mol higher than that of $CrGa_4$. The $PtHg_4$ structure of $CrGa_4$ and $MnGa_4$ is stable up to pressures of about 100 kbar. Full-potential linearized augmented plane wave calculations reproduced very well the experimental structural properties of $CrGa_4$ and $MnGa_4$ and showed strong directional (covalent) bonding between transition metal atoms and Ga atoms in both compounds. The directional bonding is due to a large hybridization of the narrow d bands with the Ga sp bands. As a consequence a large pseudogap at the Fermi level for $CrGa_4$ and slightly above the Fermi level for $MnGa_4$ is produced. This pseudogap is characteristic and decisive for structural stability of electron compounds with the $PtHg_4$ structure. We find that structural stability appears as a competition between optimizing the pseudogap and minimizing the compound equilibrium volume. Therefore, stable electron compounds are confined to systems $T\mathrm{Ga}_4$ with T being a transition metal from group 6 or 7. A complete substitution of Ga for isovalent Al or In is not possible.

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I. INTRODUCTION

The interpretation of structural stability and chemical bonding in intermetallic compounds is a continuous challenge for physicists and chemists because metallic systems evade the simple and powerful valence rules applicable to semiconducting and insulating solids which allow the linking of electron counts to particular geometrical arrangements of atoms.[1,2] However, there exists a number of intermetallics where the valence electron concentration [(VEC), average number of valence electrons per atom] plays a decisive role for structural stability and these compounds are usually classified as electron compounds[3] or Hume-Rothery compounds.[4] One group of such intermetallic electron compounds comprises E-rich systems T_mE_n ($n/m\geqslant3$) where T is a transition metal from the groups V-Fe and E is preferably Al or Ga. In these compounds the transition metal atoms appear uniformly distributed in a matrix of E atoms and the resulting structures (e.g., VAl_{10}, WAl_{12}, $MnAl_6$, Ru_4Al_{13}, $MnGa_4$, V_8Ga_{41}, V_7Al_{45}) are very often large and complex. Characteristically the T atoms are separated by the largest distance possible and, thus, are only coordinated by E atoms in the first coordination sphere. The resulting TE_p coordination polyhedra are rather regular with p ranging from eight to twelve and appear as discrete entities (VAl_{10}, WAl_{12}), as vertex linked ($MnGa_4$, V_8Ga_{41}) or edge linked ($MnAl_6$). According to Trambly de Laissardiere *et al.*[5] who performed electronic structure calculations of a large number of T-Al Hume-Rothery compounds the origin of the important role of VEC for the stability of this class of compounds lies in the occurrence of a pronounced pseudogap at the Fermi level in the density of states (DOS). This pseudogap is an effect of strong $d(T)$-$sp(E)$ hybridization and separates bonding from antibonding states. As a consequence the TE_p coordination polyhedra should represent strongly bonded entities and the position of the pseudogap determines the optimum VEC, or in the case of broad pseudo gaps a range of optimum VEC, for a particular Hume-Rothery compound.

In this paper we discuss structural stability and chemical bonding of T-E electron compounds with the simplest structure occurring among this class of compounds. It is the body centered cubic $PtHg_4$ structure type with the space group $Im\overline{3}m$. Three Hume-Rothery compounds adopt this structure type, namely $CrGa_4$, $MnGa_4$, and $ReGa_4$. The transition metal atoms occupy position $2a$ (0,0,0) and the Ga atoms position $8c$ ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$). The structure can easily be regarded as a defect CsCl structure where $\frac{3}{4}$ of the Cs atoms have been removed in such a way that an array of corner connected cubes $[\mathrm{TGa}_{8/2}]$ is formed as depicted in Fig. 1. The removal of Cs atoms reduces maximum space filling (if defined geometrically from a packing of equally sized spheres) from 68% in the CsCl structure to 42.5% in the $PtHg_4$ structure. The formation of loosely packed intermetallic structures is a strong indicator of the presence of directional (covalent) bonding (e.g., the CoSn structure[6]).

The compounds $CrGa_4$ and $MnGa_4$ were reported already some 30 years ago,[7] although there seems to be some contradiction in the composition because both were also published as nonstoichiometric TGa_3.[8] $ReGa_4$ was discovered

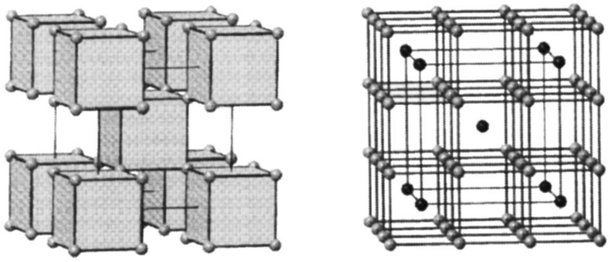

FIG. 1. The $PtHg_4$ structure type represented as a framework of corner connected $PtHg_{8/2}$ coordinations polyhedra (left) and as a stuffed simple cubic array of Hg atoms (right). Dark spheres indicate Pt atoms, light spheres Hg atoms.

just recently.[9] We reinvestigated composition and structure of $CrGa_4$ and $MnGa_4$ and determined their bulk moduli from single crystal high pressure experiments as well as their magnetic and conductivity properties. Finally we completed our study with a detailed bonding analysis of T-E electron compounds with the $PtHg_4$ type which—due to the simplicity of the structure—represent an excellent prototype system for a more general insight into structural stability and bonding of d-sp bonded Hume-Rothery compounds.

The experimental and computational details are given in Secs. II and III, respectively. Section IV is devoted to the obtained results and their discussion. A summary is given in Sec. V.

II. EXPERIMENTAL DETAILS

A. Sample preparation and analysis

The compounds $CrGa_4$ and $MnGa_4$ were prepared from mixtures of the pure elements with a molar ratio of 1:50 and 1:6, respectively. The samples with a weight of 5 g were loaded into quartz ampoules which were sealed under vacuum. The Cr/Ga sample was heated to 960 °C, kept at this temperature for 15 h, cooled to 250 °C at a rate of 200 °C per hour and annealed at this temperature for 72 h. The Mn/Ga sample was first heated to 800 °C, held at this temperature for 50 h and then cooled to room temperature at a rate of 25 °C per hour. Excess Ga was dissolved with 3 molar HCl yielding highly crystalline products of $CrGa_4$ and $MnGa_4$. The crystals of both samples have a silvery color and are well shaped (often truncated octahedra) with sizes in the range of one tenth of a millimeter up to one millimeter.

