

# Electronic structure of $RAuMg$ and $RAgMg$ ( $R=Eu, Gd, Yb$ )

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(Received 21 November 2005; revised manuscript received 30 May 2006; published 16 August 2006)

We have investigated the electronic structure of the equiatomic  $EuAuMg$ ,  $GdAuMg$ ,  $YbAuMg$ , and  $GdAgMg$  intermetallics using x-ray photoelectron spectroscopy. The spectra revealed that the Yb and Eu are divalent while the Gd is trivalent. The spectral weight in the vicinity of the Fermi level is dominated by the mix of Mg  $s$ , Au/Ag  $sp$ , and  $R$   $spd$  bands. We also found that the Au and Ag  $d$  bands are extraordinarily narrow, as if the noble metal atoms were impurities submerged in a low density  $sp$  metal host. The experimental results were compared with band structure calculations, and we found good agreement provided that the spin-orbit interaction in the Au and Ag  $d$  bands is included and correlation effects in an open  $4f$  shell are accounted for.

DOI: 10.1103/PhysRevB.74.073102

PACS number(s): 71.20.Eh, 79.60.-i

Many equiatomic rare-earth ( $R$ ) transition-metal ( $T$ ) magnesium intermetallics have been synthesized in the last decade.<sup>1–12</sup>  $RTMg$  materials with Yb and Eu as rare-earth elements crystallize in the orthorhombic  $TiNiSi$  structure,<sup>13</sup> while those with the other rare earths adopt the hexagonal  $ZrNiAl$  structure,<sup>14–16</sup> see Fig. 1. A wealth of interesting magnetic properties has been observed.  $CePdMg$ ,  $CePtMg$ , and  $CeAuMg$  show long-range magnetic ordering below 2–3 K.<sup>9</sup>  $EuAgMg$  and  $EuAuMg$  order ferromagnetically with  $T_C$  of 22 and 37 K, respectively.<sup>6</sup> Also the Gd materials  $GdPdMg$ ,  $GdPtMg$ , and  $GdAgMg$  are ferromagnetic, with relatively high  $T_C$  of 96, 98, and 39 K, respectively.<sup>10</sup>  $GdAuMg$ , by contrast, orders antiferromagnetically, with  $T_N=81$  K.<sup>12</sup>

Not much is presently known about the electronic structure of these materials. Basic spectroscopic determination of the  $4f$  valence of the rare earths is lacking, and it is also unclear how band structure effects will play out for the  $T$   $d$  bands in view of the rather peculiar crystal structure. We have therefore set out to perform valence band and core level photoelectron spectroscopy measurements. Here we choose for  $EuAuMg$ ,  $GdAuMg$ ,  $YbAuMg$ , and  $GdAgMg$  as model materials, since with the  $d$  shell of the Au and Ag constituents being closed, we can avoid complications which otherwise could occur as a result of the intricate interplay between band formation and correlation effects usually present in an open  $T$   $d$  shell system. We also have calculated the band structure of these materials using the local density approximation (LDA) and local density approximation+Hubbard  $U$  (LDA+ $U$ ) scheme,<sup>17</sup> where the  $U$  is used to account for correlation effects in an open atomiclike  $4f$  shell. As it turns out later, it was necessary to include as well the spin-orbit coupling for the Au and Ag  $d$  shells.

The starting rare earth, noble metal and magnesium materials were mixed in the ideal 1:1:1 atomic ratios and sealed in niobium or tantalum tubes under an argon pressure of  $\approx 800$  mbar. These tubes were first rapidly heated to  $\approx 1370$  K and subsequently annealed at  $\approx 870$  K for 2 hours. The samples were separated from the tubes by mechanical fragmentation. No reaction with the metal tubes was observed. The polycrystalline samples with dimensions of about  $2 \times 1 \times 1$  mm<sup>3</sup> are light grey with metallic luster. All samples are pure phases on the level of x-ray powder dif-

fraction, and their transport and thermodynamic properties have been analyzed recently.<sup>18</sup>

