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Structure and Bonding in Yb_4MgGe_4: Yb^{2+}/Yb^{3+} Mixed-Valency and Charge Separation

Paul H. Tobash and Svilen Bobev*

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

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The family of intermetallic compounds with a general formula RE_5Tt_4 (RE = Rare-earth; Tt = Tetrel = Si, Ge, i.e., group 14 element) has long been known,[1] however, these materials captured the interest of the solid-state community only very recently.[2−4] The discovery of the giant magnetocaloric effect, magnetostriction and magnetoresistance in the Gd_5Si_4−Gd_5Ge_4 system prompted more systematic studies of the magnetic and crystallographic transformations in this and related phases.[2−4] Nowadays, it is well understood that the diverse and unique properties of these materials are stemming from the reversible breaking of specific Tt-Tt bonds in the crystal structure.[3,4] It has been shown that these structural first-order transformations can be controlled via several parameters such as temperature, pressure, applied magnetic field, and chemical composition.[3] The latter presents a powerful tool for fine-tuning properties through substitution of Ge with the isoelectronic but smaller Si for example, as demonstrated with comprehensive work on the $Gd_5(Si_xGe_{1-x})_4$ system.[2−4] Likewise, partial substitution of Ge by electron poorer Ga changes the valence electron count and affects the bond-making/breaking "processes" concomitant with the magnetic ordering.[4a] These and other possibilities for exchanging Tt elements have been explored in the past.[2−4]

With this communication, we report the synthesis and the structural characterization of a new derivative of the RE_5Tt_4 family, $Yb_{5-x}Mg_xGe_4$ ($x \approx 1$, Yb_4MgGe_4 hereafter). This phase is a rare example of a substitution of a lanthanide metal (Yb) with a nonmagnetic element, Mg in this instance (Figure 1) within the Gd_5Si_4 type.[5] Similar approach has been recently used in probing the limits of electron-deficiency in related $La_{5-x}Ca_xGe_4$ and $Ce_{5-x}Ca_xGe_4$ ($3 < x < 3.8$) systems.[6] In the present case however, since the parent Yb_5Ge_4 compound exhibits an intermediate valent behavior,[7] there exists the possibility for interchanging Mg for either trivalent or divalent Yb, which broadens the possibilities for rational structure alteration. Moreover, unlike all previous reports on RE_5Tt_4, where satisfying the Zintl−Klemm concept[8] has been claimed inessential, our results are best interpreted if one recognizes the tendency of all atoms for closed-shell configuration.

Yb_4MgGe_4 was serendipitously discovered from a reaction of the elements designed to produce the hitherto unknown compound Yb_2MgGe_2 (see Supporting Information). It is the missing member of a large RE_2MgGe_2 family of intermetallics, which crystallize with an ordered ternary variant of the tetragonal U_3Si_2 structure.[1] Our interest in that system was sparked by the discovery of Yb_2InGe_2 and a series of RE_2InGe_2 phases (RE = Sm, Gd, Tb, Dy, Ho), isotypic with RE_2MgGe_2.[9] According to the Zintl concept,[8] the electron count in these compounds can be rationalized as $(RE^{3+})_2(In^{3+})(Ge^{3-})_2(e^-)_3$. Although an oversimplification, bonding in the isostructural RE_2MgGe_2 can be rationalized in an identical manner, however there will be a surplus of only two electrons.[10] These speculations do not apply to Yb_2InGe_2 for which experimental data confirm Yb^{2+} (i.e. $[Xe]f^{14}$) ground state.[9] Therefore, the formal electron count in Yb_2InGe_2 will lead to one extra electron per formula, while the hypothetical Yb_2MgGe_2 with the same structure would be charge-balanced according to $(Yb^{2+})_2(Mg^{2+})(Ge^{3-})_2$. As a result, this material could present a ground state where the Yb^{2+}/Yb^{3+} configurations might compete, thereby leading to interesting physical properties.