The homogeneity of the products was confirmed by powder x-ray diffraction patterns taken on a Guinier powder camera with Cu$K\alpha$ radiation. The lattice constant of the compounds was obtained from a least squares from 11 measured and indexed lines using Si (NIST) as an internal standard. The elemental composition was verified by means of semiquantitative elemental analyses of 30 crystallites from each sample with the energy disperse x-ray (EDX) method in a JEOL scanning microscope.

B. High-pressure investigations

Single crystal high-pressure investigations on $CrGa_4$ and $MnGa_4$ were performed using a Merril-Basset type of diamond anvils cell (DAC) with diamond culet diameters of 0.6 mm and preindented stainless steel gaskets with mechanically drilled hole diameters of about 0.25 mm. A mixture of methanol:ethanol:water (16:3:1) served as pressure transmitting medium. The diffraction measurements were performed with a four-circle diffractometer (Siemens P4/RA) using rotating anode generated Mo$K\alpha$ radiation (5 kW for a filament size of 0.3×3 mm). Cell parameters were determined from about 8-10 θ-values for well centered reflections in a range of $14<2\theta<30°$. Pressure calibration was performed using the ruby R_1 fluorescence line shift of 2.74 Å /kbar.[10] The estimated standard deviation for the measured pressures amounts to 0.6 kbar, except for pressures above 80 kbar when it becomes 1 kbar (fluorescence line broadening).

C. Magnetic and electric measurements

The magnetic susceptibilities of polycrystalline samples of $CrGa_4$ and $MnGa_4$ obtained from crushed single crystals were determined with a SQUID magnetometer (Quantum design, Inc.) in a temperature range between 4.2 and 300 K with a magnetic flux density of 1 T. We also performed magnetization measurements by varying the flux density between 0.01 and 5 T at different temperatures (1.75, 4.12, 10, 40, 70, and 293 K). Resistivities were measured on small blocks with a conventional four-probe technique between 11 and 300 K.

III. COMPUTATIONAL DETAILS

Nonspin-polarized energy band structure calculations for the compounds TGa_4 ($T=$V, Cr, Mn, Fe, Ta, W, Re, and Os), $CrAl_4$, and $CrIn_4$ have been performed with the full-potential linearized augmented plane wave (FLAPW) method.[11] In full-potential techniques within the density functional theory basis functions, electron densities, and potentials are calculated without any shape approximation. Concerning the FLAPW calculations, well-converged plane wave sets with a cutoff parameter $R_{mt}K_{\max}=8.0$ and atomic sphere sizes of 2.2 Bohr (V, Cr, Mn, Fe, Al, and Ga) and 2.2 Bohr (Ta, W, Re, Os, and In) were used. The T atom $3p$ ($T=3d$ transition metal) and T atom $5p$ and $4f$ ($T=5d$ transition metal) as well as the Ga $3d$ and In $4d$ states were described as so-called local orbitals. The exchange-correlation potential was treated with the generalized gradient approximation (GGA) (Ref. 12) and the results were sometimes compared with those of the less advanced local density approximation (LDA).[13] The reciprocal space integrations were performed with the tetrahedron method using 120 k points in the irreducible wedge of the Brillouin zone.

IV. RESULTS AND DISCUSSION

A. Experimental Results

The lattice parameters of $CrGa_4$ and $MnGa_4$ at ambient conditions were refined to $a=5.6508(4)$ Å and $a=5.5943(3)$ Å , respectively, just slightly different (but more precise) as the ones reported by Schubert *et al.* (5.64 Å for $CrGa_4$ and 5.59 Å for $MnGa_4$).[7,8] The relevant inter-

TABLE I. Interatomic distances in the compounds $CrGa_4$, $MnGa_4$, and $ReGa_4$.

d (Å)	$CrGa_4$	$MnGa_4$	$ReGa_4$
Ga-Ga	2.825	2.797	2.882
T-Ga	2.447	2.422	2.496
T-T	4.894	4.845	4.992

atomic distances are compared in Table I, including those of $ReGa_4$. The Ga-Ga distance (edge of the cubes) of about 2.8 Å in the three compounds indicate (weak) bonding interaction between Ga atoms when comparing to the range of nearest neighbor distances in elemental α-Ga which is between 2.48 and 2.79 Å . The EDX analyses yielded average compositional values of 17.8(8) % Cr, 82.2(8)% Ga, and 18.5(4)% Mn, 81.5(4)% Ga, respectively. These small deviations from the ideal stoichiometry 1:4 could indicate the occurrence of a small amount of transition metal defects (7–10 %). However, the accuracy of the (semiquantitative) EDX method is usually not considered to be better than 1 to 2 at. % and we regard $CrGa_4$ and $MnGa_4$ to be line phases with no range of homogeneity.

The high pressure behavior of $CrGa_4$ and $MnGa_4$ was investigated in a pressure range between 6 and 99 kbar and 3 and 66 kbar, respectively. There was no indication of a structural phase transition within these pressure ranges. The change of the unit cell parameters as a function of pressure is summarized in Fig. 2. The observed relative changes in the unit cell volumes were fitted to the Birch-Murnaghan equation of states[14] in order to determine bulk moduli B and their pressure derivatives B'. The results for $CrGa_4$ are 84(2) GPa for B and 3.8(6) for B'. For $MnGa_4$ we found $B=88(5)$ GPa and $B'=5.6(19)$. The B values are considerably higher than that of elemental Ga which is 56.9 GPa,[15] manifesting a large covalent T-Ga bonding contribution in these Ga-rich Hume-Rothery compounds.

