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Journal of Alloys and Compounds 275–277 (1998) 468–471

Journal of ALLOYS AND COMPOUNDS

Local spin density functional investigations of the ternary systems UT_2Ge_2 (T=Mn,Fe)

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Abstract

The electronic and magnetic structures of the ferromagnetic UMn_2Ge_2 and the paramagnetic UFe_2Ge_2 intermetallic systems are investigated ab initio and self-consistently within the Local Spin-Density Functional (LSDF) using the Augmented Spherical Wave (ASW) method. Agreement with experiment for the magnetic ordering as well as for the magnitudes of magnetization are found when spin-orbit coupling effects are included. Further, we discuss the chemical bonding within these systems from the Crystal Orbital Overlap Populations (COOP) which allow to assign a bonding or anti-bonding character for pair interactions. © 1998 Elsevier Science S.A.

Keywords: Ternary uranium intermetallics; ASW; LSDF; Band structure; Chemical bonding

1. Introduction

The family of ternary intermetallic systems UT_2X_2 (T=d metal, X=p element) is well known to exhibit a wide variety of electronic and magnetic properties [1,2]. This diversity is due to the interplay between the magnetism and the mixing between the states of the different constituents in the crystal lattice. Besides structural factors, the mechanism of intra-band spin polarisation in uranium intermetallic systems is based on the interactions within the uranium sublattice as well as on the hybridisation of uranium states with the respective transition metal and X-element ones, i.e. 5f–d and 5f–p. The interaction between uranium atoms in the lattice depends on the so-called Hill critical distance ($d_{U-U} \approx 3.5$ Å). Generally below this value there is no intra-band spin polarisation because the U 5f bands broaden due to the direct overlap between them. The hybridisation involving uranium and transition metal neighbours (T) depends on the position of T in the *n*d series and the distance between uranium and the transition metal site. The combination of these effects in 1:2:2 intermetallics leads to their various magnetic ground states. For instance, UMn_2Ge_2 is ferromagnetic, UFe_2Ge_2 is a Pauli paramagnet. This work reports on a study of these two compounds as a part of systematic investigations within the LSDF of uranium intermetallic systems prepared and characterised at the ICMCB-CNRS [3–5]. For this purpose we apply the ASW method [6] in a scalar relativistic implementation [7], including spin-orbit coupling. For exchange and correlation, the parametrisation schemes of von Barth and Hedin [8], and Janak [9] were used. Similar studies using this method were recently reported on homologous silicides [10]. Using the Atomic Sphere Approximation (ASA), the ASW method assumes overlapping spheres centered on the atomic sites. The volume of the atomic spheres is enforced to equal the cell volume. This is a good approximation for compact structures such as that of $ThCr_2Si_2$. Our 'non unique' choice of the Atomic Sphere (AS) radii was the following: $r_U/r_T=1.306$ and $r_{Ge}/r_T=1.048$. These values were found to minimise the overlap between the AS. We used up to 1728 *k*-points within the first Brillouin Zone (BZ), i.e. twelve points in each direction, in order to obtain reliable results. Self-consistency was achieved using the criteria $\Delta Q<10^{-8}$ and $\Delta E<10^{-8}$ Ry respectively for charge transfers and total energy.

Besides magnetic moment formation in these compounds, we discuss their chemical bonding using the concept of COOP. In short the COOP is based on the expectation values of operators which consist of the non-diagonal elements of the overlap population matrix,

$$c^*_{ni}(\boldsymbol{k})S_{ij}c_{nj}(\boldsymbol{k}) = c^*_{ni}(\boldsymbol{k}) < \chi_{ki}(\boldsymbol{r})|\chi_{kj}(r) > c_{nj}(\boldsymbol{k})$$

where S_{ij} represents an element of the overlap matrix of the basis functions and the $c_{nj}(\boldsymbol{k})$ are the expansion

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PII: S0925-8388(98)00373-9

coefficients entering the wave function of the nth band. Partial COOP coefficients $C_{ij}(E)$ are then obtained by integrating the above expression over the BZ:

$$C_{ij}(E) = C_{ji}(E)$$
$$= 1/\Omega_{\mathrm{BZ}} \sum_n \int_{\mathrm{BZ}} d^3\boldsymbol{k} \mathrm{Re}\{c^*_{ni}(\boldsymbol{k}) S_{ij} c_{nj}(\boldsymbol{k})\} \delta(E - \varepsilon_{nk})$$

(Dirac notation delta) which, in a somewhat lax notation, is often designated as the overlap-population-weighted-Density of State (DOS). The total COOP are then evaluated as the sum over all non-diagonal elements, i.e. $C(E) = \Sigma_{ij\ (i \neq j)} C_{ji}(E)$. For a detailed description and for significant examples we refer the reader to the work of Eyert [11].

