Doping-induced valence change in $Yb_5Ge_{4-x}(Sb, Ga)_x$: $(x \leq 1)$

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Abstract Following our earlier observation that the ytterbium valence distribution in $Yb_5Ge_{4-x}Si_x$ was independent of x, we use ^{170}Yb Mössbauer spectroscopy to follow the Yb valence distribution in Sb and Ga doped Yb_5Ge_4. The crystal structure does not change for either dopant and the Yb valence, while affected, proves quite resistant to change, with only one third of the electrons added or removed by the dopants leading to $Yb^{3+} \leftrightarrow Yb^{2+}$ conversion.

Keywords Lanthanide · Valence · Mössbauer spectroscopy

1 Introduction

The R_5X_4 (R = Y, La–Lu; X = Si, Ge, Sn) compounds became the subject of intense investigation after the discovery of a giant magnetocaloric effect in $Gd_5Si_2Ge_2$ [1]. Systematic phase relationship and structural data have been obtained for most of

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the $R_5Ge_{4-x}Si_x$ systems and two key parameters have been identified which affect the balance between the magnetic and structural energies in the R_5X_4 phases. The first is the ratio of the ionic radius of the rare earth, r_R, to the weighted average radius of the metalloid elements, r_X [2] and the second is the valence electron concentration [3]. As the ratio r_R/r_X decreases, the crystal structures of most R_5X_4 compounds change in the sequence: tetragonal $Zr_5Si_4 \rightarrow$ orthorhombic $Gd_5Si_4 \rightarrow$ monoclinic $Gd_5Si_2Ge_2 \rightarrow$ orthorhombic Sm_5Ge_4 [2]. The Yb_5X_4 compounds are of particular interest because Yb can occur in two valence states: Yb^{2+} ($r_R = 1.94$ Å) and Yb^{3+} ($r_R = 1.74$ Å). This allows us to explore the effects of both the valence electron concentration and the relative metallic radii (r_R/r_X). Surprisingly, $Yb_5Ge_{4-x}Si_x$ adopts the orthorhombic Gd_5Si_4-type (*Pnma* #62) structure, with a constant $Yb^{2+}:Yb^{3+}$ population ratio of 1.09(4) for all x [4]. In this paper, we investigate the effects of Sb and Ga doping in Yb_5Ge_4. Sb and Ga have respectively one more and one less electron in their outer shell than Ge, allowing us to drive $Yb^{3+} \leftrightarrow Yb^{2+}$ interconversion directly, while the very different metallic radii of Sb (1.59 Å) and Ga (1.41 Å), both larger that that of Ge (1.37 Å), could drive the Yb valence towards the larger Yb^{2+}, effectively maintaining an approximately constant r_R/r_X ratio.

2 Experimental methods

The samples used in this study ($Yb_5Ge_{4-x}Sb_x$ (x = 0.5, 0.75, 1), $Yb_5Ge_{4-x}Ga_x$ (x = 0.5, 1) and Yb_5Ge_4) were prepared at the Ames Laboratory by induction melting stoichiometric mixtures of the pure elements following the standard procedure described elsewhere [5]. X-ray powder diffraction was used to verify the structure and phase composition of the materials. All of the materials were found to crystallize in the orthorhombic Gd_5Si_4-type *Pnma* structure. A second phase (11:10) is present in the Sb doped samples, amounting to ∼5–15 mol % of the materials.

[170]Yb Mössbauer spectroscopy was used to determine the relative proportions of Yb^{2+} and Yb^{3+}. A 20mCi [170]Tm source was prepared by neutron activation of ∼20 mg of Tm as a 10 wt% alloy in aluminium. The source and sample were mounted vertically in a helium flow cryostat and the drive was operated in sine mode. The 84.25 keV Mössbauer γ-photons were isolated from the various x-rays emitted by the source using a high-purity Ge detector. The spectrometer's drive velocity was calibrated with a laser interferometer and velocities were cross-checked against [57]Co**Rh**/α-Fe at room temperature. All spectra were obtained at 5 K (except for Yb_5Ge_4 which was part of the earlier study [4] and was taken at 8 K) and fitted using a nonlinear least-squares minimization routine with line positions and intensities derived from an exact solution to the full Hamiltonian [6].