The photoemission spectra were recorded at room temperature in a spectrometer equipped with a Scienta SES-100 electron energy analyzer and a Vacuum Generators twin crystal monochromatized Al- $K_\alpha$  ( $h\nu=1486.6$  eV) source. The overall energy resolution was set to 0.4 eV, as determined using the Fermi cutoff of a Ag reference, which was also taken as the zero of the binding energy scale. The base pressure in the spectrometer was  $1 \times 10^{-10}$  mbar, and the pressure raised to  $2 \times 10^{-10}$  mbar during the measurements due to the operation of the x-ray source. The samples were cleaved *in-situ* to obtain clean surfaces.

The left-hand panels of Fig. 2 show the valence band photoemission spectra of (from top to bottom)  $YbAuMg$ ,  $EuAuMg$ ,  $GdAuMg$ , and  $GdAgMg$ . A weak but clear cutoff at the Fermi level (0 eV binding energy) can be observed, consistent with these materials being metals.<sup>18</sup> The three Au samples have in common that their valence bands contain a two-peak structure at 5.0 and 6.4 eV binding energy. We therefore can assign these two peaks to the Au  $5d$ . Consequently, the other peaks in the spectra can be attributed to the rare-earth  $4f$ .  $YbAuMg$  shows a very sharp two-peak structure at 0.5 and 1.9 eV binding energy. The line shape as well as the energy separation of these two peaks is characteristic for the Yb  $4f_{7/2}, 4f_{5/2}$  spin-orbit split  $4f^{13}$  photoemission fi-

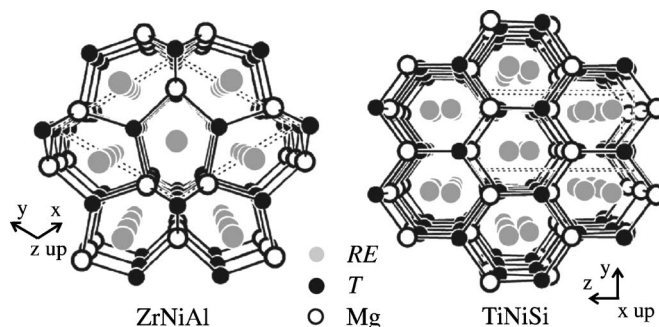


FIG. 1. The two structures of the intermetallic  $RTMg$  (from Ref. 5). On the left-hand side, the  $ZrNiAl$  structure which is adopted by the materials with trivalent rare earth and on the right-hand side, the  $TiNiSi$  structure for those with divalent rare earths.