2. Crystal structure

The systems under study crystallise in the body centered tetragonal $\mathrm{ThCr_2Si_2}$-type structure (space group $I4/mmm$) with two formula units (f.u.) per unit cell. Perpendicular to the c-axis, U atoms form planes at $z=0$ and $z=\frac{1}{2}$ which are interlayered by motifs containing T ($z=\frac{1}{4}$ and $\frac{3}{4}$) and Ge ($z \approx \pm 0.375$ and ± 0.125) atoms respectively. Hence the structure can be described as a succession of $\{\mathrm{T_2Ge_2}\}$ entities perpendicular to the c-axis with the sequence U–(T,Ge)–U–(T,Ge). The shortest U–U distance is equal to the a lattice constant which is systematically around 4 Å. This distance being larger than the Hill critical value leads us to expect a sufficient localisation of the U 5f states to carry a magnetic moment. The lattice constants used throughout the calculations are derived from experimental investigations [2].

3. Non-spin polarised calculations

Calculations were firstly performed assuming non-magnetic ground states, i.e. we enforced spin degeneracy for all states. From the results of such Non-Spin Polarised (NSP) calculations the features of chemical bonding can be addressed. This is because the spin polarised bands, to a large extent, result from the NSP bands by a rigid energetic shift. Hence, it is well justified to discuss the chemical bonding already from the NSP results.

In the ASA, charge transfers are not a relevant issue in as far as they depend on the choice of the atomic spheres radii which is not unique. We notice however from the calculations a small charge transfer between the different constituents. This leads to suggest that the bonding mechanism is not based on charge transfer in such systems, but rather results from the mixing between the different l-states as we have shown before for other ternary uranium intermetallics [3–5]. This can be discussed from the analysis of the DOS.

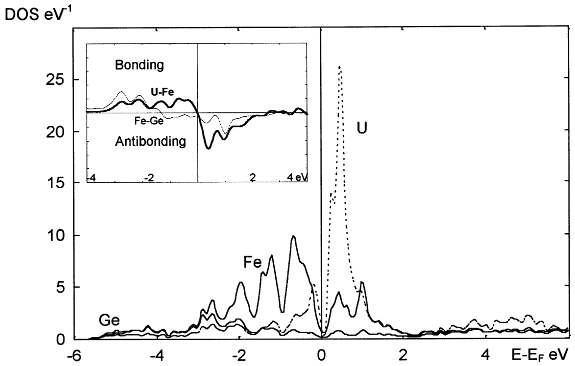

Fig. 1. Non magnetic site projected DOS of $\mathrm{UFe_2Ge_2}$. Energy reference is with respect to Fermi level. The insert shows the COOP of pair interactions around E_F.

In Fig. 1 the site projected DOS are shown for $\mathrm{UFe_2Ge_2}$. The energy scale along the horizontal axis is taken with reference to E_F. Low-lying Ge(s)-related states below −6 eV are not shown. Uranium states are mainly of 5f character around E_F showing the sharp DOS. U 6d states, which have more itinerant behaviour, contribute to the bonding below E_F. Fe DOS are almost exclusively of d-type and Ge DOS are dominated by 4p states. From the resemblance and relative intensities of the partial DOS, the mixing between Ge and Fe states can be seen to occur in the energy range {−6, −2 eV}. Although present over the whole range of the valence band (see COOP discussion in the next paragraph), the metallic bonding involving U and Fe sublattices is dominant at a higher energy and in the close neighbourhood of E_F. The lower part of U 5f DOS is crossed by Fermi energy. This follows from the 'close-to-free-atom filling' of the 5f band with roughly 3 electrons. The DOS minimum for all states observed at Fermi level is an interesting feature that we discuss in the next paragraph.