3 Results and discussion

The 84.25 keV $2^+ \rightarrow 0^+$ transition in [170]Yb involves a rotational change at almost constant nuclear volume, so the isomer shift is essentially independent of valence. However, the electric field gradients (EFG) associated with the two valence
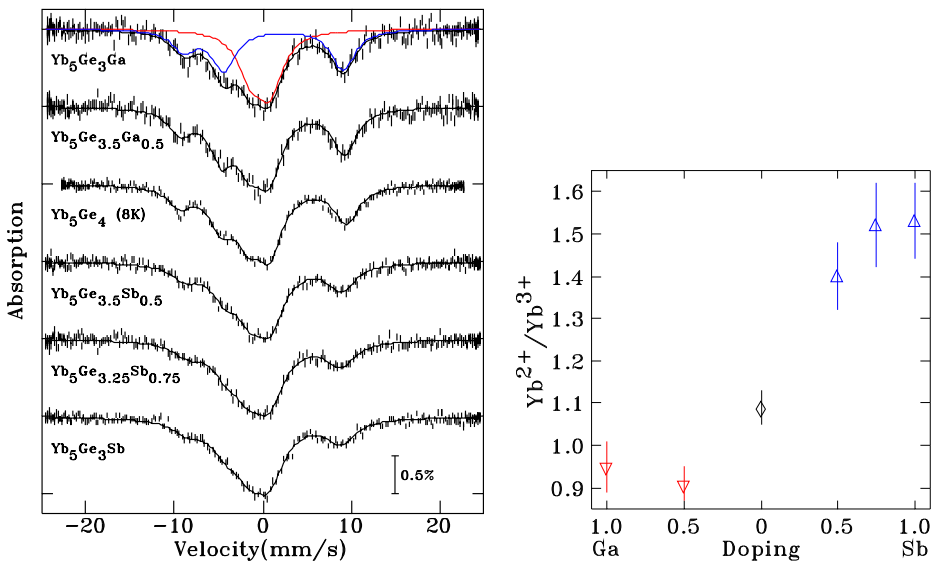
Fig. 1 (*Left*) ^{170}Yb Mössbauer spectra of $Yb_5Ge_{4-x}(Sb, Ga)_x$: $(x \leq 1)$, obtained at 5 K (except for Yb_5Ge_4, taken at 8 K). The *solid lines* are fits to a full Hamiltonian solution as described in the text. For the top spectrum (Yb_5GaGe_3) we also show the two components Yb^{2+} (*red*) and Yb^{3+} (*blue*). (*Right*) Dopant dependence of the Yb^{2+}:Yb^{3+} area ratio, deduced from fits to the ^{170}Yb Mössbauer spectra

states are quite different. Yb^{2+} has a nonmagnetic, closed shell $4f^{14}$ electronic configuration, leaving only a small contribution to the EFG from the lattice, whereas Yb^{3+} has a $4f^{13}$ configuration which results in a significant 4f contribution to the EFG. The ^{170}Yb Mössbauer spectra of the studied compounds are shown in the left panel of Fig. 1. Each spectrum consists of two paramagnetic components, corresponding to the two valence states of Yb. As with $Yb_5Ge_{4-x}Si_x$ [4], it was not possible to resolve the contributions from the three ytterbium sites, and only a valence separation was possible. The right panel of Fig. 1 shows the Yb^{2+}:Yb^{3+} subspectral area ratio plotted against the dopant content. Doping with Sb strongly increases the Yb^{2+}:Yb^{3+} ratio, whereas Ga doping produces a smaller decrease. This difference in the strength of the doping effects may derive from the larger size of the dopants supporting (in the case of Sb) or competing with (in the case of Ga) the valence shift. One way to separate out the effects of dopant size (r_X) is to combine our data with those from $Yb_5Ge_{4-x}Si_x$ [4] in the left panel of Fig. 2, where it is clear that doping with the larger Ga actually leads to a cell volume *decrease* while the increase with Sb doping is slower than expected. Both departures from the trend established by $Yb_5Ge_{4-x}Si_x$ are due to $Yb^{3+} \leftrightarrow Yb^{2+}$ conversion.