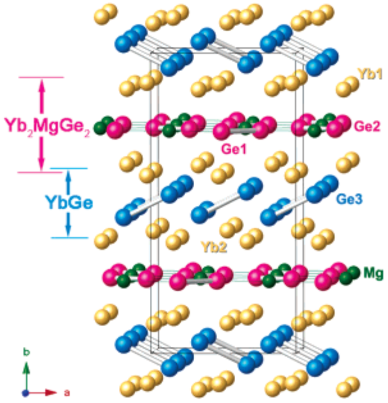

Figure 1. Ball-and-stick representation of the orthorhombic crystal structure of Yb_4MgGe_4 (unit cell outlined). The Yb and Mg atoms are shown as yellow and dark-green spheres, respectively. The two different kinds of Ge atoms are drawn as magenta (Ge1 and Ge2) and blue (Ge3) spheres, respectively.

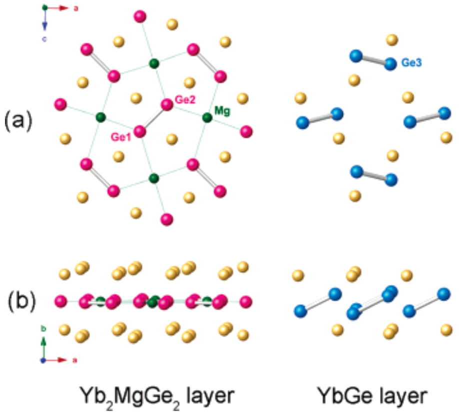

Figure 2. (a) Top and (b) side views of the basic building fragments of the Yb_4MgGe_4 structure—the hypothetical Yb_2MgGe_2 and YbGe.

All attempts to make Yb_2MgGe_2 have proven unsuccessful and yielded Yb_4MgGe_4 as a major product. This is not surprising if one realizes that both structures are closely related. The tetragonal Yb_2MgGe_2 (ordered U_3Si_2 type) can be viewed as flat infinite $[MgGe_2]^{4-}$ layers, which are stacked above one another, with Yb cations between them. The $[MgGe_2]^{4-}$ layers, in turn, can be regarded as $[Ge_2]^{6-}$ dimers, "stitched" together through Mg−Ge interactions (Figure 2a). The same motifs are present in the structure of Yb_4MgGe_4, although their arrangement is slightly different. As can be seen from Figure 1, the flat $[MgGe_2]^{4-}$ layers propagate in

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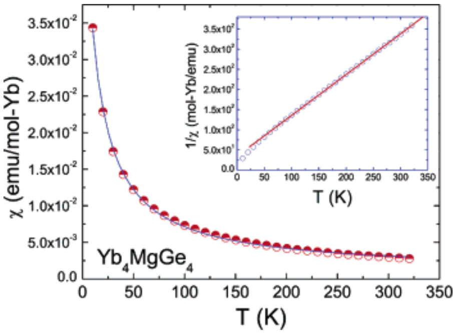

Figure 3. Magnetic susceptibility $\chi(T)$ plot in an applied magnetic field of 500 Oe. (Inset) Inverse magnetic susceptibility $\chi^{-1}(T)$ plot. Solid lines indicate fits to the Curie−Weiss law, respectively.

two dimensions (*a* and *c*), but they are not eclipsed as in Yb_2MgGe_2. Instead, the layers are offset by a distance of 1/4•*a* with respect to one another and are interspaced with layers of $[Ge_2]^{6-}$ dimers and Yb cations filling the space between them (Figure 1).[11] The corresponding Ge−Ge distances of 2.557(2) and 2.600(2) Å, respectively, indicate strong covalent character for these bonds and compare well with those reported for RE_2MgGe_2 and RE_2InGe_2.[9,10]