Similar DOS features are observed for NSP $\mathrm{UMn_2Ge_2}$, therefore we do not show them here. This is mainly exhibited by the presence of U and Mn states in a rather broad energy range around E_F; however large DOS magnitude is found at E_F contrary to the Fe compound. The mixing of the relevant states and the large band width, Mn 3d and U 5f, 6d, leading to a lesser localisation of metal states, are features which should lead to the absence of polarisation for both constituents when SP calculations are undertaken subsequently. However U and Mn carry their own magnetic moments and $\mathrm{UMn_2Ge_2}$ is a ferromagnet [1]. This apparent contradiction can be explained by a factor relative to the geometry. The large c/a ratio ($c/a=2.71$) leads to a large U–Mn distance. From this there is a reduction of the mixing effects between the two elements and local moments may appear both on Mn and U. Just like in the former germanide, Fe 3d states in $\mathrm{UFe_2Ge_2}$ are close to the Fermi level. This energetic effect, combined with the one of a reduced c/a ratio ($c/a=2.48$) with respect to $\mathrm{UMn_2Ge_2}$, leads to a large mixing between the states of uranium and iron. This induces a loss of magnetic moments and a non-magnetic ground state is found (experimentally exhibited by a Pauli paramagnetic behaviour). Furthermore, in the converged calculations, the electronic configurations of Fe and Mn are found to be close to the free atom filling (6 and 5 3d electrons, respectively). Thus in UFe_2Ge_2, there is a filling of 3 out of the 5 3d orbitals leading to their energetic downshift. This explains the DOS minimum at E_F for Fe states which, through their mixing with those of uranium states, lead to the DOS minimum at E_F as well. From this one may understand why the Fermi level falls in a large DOS magnitude from the half filled Mn 3d subshell in UMn_2Ge_2.

The insert in Fig. 1 shows the COOP for U–Fe and Fe–Ge pair interactions given in bold and dashed lines. Upper and lower panels show bonding and antibonding interactions, respectively. Within the 'Fe_2Ge_2'-like entities, the T–Ge COOP are bonding from -4 to -2 eV. Low intensity anti-bonding interactions are observed when the transition metal states are involved with the metallic bonding in the plane as well as with the uranium states, i.e. between -2 eV and E_F. The U–Fe COOP are bonding up to the Fermi level. From this the stability of 1:2:2 intermetallic systems involves in-plane T–Ge as well as out-of-plane metal U–T interactions because they are mainly bonding in the energy range of the valence band. The passage from bonding to anti-bonding U–Fe states occurs exactly at E_F. This interestingly follows the DOS minimum at E_F. Such a feature can help to understand the evolution of U–T bonding throughout the T = 3d series of UT_2Ge_2 germanides if one adopts a rigid band scheme. The U–T COOP at E_F will be bonding for T = Mn (one less electron than Fe) and more and more antibonding for T = Co, Ni and Cu which have an increasing number of d electrons. This is further evident in [12].

4. Spin polarised (SP) calculations

SP spin-only calculations were done by initially allowing for two spin occupations for all atomic species, then self-consistently converging the charges and the magnetic moments. In a second step, spin-orbit coupling calculations were carried out. The features of hybridisation and bonding formerly discussed are relevant here because SP results are NSP ones with spin splitting within a rigid band model. Thus, we only discuss the signs and magnitudes of the magnetic moments and confront them with experiment.

SP calculations for UFe_2Ge_2 give equal spin populations for the majority (↑) and minority (↓) spin directions. With zero exchange splitting energy between the (↑) and (↓) bands, zero magnetic moments were found both on U and Fe. This result is in agreement with the experimental findings of the absence of any magnetic order for this compound down to 0 K [1,2]. For UMn_2Ge_2, the total energy is found to be 0.028 Ry lower than the NSP one due to the gain in exchange energy.

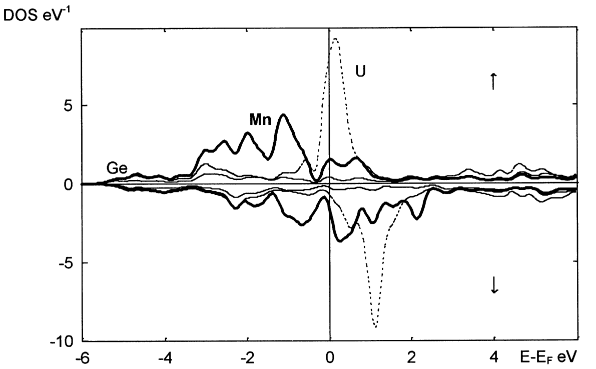

Fig. 2. Site projected DOS of spin polarised ferromagnetic UMn_2Ge_2. Energy reference is with respect to Fermi level (E_F).