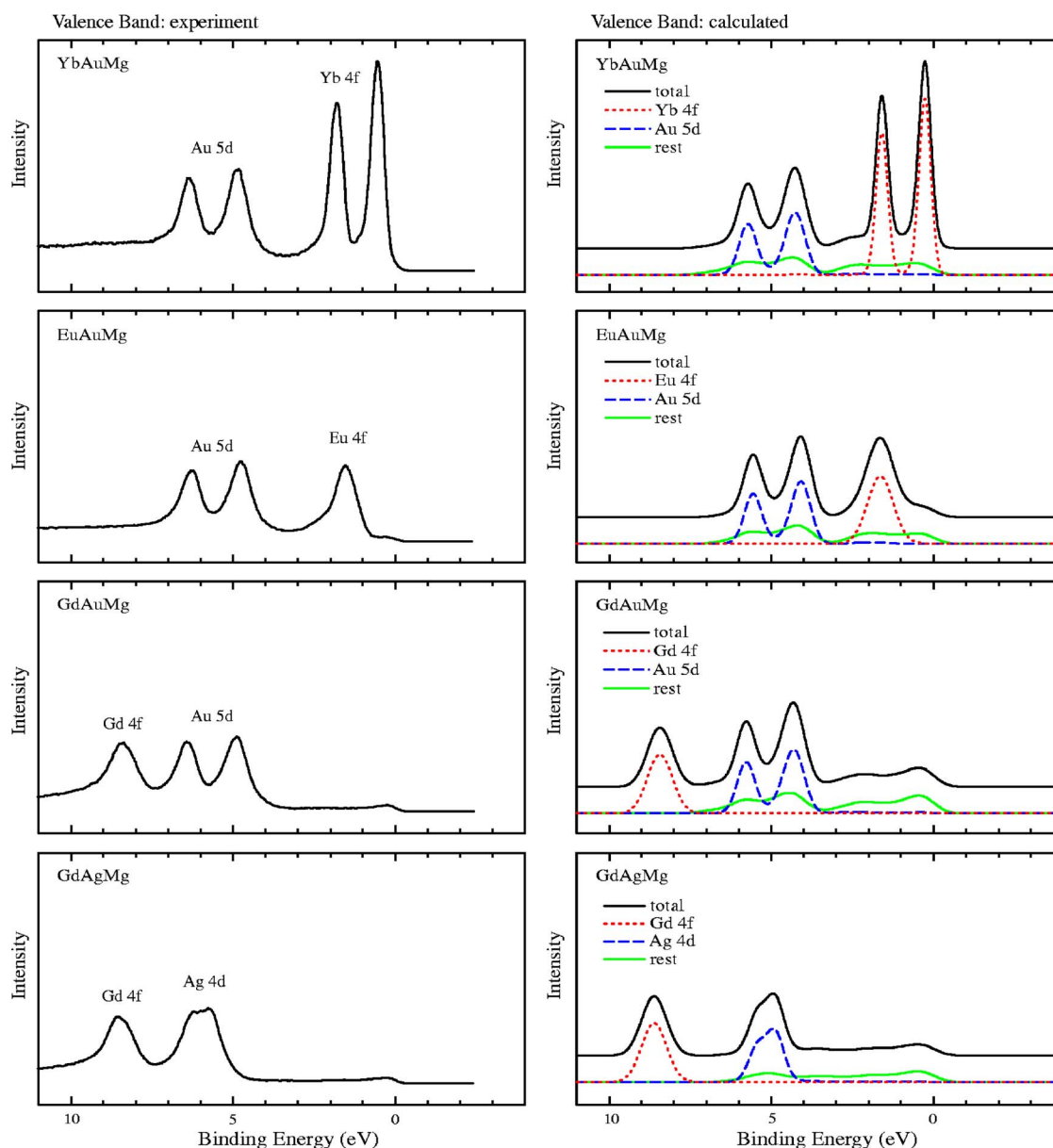


FIG. 2. (Color online) Experimental valence band photoemission spectra (left-hand panels) and calculated valence band density of states (right-hand panels) of polycrystalline YbAuMg, EuAuMg, GdAuMg, and GdAgMg (from top to bottom).

nal states,<sup>20–22</sup> indicating that the Yb in the ground state is  $4f^{14}$ , i.e., divalent, in agreement with the magnetic susceptibility.<sup>23</sup> The EuAuMg has a somewhat broader peak at 1.5 eV binding energy, very typical for the multiplet structured  $4f^6$  final states of divalent Eu compounds and intermetallics having the high-spin  $4f^7$  ground state.<sup>20,21</sup> This assignment is supported also by the fact that the integrated  $4f$  intensity of the Eu sample is close to half of the Yb  $4f$ , i.e., proportional to the number of  $f$  electrons. The peak at 8.4 eV binding energy in the GdAuMg sample is very similar in line shape and intensity to the 1.5 eV feature of the Eu sample, indicating that this peak corresponds also to a  $4f^6$  final state, and thus to a ground state having the high-spin  $4f^7$  configuration.<sup>20,21</sup> In other words, the Gd is trivalent.