The temperature dependence of the magnetic susceptibilities for $CrGa_4$ and $MnGa_4$ at $B=1$ T is shown in Fig. 3. Down to 50 K the susceptibilities are essentially temperature independent with room temperature values of $-0.7(1)\times10^{-9}$ m^3/mol ($CrGa_4$) and $4.2(1)\times10^{-9}$ m^3/mol ($MnGa_4$). The increase of the susceptibilities below 50 K is most likely due to very small amounts of paramagnetic impurities (e.g., the formation of traces of hydrated $CrCl_2$ and $MnCl_2$ on the surface of the $CrGa_4$ and $MnGa_4$ crystals when dissolving excess Ga with HCl). The measured molar magnetic susceptibility is actually a combination of the Pauli paramagnetic susceptibility with the Landau and Larmor diamagnetic susceptibilities. The estimation of those diamagnetic increments in metallic compounds is difficult and not unambiguous. As a crude estimation for the transition metals the increments of the T^0 oxidation states [Cr: -0.33×10^{-9} m^3/mol and Mn: -0.29×10^{-9} m^3/mol (Ref. 16)] and for Ga the elemental diamagnetic susceptibility of -0.28×10^{-9} m^3/mol[17] might be considered. With these increments we obtain values of -1.45×10^{-9} m^3/mol and -1.41×10^{-9} m^3/mol for the core diamagnetism of $CrGa_4$ and $MnGa_4$, respectively and the Pauli paramagnetic susceptibilities become 0.75×10^{-9} m^3/mol ($CrGa_4$) and 5.61×10^{-9} m^3/mol ($MnGa_4$). However, despite the shortcoming of this correction we can safely state that when taking into account underlying diamagnetism $CrGa_4$ will become weakly Pauli paramagnetic and the difference of the susceptibility values of $MnGa_4$ and $CrGa_4$ $\Delta\chi_{mol}\approx5\times10^{-9}$ m^3/mol will remain unchanged because the diamagnetic increments of Cr and Mn should differ only slightly.

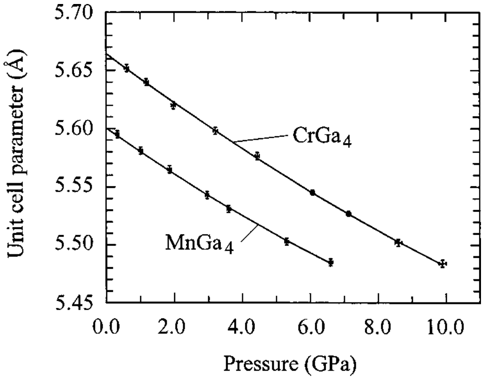

FIG. 2. Unit cell parameter changes of $CrCa_4$ and $MnGa_4$ with pressure.

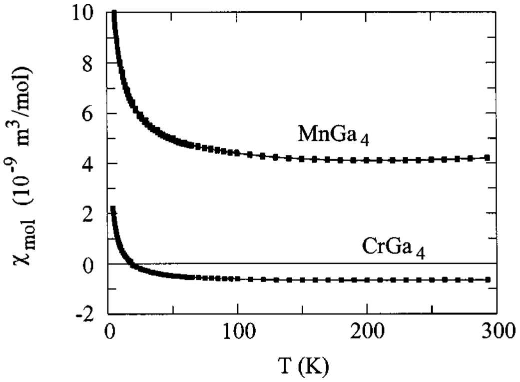

FIG. 3. Temperature dependence of the magnetic susceptibilities of $CrCa_4$ and $MnGa_4$.

The resistivity measurements reveal metallic conductivity for both compounds over the investigated range of temperature. Unfortunately the specific resistivities could not be determined. Instead the normalized resistivity $\rho(T)/\rho(300\text{ K})$ is shown in Fig. 4. At 11.5 K the resistivity for $MnGa_4$ has dropped to about 35% whereas the one of $CrGa_4$ is still above 80%. Importantly, no anomalies at low temperatures indicating (magnetic) structural transitions are observed, which is in agreement with the temperature dependence of the magnetic susceptibilities.

B. Calculational results

1. Structural properties

The calculated structural properties equilibrium volume, bulk modulus, and its pressure derivative, and the heat of formation for the compounds $CrGa_4$, $MnGa_4$, and $ReGa_4$ are listed in Table II and compared with experiment. For $CrGa_4$

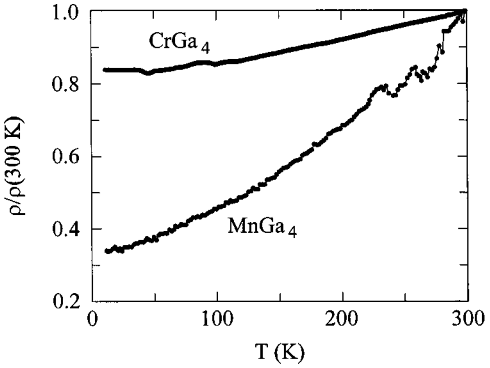

FIG. 4. Normalized resistivity versus temperature data for $CrCa_4$ and $MnGa_4$.

and $MnGa_4$ LDA calculations yield equilibrium volumes of about 5% lower than the experimental ones (and too high bulk moduli), which is in the range of overbinding typically observed for this approximation. The GGA calculations, however, reproduce very well the experimental equilibrium volumes and bulk moduli of these compounds. For $ReGa_4$ the LDA and GGA obtained volumes deviate symmetrically by -3% and $+3\%$ from the experimental value. Heats of formation $\Delta E = E(T\mathrm{Ga}_4) - E(T) - 4 \times E(\mathrm{Ga})$ were calculated with respect to the α-Ga structure and the respective T ground state atomic and magnetic structures. For $T=\mathrm{Mn}$, $E(T)$ was calculated for the (nonmagnetic) fcc high temperature modification (γ-Mn) and $E(\alpha\text{-Mn})$ estimated by adding the energy equivalent of the transition temperature (1375 K).[18] The obtained results from full-potential calculations are supposed to be as reliable as experimentally obtained values.[19] The attained values (from GGA calculations) are negative but small for all three stable compounds. The narrow range is between -0.083 eV/atom (-8.01 kJ/g atom) for $ReGa_4$ and -0.121 eV/atom (-11.67 kJ/g atom) for $MnGa_4$.