In Fig. 2 the site projected DOS of UMn_2Ge_2 is shown. Exchange splitting can be seen to occur for both U and Mn, whereby the majority spin (↑) states are shifted to lower energy and minority spin states (↓) are shifted to higher energy. The splitting for Mn states shown in bold lines is large for a 3d element in uranium intermetallics where mostly uranium states are affected by spin polarisation [4,5,10]. The calculated magnetic moment of uranium mainly arises from the polarisation of 5f states $M(\text{U 5f}) = 1.88\ \mu_B$ whereas 6d states carry a small magnetic moment of 0.04 μ_B; the resulting moment of uranium is thus 1.92 μ_B. The large intraband splitting which can be visualized from the DOS figure leads to a large moment of Mn: $M(\text{Mn}) = 1.88\ \mu_B$. The total magnetisation of 5.66 μ_B per f.u. is found to be larger than the experimental one of 4.2 μ_B [2], so that accounting for spin only is not sufficient for such a system. Looking at the atomic number of uranium as well as at the relatively small band width of the U 5f band (it remains broader than a Rare Earth 4f), we expect significant changes of uranium magnetic moments upon including the effects of spin orbit (LS) coupling. Because the magnitude of spin-orbit coupling in the actinides is of the same order as their 5f band width, the effects of LS-coupling will be well pronounced [13,14]. As a matter of fact the ground state energy is largely stabilised by -0.1 Ry in UMn_2Ge_2 due to LS coupling. The new value of the spin only moments of $M'(\text{U}) = 1.14\ \mu_B$ and $M'(\text{Mn}) = 1.77\ \mu_B$ are smaller than in former calculations but should be considered as more precise because the Hamiltonian is more complete when LS-coupling is accounted for. The orbital moment of U is $-2.26\ \mu_B$. Its opposite alignment to the spin only moment is readily assessed within Hund's third rule for less than a half filled subshell $5f^3$. Orbital contribution to the 3d element Mn is very small ($+0.01$). The same alignment between spin and orbital moments for Mn is again due to Hund's rule but for more than a half filled d subshell. The total magnetisation is 4.76 μ_B per f.u. which is now in better agreement with the experiment.

References

[1] Z. Zolnierek, J. Mulak, J. Magn. Magn. Mater. 140–144 (1995) 1393.
[2] A.J. Dirkmaat, T. Endstra, E.A. Knetsch, A.A. Menovsky, G.J. Nieuwenhuys, J.A. Mydosh, J. Magn. Magn. Mater. 84 (1990) 143.
[3] S.F. Matar, V. Eyert, J. Magn. Magn. Mater. 166 (1997) 321.
[4] S.F. Matar, J. Magn. Magn. Mater. 151 (1995) 263.
[5] S.F. Matar, B. Chevalier, J. Etourneau, J. Magn. Magn. Mater. 137 (1994) 293.
[6] A.R. Williams, J. Kübler, C.D. Gelatt Jr., Phys. Rev. B 19 (1979) 6094.
[7] D. Koelling, B.N. Harmon, J. Phys. C 10 (1977) 3107.
[8] J. von Barth, D. Hedin, J. Phys. C 5 (1972) 1629.
[9] J.F. Janak, Solid State Commun. 25 (1978) 53.
[10] L.M. Sandratskii, J. Kübler, Phys. Rev. B50 (1994) 9258.
[11] V. Eyert, Electronic structure calculations for crystalline materials, in: M. Springborg (Ed.), Density Functional Methods: Applications in Chemistry and Materials Science, Wiley, Chichester, 1997, pp. 233–304.
[12] S.F. Matar, V. Eyert, A. Mavromaras, S. Najm, B. Chevalier, J. Etourneau, J. Magn. Magn. Mater. 174 (1997) 219.
[13] O. Eriksson, M.S.S. Brooks, B. Johansson, Phys. Rev. B41 (1990) 9087.
[14] O. Eriksson, Ph.D. Thesis, University of Uppsala, Sweden, 1989.