Following this formalism, the structure of Yb_4MgGe_4 can be rationalized as an intergrowth of imaginary Yb_2MgGe_2 and YbGe lattices (Figures 1 and 2). If we extrapolate the data from Yb_2InGe_2 and assume that Yb ions in the Mg analogue are also divalent, to achieve charge balance in Yb_4MgGe_4, the Yb ions in the YbGe moiety will have to be trivalent according to $[(Yb^{2+})_2(Mg^{2+})(Ge^{3-})_2][(Yb^{3+})(Ge^{3-})]_2$. Indeed, more careful analysis of the coordination of the cation sites shows that the distances of Yb1 to its closest neighbors are almost 0.2 Å shorter than the distances of Yb2 to the nearest germanium atoms. Based on the above, a plausible conclusion is that Yb_4MgGe_4 is a *heterogeneous mixed-valent* compound, i.e. a system where one of the two Yb sites (Yb2) has atoms in nonmagnetic Yb^{2+} configuration, whereas the Yb^{3+} cations occupy the Yb1 site. Furthermore, since the ionic radius of Yb^{3+} is very similar to that of Mg^{2+}, one might speculate that additional Mg substitutions (if possible without a structural change) will lead to the displacement of Yb^{3+}, thereby creating a possibility for continuous variations of the magnetic properties through Mg^{2+}/Yb^{3+} exchange. Preliminary results confirm that in the Mg-richer systems Yb1 is the site that takes up the extra Mg—refinements on $Yb_{3.76}Mg_{1.24}Ge_4$ and $Yb_{3.45}Mg_{1.55}Ge_4$ from single-crystal data provide unequivocal evidence for a 88(1):12(1) statistical mixture of Yb and Mg on the Yb1 site in the former and 72(1):28(1) in the latter (see Supporting Information). These results are in agreement with the magnetic properties of Yb_4MgGe_4 and $Yb_{3.76}Mg_{1.24}Ge_4$.

The molar magnetic susceptibility ($\chi = M/H$, normalized per Yb) of polycrystalline Yb_4MgGe_4 is shown in Figure 3. The compound does not order magnetically down to 10 K, and the temperature dependence $\chi(T)$ in the interval 10−325 K indicates a Curie−Weiss paramagnetic behavior. The $\chi^{-1}(T)$ data above 40 K were linearly fit (inset Figure 3), which resulted in an effective moment $\mu_{eff} = 2.7\ \mu_B$/Yb. This value is almost 60% of the value expected for free-ion Yb^{3+} (f^{13} with $g_J[J(J+1)]^{1/2} = 4.54\ \mu_B$),[12] in good agreement with the mixed valency reported for Yb_5Si_4−Yb_5Ge_4 pseudobinary systems.[7] Nevertheless, departures from the straight line are clearly seen below ca. 30 K; therefore, the data were fit with the modified Curie−Weiss law $\chi(T) = \chi_o + C/(T - \theta_p)$, where χ_o is the sum of the temperature-independent contributions, e.g. van Vleck paramagnetism, paramagnetism due to conduction electrons, and core−electron diamagnetism, $C = N_A\mu_{eff}^2/3k_B$ is the Curie constant, and θ_p is the Weiss temperature.[12] A nonlinear least-squares fit to this equation resulted in $\chi_o = 9 \times 10^{-4}$ emu/mol, $\theta_p = -11$ K, and an effective moment of 2.3 μ_B/Yb. Similar analysis for the Mg-richer $Yb_{3.76}Mg_{1.24}Ge_4$ gives a moment of 2.2 μ_B/Yb, indicating fewer Yb^{3+} ions (see Supporting Information). This means that the ratio of magnetic Yb^{3+} to nonmagnetic Yb^{2+} in the lattice of Yb_4MgGe_4 is almost 1:1, while that in $Yb_{3.76}Mg_{1.24}Ge_4$ is 0.9:1, which corroborates the analysis based upon bond distances: Yb1 is trivalent, while Yb2 is divalent (above). In that regard, Yb_4MgGe_4 is rather unusual compared to other Yb-intermetallics where *intermediate* valency has been reported—in those systems, the energies of the $[Xe]f^{13}$ and $[Xe]f^{14}$ configurations are close, and the valence of Yb atoms occupying a single site can oscillate between the two states.

Since the structure of Yb_4MgGe_4 is robust and can adapt slightly higher or lower Mg concentrations and since Mg^{2+} cations substitute for magnetic Yb^{3+}, this system provides an attractive way for tunable valence transitions via controlled structure modifications. Such approach has a high potential for discovering new compounds with unique physical properties, and more designed syntheses in the related *RE*−Mg−Ge systems are currently underway.

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Supporting Information Available: Experimental details, crystallographic tables, combined single-crystal X-ray crystallographic information file (CIF), and additional magnetic susceptibility data. This material is available free of charge via the Internet at http://pubs.acs.org.

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