In comparing the two Gd samples, i.e., GdAuMg and GdAgMg, one can clearly see that the line shape differs

mainly in the spectral range between 5 and 7 eV binding energy. We then can ascribe the flattened peak at 6 eV in the GdAgMg to the Ag  $4d$  band. Remarkable is that the line shapes of both the Au  $5d$  and the Ag  $4d$  bands in these materials are vastly different from those Au  $5d$  and Ag  $4d$  bands of the elements, as shown in Fig. 3. The noble metal  $d$  bands in these rare-earth magnesium intermetallics are so narrow that one can clearly observe the splitting due to the spin-orbit interaction. The bands are much less than 1 eV wide, i.e., about a factor of 5 smaller than in the corresponding elements.

To facilitate the interpretation of the experimental results, we have carried out band structure calculations using the LDA and LDA+ $U$  methods,<sup>17</sup> where the  $U$  refers to the on-site Coulomb energy in an open  $4f$  shell. We have also included the spin-orbit coupling for the Au and Ag  $d$  shells.

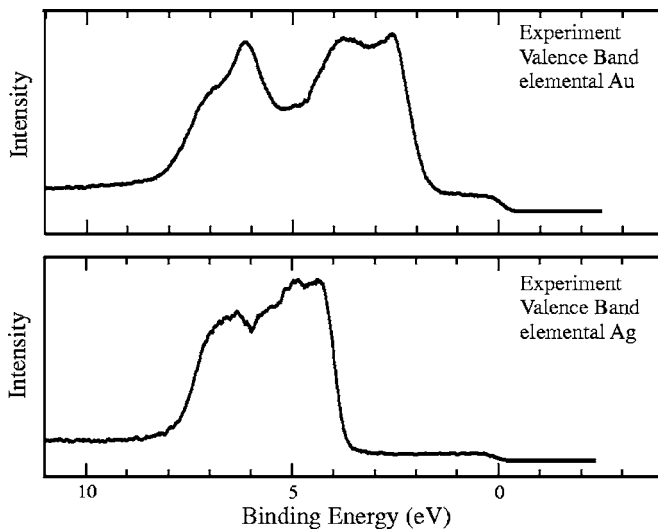


FIG. 3. Experimental valence band photoemission spectra of elemental Au (top panel) and Ag (bottom panel).

Our calculations were performed by using the full-potential augmented plane waves plus local orbital method.<sup>19</sup> We took the crystal structure as determined by x-ray diffraction.<sup>4,10,12</sup> The muffin-tin sphere radii are chosen to be 3.2, 2.5, 2.6, and 2.7 Bohr for rare-earth, gold, silver, and magnesium atoms, respectively. The spin-orbit coupling is included by the second-variational method with scalar relativistic wave functions.<sup>19</sup> We calculated the EuAuMg and GdAuMg in the ferromagnetic, the GdAuMg in the antiferromagnetic and the YbAuMg in the paramagnetic state. The easy magnetization direction is set along the  $c$  axis.

The right-hand panels of Fig. 2 depict the results of the

LDA and LDA+ $U$  calculations. One can clearly see that the density of states reproduces all the spectral features quite well, including the very narrow and spin-orbit split bands of the Au 5d and the Ag 4d. Apparently, the crystal structure is such that the overlap between the noble metal  $d$  orbitals is negligible. This can indeed be related to the fact that the Ag-Ag or Au-Au nearest-neighbor distances are more than 4.0 Å, i.e., much larger than the 2.8 Å in elemental Ag or Au. The line shape of these narrow bands is in fact reminiscent of that of noble metal impurities submerged in a low density  $sp$  metal host.<sup>24</sup> The calculations indeed indicate the presence of such an extremely broad  $sp$  like band. This band, which extends from 7 eV binding energy all the way to above the Fermi level, is labelled as rest in Fig. 2, and consists of Mg  $s$ , Au/Ag  $sp$ , and  $R spd$  bands. They in fact build up the relevant states in the vicinity of the Fermi level. The contribution of the  $R 4f$  bands to these is negligible, with the exception perhaps for the Yb system.