2. Bonding properties

In Fig. 5 the DOS together with the band structure of $CrGa_4$ and $MnGa_4$ at equilibrium volume is shown. For $CrGa_4$ the characteristic features of the electronic structure of a T-E electron compound[5] are displayed in a very prominent way: First, at low energy the density of states is dominated by approximately parabolically distributed nearly free-electron-like states stemming from the sp bands of the Ga matrix [i.e., the simple cubic (sc) Ga partial structure]. Secondly, the d band of the Cr atoms hybridizes strongly with the Ga p band (see the local d DOS on Cr and the local p DOS on Ga in Fig. 5). [Note, that in the $T\mathrm{Ga}_4$ compounds with the $PtHg_4$ structure d-d interactions are not possible because the transition metal atoms are separated by a distance of almost 5 Å (see Table I)]. As a consequence of the Cr(d)-Ga(p) interactions the d band is split into a bonding and an antibonding part, thus creating a pseudogap in which the Fermi level is located. However, the features of the pseudogap in $CrGa_4$ confined by two pronounced d band singularities are most remarkable. Its size is about 1.7 eV and the value of the DOS at the Fermi level is extremely low [just 0.07 states/(eV atom)]. The band structure of $MnGa_4$ displays a perfect rigid-band behavior when compared to the

TABLE II. Structural properties of the compounds $CrGa_4$, $MnGa_4$, and $ReGa_4$.

Property	$CrGa_4$	$MnGa_4$	$ReGa_4$
V_0-LDA (Å ^{3})	83.92	80.98	92.41
V_0-GGA (Å ^{3})	91.03	87.55	98.37
V_0-exp (Å ^{3})	90.22	87.54	95.76
B-LDA (GPa)	109.0	116.0	128.5
B-GGA (GPa)	89.9	95.1	105.5
B-exp (GPa)	84	88	
B'-LDA	4.4	5.1	5.1
B'-GGA	4.2	4.8	4.9
B'-exp	3.8	5.6	
ΔH (eV/atom)	-0.096	-0.121	-0.083

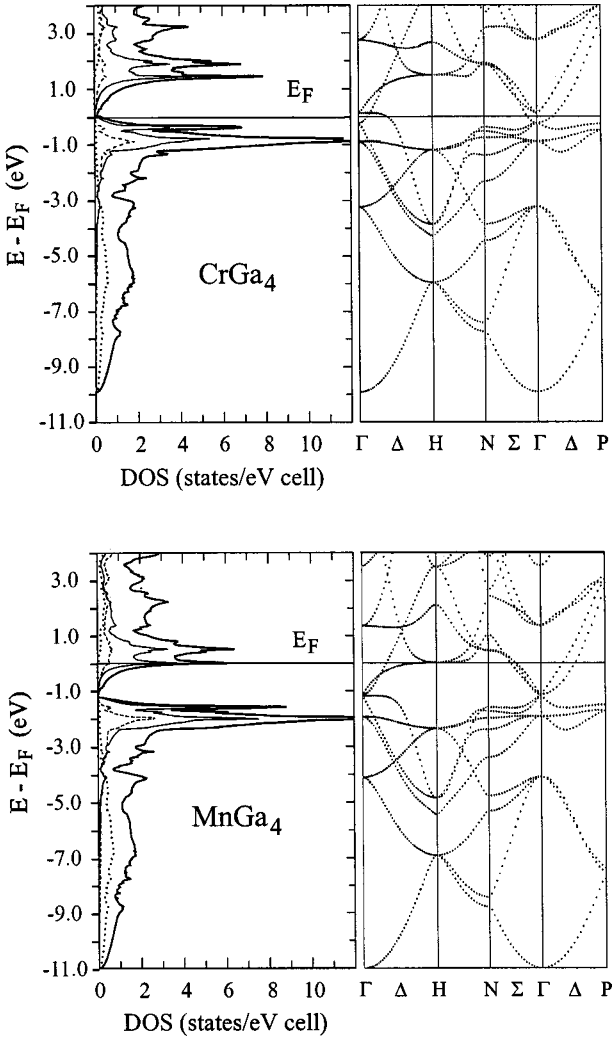

FIG. 5. The density of states (DOS, left) and band structures (right) of $CrCa_4$ and $MnGa_4$. The DOS is decomposed into T-d contributions (thin solid lines), Ga-p contributions (dashed lines), and Ga-s contributions (dotted lines).

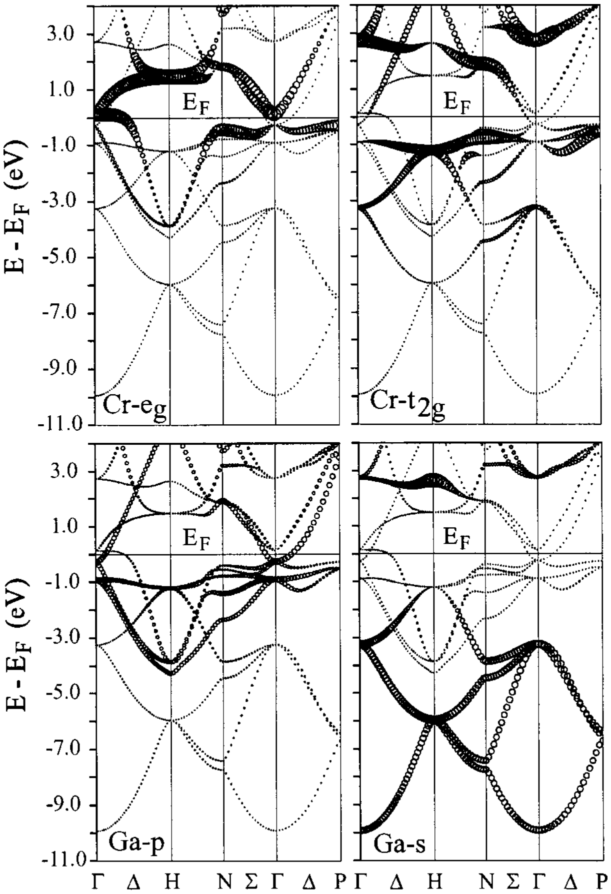

FIG. 6. Orbital character of the band structure of $CrGa_4$.