Finally, in the right panel of Fig. 2 we show the total valence electron count, per formula unit, as a function of dopant (Ga = 3; Ge = 4; Sb = 5 with the Yb value derived from the measured Yb^{2+}:Yb^{3+} ratio). No valence conversion would give a slope of unity, while full dopant-induced conversion would yield zero slope. The
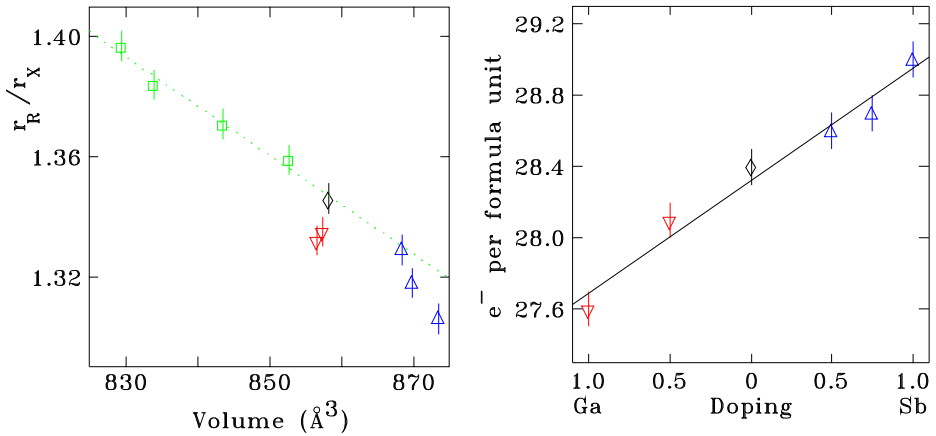
Fig. 2 (*Left*) Cell volume dependence of the atomic radii ratio (r_R/r_X). □ (*green*) and the *dashed line* show the trend for $Yb_5Ge_{4-x}Si_x$ [4]. ▽ (*red*) and △ (*blue*) show data for gallium and antimony doping respectively. (*Right*) Dopant dependence of the weighted valence electron count

fitted slope of 0.63(6) indicates that the Yb valence distribution is rather robust, with only about *one-third* of the valence electrons donated by the dopants actually leading to $Yb^{3+} \leftrightarrow Yb^{2+}$ valence conversion, with the other two-thirds entering the conduction band.

In order to obtain more information on the relative importance of dopant size and valence, we plan to investigate the effects of In (over-sized acceptor) and As (size-matched donor) doping in this system.

4 Conclusions

We have examined the effect of Ga and Sb doping on the $Yb^{2+}:Yb^{3+}$ population ratio in the $Yb_5(Ge, Ga, Sb)_4$ system by ^{170}Yb Mössbauer spectroscopy. Sb doping has a large effect on the Yb valence ratio, due to the combined effects of the increased atom size and the increase in valence electron concentration. In the case of Ga doping, the competing effects of the increased atom size and the reduced electron valence concentration lead to significantly smaller changes in the $Yb^{2+}:Yb^{3+}$ ratio. Finally, the crystallographic cell volume increases with Sb doping, and decreases with Ga doping, an effect which is explained in part by the change in average weighted volume of the Yb ions, due to the change in the $Yb^{2+}:Yb^{3+}$ ratio.

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