To address the issue concerning the  $4f$  shell, we used the LDA method for the Yb system in which we also include the spin-orbit interaction in the  $4f$ . The calculation finds correctly the closed shell  $4f^{14}$  configuration for the Yb, and the peak positions are in good agreement with the experiment. For the Eu and Gd system, however, we must resort to the LDA+ $U$  method, in which  $U$  in the  $4f$  shell is set to 6 eV for the Eu and 7 eV for the Gd. This is necessary to account for correlation effects in the open atomiclike  $4f$  shell: both Eu and Gd have the  $4f^7$  configuration as found from experiment and calculation. If  $U$  were set to zero, the Eu and Gd  $4f$  states would move sizeably to the Fermi level, and the experimental peak positions would not have been reproduced.

Despite the apparent successes of these band structure calculations, we also can observe small deviations between

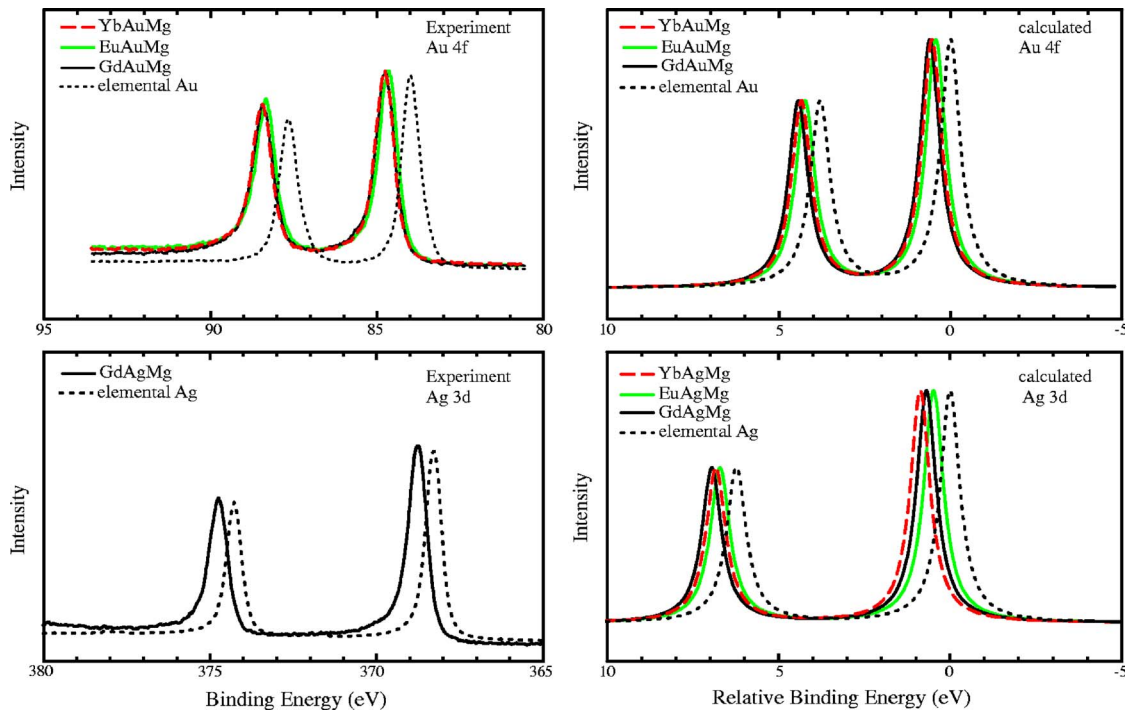


FIG. 4. (Color online) Left-hand panels: experimental Au 4f and Ag 3d core level spectra of YbAuMg, EuAuMg, GdAuMg, GdAgMg, and elemental Au and Ag. Right-hand panels: simulated spectra based on the calculated Au 4f and Ag 3d energy positions.

theory and experiment. A closer look at the calculated positions of the closed shell Au and Ag  $d$  bands as well as of the closed shell Yb  $4f$  orbitals, reveals that they are too close to the Fermi level by several tenths of an eV. We attribute such deviations as being caused by the inherent limitations of these mean-field methods to calculate the dynamical response of a system.