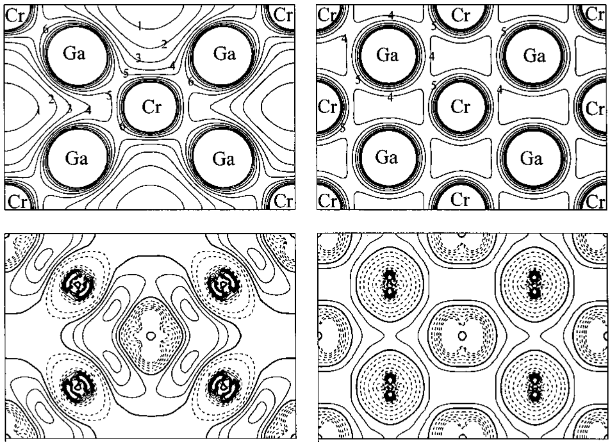

FIG. 7. The upper panel shows the charge density distribution in the plane (110) of $CrGa_4$ (left) and CrGa (right) at equilibrium volume. The separation of the contours is 0.01 e/Bohr^3, the unit of the contours in the plots is 10^{-2} e/Bohr^3. The lower panel displays the corresponding difference density plots in the range of -0.02 and 0.02 e/Bohr^3. The separation of the contours is 0.004 e/Bohr^3, dashed contours represent regions of depletion, solid contours those of charge accumulation. The zero level corresponds to the bold solid line.

one of $CrGa_4$. The increased electron count (VEC is 3.8 electrons/atom in the 19 electron compound $MnGa_4$ compared to 3.6 electrons/atom in the 18 electron compound $CrGa_4$) puts the Fermi level exactly at the singularity defining the upper boundary of the pseudogap. Otherwise the band structure remains unchanged. In Fig. 6 the orbital character of the band structure of $CrGa_4$ is displayed (the orbital character of the band structure of $MnGa_4$ is virtually identical). More clearly than from the DOS we notice the large bonding-antibonding *d* band splitting of about 3 eV along some directions in reciprocal space. Further, in the range between -1 and -3 eV the bonding *d-p* hybridization takes place. The lower part of the band structure (between -10 and -3 eV)—dominated by the *s* band of the sc partial structure of the Ga atoms—is basically unaffected by the *T* atom *d* band interaction. From this discussion of the band structure strong bonding within the cubes $T\mathrm{Ga}_8$ appears as the stability determining feature for both compounds although antibonding states above the Fermi level are partly occupied in $MnGa_4$. The analysis of the charge densities corroborates this bonding picture. In Fig. 7 we compare the charge density and difference density (crystalline density minus superposed atomic densities) contour maps of $CrGa_4$ (the ones of $MnGa_4$ is basically indistinguishable) with that of the hypothetical (unstable) compound CrGa (calculated heat of formation: $+0.32$ eV/atom) with the CsCl structure in their respective plane (110). This plane contains all nearest neighbor distances *T*-Ga, Ga-Ga, and *T*-*T*. The charge density map of $CrGa_4$ display clear directional (covalent) bonding between Cr and Ga atoms with quite high values of ρ at the saddle point (bond critical point[20]) along the internuclear distances *T*-Ga. Additionally, the $\Delta\rho$ map shows a pronounced accumulation of charge in the region around the bond critical point. This is in contrast to the almost spherically distributed charge density in CrGa. (A homogeneous distribution of ρ is usually considered as the result of metallic bonding.) Interestingly in $CrGa_4$ no bond critical point occurs between pairs of Ga atoms in the sc framework although the Ga-Ga distance of about 2.8 Å in the stable $T\mathrm{Ga}_4$ compounds suggests weak bonding interactions between Ga atoms [the distances occurring in the first coordination shell in α-Ga are not much shorter (2.48–2.79 Å)].

The location of the Fermi level above the pseudogap in $MnGa_4$ may account for the much larger decrease of the normalized resistivity at lower temperatures compared to $CrGa_4$ (see Fig. 4). However, this feature in the electronic structure is especially mirrored in the large difference in the Pauli paramagnetic susceptibilities of $MnGa_4$ and $CrGa_4$ because those susceptibilities are proportional to the value of the DOS at the Fermi level.[15] Moreover the DOS for $MnGa_4$ at the Fermi level has a singularity. This indicates an instability because a splitting of electronic states around the Fermi energy always decreases the one electron term of the total energy and thus often stimulates changes in the system (i.e., a structural distortion or magnetism). Indeed, spin-polarized calculations find that an antiferromagnetic state is favored over the nonspin-polarized state.[21] However, from the temperature dependent magnetic susceptibility and resistivity data there is no experimental evidence for a magnetic transition at low temperatures. Further, we performed transmission electron microscopy investigations on various

$MnGa_4$ crystals. The electron diffraction patterns did not show any deviation from the high-symmetry $PtHg_4$ structure for this compound caused by a structural distortion or the presence of intrinsic defects. Therefore we assume that electron-electron interactions not properly described in our calculational method will split the narrow band at the Fermi level. These findings remind very much on the classic problem FeAl (FeAl has the CsCl structure) where spin-polarized calculations find a ferromagnetic ground state which is not observed experimentally[22] and we will give a detailed analysis in a separate publication.[23]

3. Structural stability

a. Variation of T. In order to investigate structural stability of T-E electron compounds with the $PtHg_4$ structure we calculated the structural properties and the band structures at equilibrium volume for the compounds $T\mathrm{Ga}_4$ ($T=$V-Fe; Ta-Os). The band structures are displayed in Fig. 8. The location of the stability determining pseudogap is virtually independent from the kind of T atom within a row. The center is 9.9 and 9.3 eV above the bottom of the Ga $4s$ band for first row and third row transition metal compounds, respectively. This corresponds to a filling of nine states and makes the band structures very well described by a rigid-band behavior. Optimum band filling is obtained for the 18 electron compounds containing group six transition metals. As expected $5d$ bands interact more strongly with the Ga framework sp states than $3d$ bands.[2] This is manifested in a twice as large dispersion of the d-sp hybridized bands and the larger pseudogaps in compounds $T\mathrm{Ga}_4$ containing $5d$ transition metals. The strength of $d(T)$-$sp(\mathrm{Ga})$ bonding in the series of compounds $T\mathrm{Ga}_4$ might be estimated (i) from the size of the pseudogap, (ii) from the degree of the t_{2g}-e_g bonding-antibonding splitting at Γ, (iii) from the value ρ_b of the charge density ρ at the bond critical point along the distances T-Ga, and (iv) from the bulk moduli. The values are listed in Table III. Within a transition metal series the pseudogap and t_{2g}-e_g splitting are largest for group 6 and 7 compounds, i.e., for the stable compounds. ρ_b increases most when going from group 5 to group 6 transition metals, i.e., when the bonding states are getting completely filled. The trend in the bulk moduli parallels that of ρ_b.

The largest heats of formation occur for 19 electron compounds and not for the compounds with the Fermi level exactly at the pseudogap. This reflects the stability trend within the transition metal series: transition metals of group 5 and 6 have the largest cohesion energies (and melting points). Even compounds $T\mathrm{Ga}_4$ with T being a group 8 transition metal have negative heats of formation in spite of the filling of one antibonding state per formula unit. However, in these systems compounds $T\mathrm{Ga}_3$ with the $FeGa_3$ structure type represent the Ga richest composition and indeed calculations show that the decomposition $FeGa_4 \rightarrow FeGa_3 + Ga$ is favored by at least 40 kJ/mol. WGa_4 has a heat of formation of about half of that of $CrGa_4$. In the system W/Ga no compounds are reported[24] and we were not able to prepare WGa_4 from the elements. This is probably due to the fact that the low heat of formation requires too low synthesis temperatures for obtaining a reaction of Ga with the quite inert metal tungsten.

Naturally, size and electronegativity factors are not considered to be important to structural stability of Hume-Rothery compounds. However, for the T-E electron compounds especially electronegativity differences T-E are rather small and not really variable. A consequence of different electronegativities is the occurrence of charge transfer under compound formation which is usually accompanied with a substantial variation (reduction) of the elemental atomic volumes.[25] In Fig. 9 the the equilibrium volumes of the compounds $T\mathrm{Ga}_4$ are compared with the sum of the elemental atomic volumes. For the stable compounds $CrGa_4$, $MnGa_4$, and $ReGa_4$ we note that the compound volumes and the sum of the elemental atomic volumes are quite similar. Therefore, one might exclude a considerable charge transfer in these compounds, yet this finding seems to bear a contradiction. If considering the $PtHg_4$ structure type as a loosely packed structure one could actually suspect a volume expansion under compound formation. The reason for the ''volume anomaly'' is that especially the Ga atoms suffer a considerable decrease in size when changing the environment from the predominantly metallic bonded elemental structure (but note, that there is also a considerable covalent bonding contribution in the orthorhombic ground state structure of gallium[26]) to the covalently bonded $T\mathrm{Ga}_4$ Hume-Rothery compounds. The locations of the bond critical point can be used to define radii r_T and r_{Ga} in the compounds $T\mathrm{Ga}_4$. The obtained values are included in Table III. One recognizes that r_{Ga} decreases most when going from the 17 electron compounds (with the group 5 transition metals) to the 18 electron compounds with all bonding states completely filled. After that r_{Ga} decreases only slightly when traversing further along the transition metal rows which reflects the slightly increasing electronegativity of T in this direction. The value of r_{Ga} for the stable compounds $T\mathrm{Ga}_4$ is about 1.25 Å and, interestingly, this value of r_{Ga} agrees almost exactly to the *covalent* radius of Gallium (1.26 Å),[27] whereas its metallic radius (referring to a coordination number of 12) is considerably larger (1.41 Å). If we turn to the trends of r_T it is realized that also the radii of most of the transition metals in the compounds $T\mathrm{Ga}_4$ appear diminished compared to the radii those metals attain in an elemental bcc structure at equilibrium volume [obtained from GGA calculations ($r_{T,\mathrm{bcc}}$ in Table III)]. However, r_T decreases by far not to the same extend than r_{Ga}. Consequently, the contraction of the atomic sizes of T and especially Ga in the compounds $T\mathrm{Ga}_4$ (with respect to the metallic bonded elemental structures) indicates as well the strong covalent T-Ga bonding which ensures that the open packed $PtHg_4$ structure type can be realised for compounds $T\mathrm{Ga}_4$.

b. Variation of E. The large pseudogap at the Fermi level of $CrGa_4$ raises the expectation that the isoelectronic compounds $CrIn_4$ and $CrAl_4$ might also exist with the same structure. However, we neither were able to prepare a compound $CrIn_4$ nor a solid solution $CrGa_{4-x}In_x$ with x larger than 0.2. $CrAl_4$ adopts a completely different structure, i.e., the $MnAl_4$ type.[24] We calculated the structural properties of the hypothetical compounds $CrIn_4$ and $CrAl_4$ and they are summarized together with those of the stable compound