The left-hand panels of Fig. 4 show the Au  $4f$  and Ag  $3d$  core levels of the YbAuMg, EuAuMg, GdAuMg, and GdAgMg samples (solid and long dashed lines). As reference we have also measured the corresponding core levels in elemental Au and Ag (short dashed lines). One can clearly observe that the Au and Ag core levels in the intermetallics have substantially higher binding energies than those in the elements, i.e.,  $\approx 0.7$  eV for the Au  $4f$  and  $\approx 0.5$  eV for the Ag  $3d$ . This may indicate that in the intermetallics the electron density around the Au and Ag sites are more diluted and thus giving a weaker static electric field. LDA band structure calculations confirm this picture. We have calculated that the energies of the Au and Ag core levels of the intermetallics are indeed lower (i.e., at higher binding energy) than in the elements, as shown in the right-hand panels of Fig. 4 where we have simulated the spectra based on these calculated energy positions. We note that there exist two inequivalent Au (Ag) sites in GdAuMg (GdAgMg). The calculations show, however, that the Au  $4f$  of the two sites differs by only 40 meV, and that the Ag  $3d$  by only 20 meV. The influence of different local environments<sup>25</sup> is thus negligible here. The Au and Ag sites in EuAuMg, YbAuMg, EuAgMg, and YbAgMg are all equivalent. We also note that comparing the

calculations for the intermetallics with the elements reveals that there is hardly any difference in the total amount of charge inside the Au or Ag muffin tin spheres, i.e., less than 0.05 electrons. The core level shifts are thus consistent with the rather open crystal structure: the Au and Ag atoms in the intermetallics could be considered as impurities submerged in a low density  $sp$  metal host.

To conclude, we have investigated the electronic structure of the equiatomic EuAuMg, GdAuMg, YbAuMg, and GdAgMg intermetallics by x-ray photoelectron spectroscopy and LDA/LDA+ $U$  band structure calculations. We found a closed shell  $4f$  configuration for the Yb (divalent) and a  $4f^7$  for the Eu (divalent) and Gd (trivalent). The states in the vicinity of the Fermi level are given by a broad  $sp$ -like band consisting of Mg  $s$ , Au/Ag  $sp$ , and  $R spd$  states. The contribution of the  $R 4f$  is negligible, except perhaps for the Yb system. We also found that the Au and Ag  $d$  bands are extraordinarily narrow, as if the noble metal atoms were impurities submerged in a low density  $sp$  metal host. This calls for a follow-up study of the electronic structure of equiatomic intermetallics in which the noble-metal atoms are replaced by transition-metal atoms with an open  $d$  shell, since in view of the extremely narrow bandwidth even modest electron correlation effects could already play an important role for the properties.

The authors acknowledge Lucie Hamdan for her skillful technical assistance. The authors thank the Degussa-Hüls AG for the generous gift of noble metals. This work was supported by the Deutsche Forschungsgemeinschaft through the priority programme SPP 1166 "Lanthanoidspezifische Funktionalitäten in Molekül und Material."

<sup>1</sup>A. Iandelli, J. Alloys Compd. **203**, 137 (1994).

<sup>2</sup>A. Iandelli, J. Alloys Compd. **182**, 87 (1992).

<sup>3</sup>C. Geibel, U. Klinger, M. Weiden, B. Buschinger, and F. Steglich, Physica B **237& 238**, 202 (1997).

<sup>4</sup>R. Pöttgen, R.-D. Hoffmann, J. Renger, U. Ch. Rodewald, and M. H. Möller, Z. Anorg. Allg. Chem. **626**, 2257 (2000).

<sup>5</sup>Th. Fickenscher and R. Pöttgen, J. Solid State Chem. **161**, 67 (2001).

<sup>6</sup>D. Johrendt, G. Kotzyba, H. Trill, B. D. Mosel, H. Eckert, Th. Fickenscher, and R. Pöttgen, J. Solid State Chem. **164**, 201 (2002).

<sup>7</sup>R. Kraft, G. Kotzyba, R.-D. Hoffmann, and R. Pöttgen, Z. Naturforsch., B: Chem. Sci. **57**, 488 (2002).

<sup>8</sup>Th. Fickenscher, R.-D. Hoffmann, R. Kraft, and R. Pöttgen, Z. Anorg. Allg. Chem. **628**, 667 (2002).

<sup>9</sup>B. J. Gibson, A. Das, R. K. Kremer, R.-D. Hoffmann, and R. Pöttgen, J. Phys.: Condens. Matter **14**, 5173 (2002).

<sup>10</sup>K. Łątka, R. Kmieć, A. W. Pacyna, T. Tomkowicz, R. Mishra, T. Fickenscher, H. Piotrowski, R.-D. Hoffmann, and R. Pöttgen, J. Solid State Chem. **168**, 331 (2002).

<sup>11</sup>R. Kraft, Th. Fickenscher, G. Kotzyba, R.-D. Hoffmann, and R. Pöttgen, Intermetallics **11**, 111 (2003).

<sup>12</sup>K. Łątka, R. Kmieć, A. W. Pacyna, Th. Fickenscher, R.-D. Hoffmann, and R. Pöttgen, Solid State Sci. **6**, 301 (2004).

<sup>13</sup>C. B. Shoemaker and D. P. Shoemaker, Acta Crystallogr. **18**, 900 (1965).

<sup>14</sup>P. I. Kripyakevich, V. Ya. Markiv, and E. V. Melnyk, Dopov.

Akad. Nauk Ukr. RSR, Ser. A: Fiz.-Tekh. Mat. Nauki **29**, 750 (1967).

<sup>15</sup>A. E. Dwight, M. H. Mueller, R. A. Conner, Jr., J. W. Downey, and H. Knott, Trans. Metall. Soc. AIME **242**, 2075 (1968).

<sup>16</sup>M. F. Zumdick, R.-D. Hoffmann, and R. Pöttgen, Z. Naturforsch., A: Phys. Sci. **54**, 45 (1999).

<sup>17</sup>V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).

<sup>18</sup>H. Hartmann, K. Berggold, S. Jodlauk, I. Klassen, K. Kordonis, T. Fickenscher, R. Pöttgen, A. Freimuth, and T. Lorenz, J. Phys.: Condens. Matter **17**, 7731 (2005).

<sup>19</sup>P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, <http://www.wien2k.at>

<sup>20</sup>J. K. Lang, Y. Baer, and P. A. Cox, J. Phys. F: Met. Phys. **11**, 121 (1981).

<sup>21</sup>M. Campagna, G. K. Wertheim, and Y. Baer, in *Topics in Applied Physics*, edited by L. Ley and M. Cardona (Springer-Verlag, Berlin, 1979), Vol. 27.

<sup>22</sup>G. K. Wertheim, J. H. Wernick, and G. Creelius, Phys. Rev. B **18**, 875 (1978).

<sup>23</sup>R. Mishra, R. Pöttgen, R.-D. Hoffmann, D. Kaczorowski, H. Piotrowski, P. Mayer, C. Rosenhahn, and B. D. Mosel, Z. Anorg. Allg. Chem. **627**, 1283 (2001).

<sup>24</sup>P. H. Hannah and P. Weightman, J. Phys. F: Met. Phys. **16**, 1015 (1986).

<sup>25</sup>R. J. Cole, N. J. Brooks, and P. Weightman, Phys. Rev. Lett. **78**, 3777 (1997).