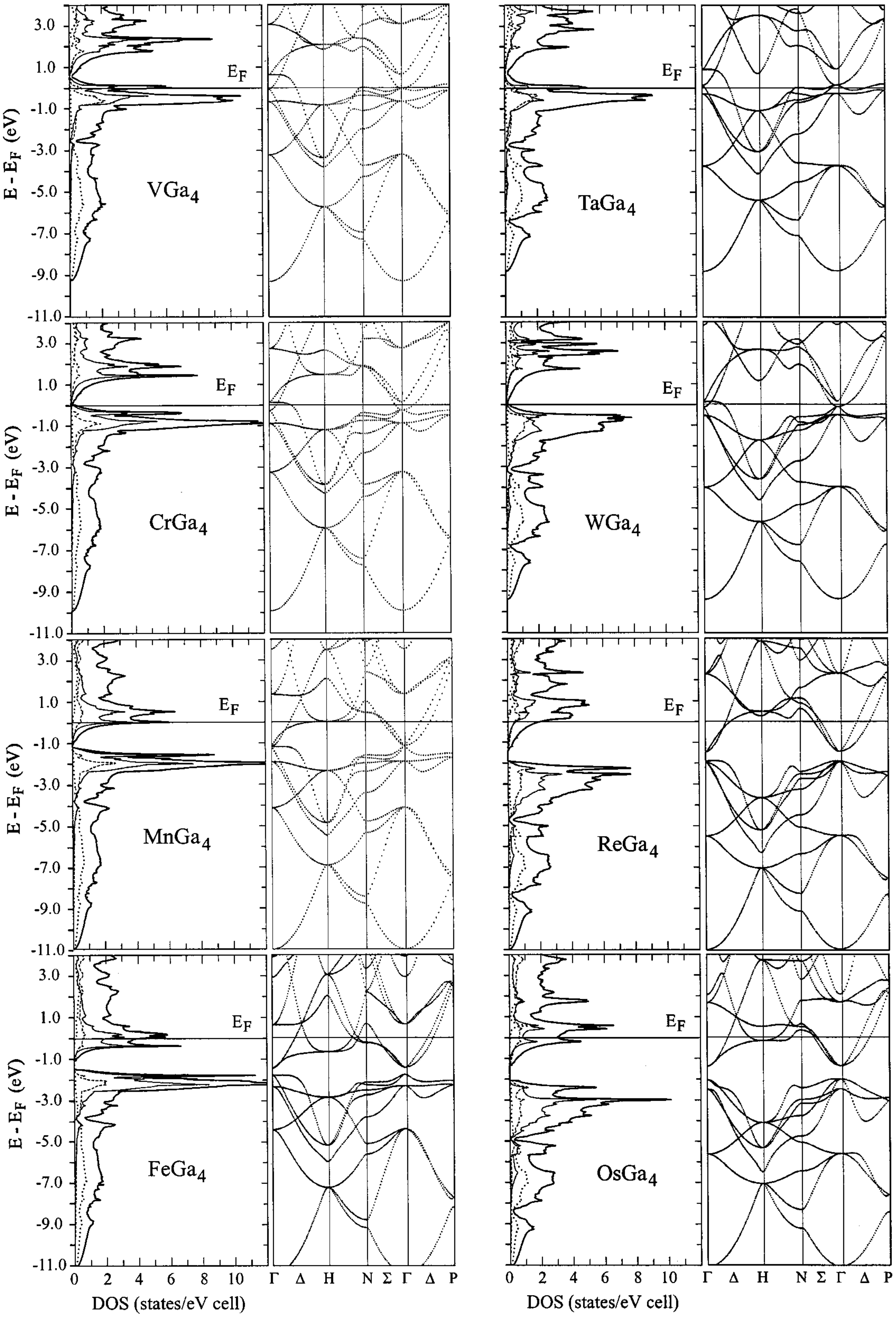

FIG. 8. Band structures of compounds TGa$_4$ with the PtHg$_4$ structure at equilibrium volume.

$CrGa_4$ in Table IV. The calculated heats of formation for $CrIn_4$ and $CrAl_4$ confirm the experimental findings because the values are close to zero. The band structures shown in Fig. 10 reveal the reason behind this difference: for $CrIn_4$ the size of the stability determining pseudogap is considerably smaller than for $CrGa_4$ indicating a substantial weaker Cr-E interaction. This is in accord with the fact that compared to the wealth of T-Al and T-Ga electron compounds just a few

TABLE III. Calculated structural properties and band structure characteristics of compounds $T\mathrm{Ga}_4$ with the PtHg_4 structure.

Property	VGa_4	CrGa_4	MnGa_4	FeGa_4
V_0 (Å ^{3})	98.12	91.03	87.55	86.00
$d_{T-\mathrm{Ga}}$ (Å)	2.516	2.454	2.448	2.469
B (GPa)	75.5	89.9	95.1	93.8
ΔH (eV/atom)	−0.015	−0.096	−0.121	−0.061
ΔE_{gap} (eV)	1.6	1.7	1.6	1.4
$\Delta E_{t_{2g}\text{-}e_g}(\Gamma)$ (eV)	2.43	2.60	2.51	2.43
ρ_b (e/Bohr^3)	0.049	0.056	0.058	0.057
r_{Ga} (Å)	1.319	1.265	1.244	1.234
r_T (Å)	1.197	1.189	1.203	1.234
$r_{T,\mathrm{bcc}}$ (Å)	1.295	1.241	1.207	1.229

Property	TaGa_4	WGa_4	ReGa_4	OsGa_4
V_0 (Å ^{3})	111.83	103.05	98.37	96.63
$d_{T-\mathrm{Ga}}$ (Å)	2.628	2.558	2.518	2.503
B (GPa)	73.4	94.6	105.5	110.3
ΔH (eV/atom)	0.064	−0.048	−0.083	−0.026
ΔE_{gap} (eV)	1.8	2.2	2.3	2.1
$\Delta E_{t_{2g}-e_g}(\Gamma)$ (eV)	3.98	4.12	4.20	3.67
ρ_b (e/Bohr^3)	0.050	0.059	0.065	0.066
r_{Ga} (Å)	1.346	1.279	1.242	1.211
r_T (Å)	1.282	1.279	1.276	1.292
$r_{T,\mathrm{bcc}}$ (Å)	1.434	1.378	1.348	1.340

T-In electron compounds are reported.[24] Concerning CrAl_4 the size of the pseudogap is much larger compared to CrIn_4 (in fact, it is as large as in CrGa_4), but on the other hand, the calculated equilibrium volume is much higher than the sum of the elemental atomic volumes, as displayed in Fig. 11, which suggests that the PtHg_4 structure type becomes too loosely packed for a composition CrAl_4 and instead the complex MnAl_4 structure type is realized. This is supported by the fact that the equilibrium volume of CrAl_4 in the MnAl_4 structure is considerably lower and very close to the sum of the elemental atomic volumes (as for CrGa_4 and CrIn_4). In the MnAl_4 structure the coordination number of the *T* atoms

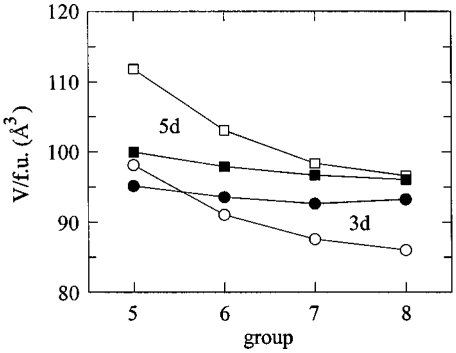

FIG. 9. Trend of the calculated equilibrium volumes per formula unit of compounds $T\mathrm{Ga}_4$ with the PtHg_4 structure. Circles: $T=3d$ elements V - Fe, squares: $T=5d$ elements Ta - Os. The solid symbols represent the corresponding sum of the (calculated) elemental atomic volumes.

TABLE IV. Calculated structural properties of the compounds CrE_4 with the PtHg_4 structure.

Property	CrAl_4	CrGa_4	CrIn_4
V_0 (Å ^{3})	92.15	91.03	121.65
$d_{T\text{-}\mathrm{Ga}}$ (Å)	2.464	2.448	2.703
B (GPa)	89.3	89.9	66.1
ΔH (eV/atom)	−0.005	−0.096	−0.008

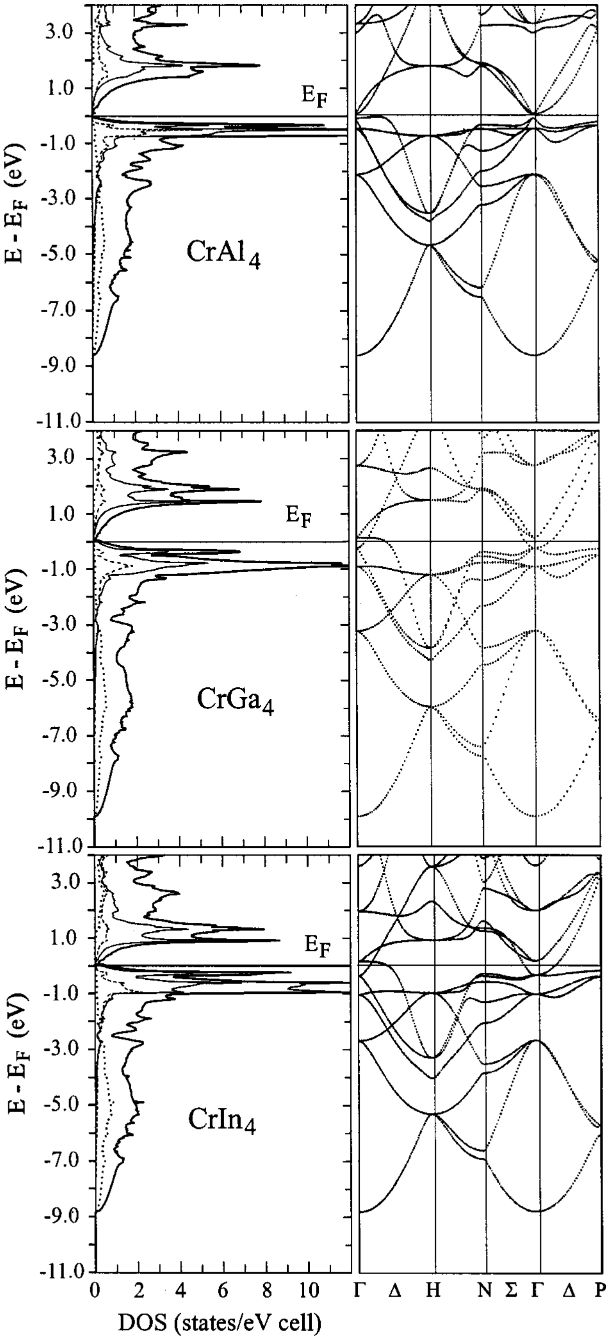

FIG. 10. The density of states (DOS, left) and band structures (right) of compounds $\mathrm{Cr}E_4$ ($E=$Al, Ga, In) with the PtHg_4 structure. The DOS is decomposed into Cr-d contributions (thin solid lines), E-p contributions (dashed lines), and E-s contributions (dotted lines).

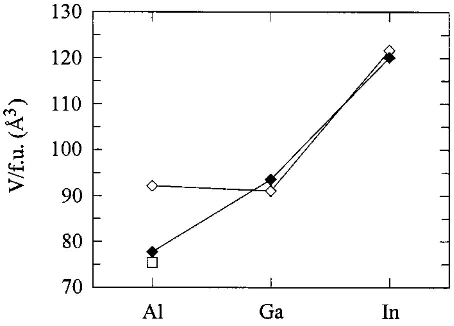

FIG. 11. Calculated equilibrium volumes per formula unit of compounds CrE_4 (E=Al, Ga, In) with the $PtHg_4$ structure. The solid symbols represent the corresponding sum of the (calculated) elemental atomic volumes. The empty square indicates the experimental volume for $CrAl_4$ in the $MnAl_4$ structure.

is increased to 12 compared to the $PtHg_4$ structure. With an increasing coordination number the distances T-E become larger which diminishes the pseudogap, but at the same time a more densely packed structure can be realised. For most intermetallic compounds structural stability is a balance between the total energy contributions band energy and electrostatic Madelung energy, whereas in semiconductors and insulators the band energy accounts almost exclusively for structural stability. For the T-Al and T-Ga electron compounds balance between band energy and Madelung energy is equivalent to a optimizing of the pseudogap and minimizing the compound equilibrium volume.

V. SUMMARY

We presented a detailed study of bonding and stability of intermetallic electron compounds with the $PtHg_4$ structure type. These systems belong to a large class of Hume-Rothery compounds consisting of homogeneously distributed transition metal (T) atoms in a matrix of Al or Ga (E) atoms. Due to strong T-E interactions a pronounced pseudogap is opened at the Fermi level which makes VEC to the prior stability controlling parameter and the TE_p coordination polyhedra (i.e., TGa_8 cubes for the compounds with the $PtHg_4$ structure) to covalently bonded entities. The general mechanism of the stabilizing pseudogap formation in T-E electron compounds is schematically summarized in Fig. 12. Due to the low concentration of T atoms the electronic structure of this class of compounds can be built up by a simple two-stage process. First the sp bands of the E atom partial structure is considered. Most partial structures represent rather close packed arrangements and therefore their electronic states can be approximately considered as free-electron-like. At higher energy the d states of the T atoms perturb and the strong d-sp hybridization produces the pseudogap which separates d-sp bonding and antibonding states. The most favorable situation concerning electron count and size of the pseudogap is obtained when the Fermi level coincides with the pseudo gap. This is the case for transition metals with an approximately half filled d shell. For those metals no substantial charge transfer occurs in the T-E Hume-Rothery compounds and the d level energy is close to the Fermi level of the E partial structure. The kind and extension of the d band splitting is dependent of the size and the local symmetry of the TE_p coordination polyhedra and the degree of d-sp band interaction.

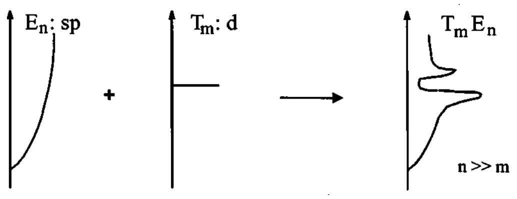

FIG. 12. Schematical construction of the DOS of the T_mE_n-Hume-Rothery compounds as a perturbation of free-electron-like states of the E atom matrix by T atom d states.

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