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Site disorder and spin-glass ordering in $PrAu_2Si_2$

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We have used ^{197}Au Mössbauer spectroscopy along with both neutron and x-ray diffraction to search for site disorder and noncollinear magnetic ordering in $PrAu_2Si_2$. There is no evidence of a transferred hyperfine field at the Au site down to 1.7 K allowing us to rule out both collinear antiferromagnetic order and spin-glass ordering of the Pr moments. Full-pattern Rietveld refinement of both neutron and x-ray diffraction data taken over a wide angle range allows us to exclude Au/Si site disorder at the 1% level. We conclude that the Pr moments do not order above 1.7 K in $PrAu_2Si_2$, and that the susceptibility peak is likely a dynamic effect. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1850271]

Frustration and disorder are necessary, but not sufficient, minimum ingredients for any spin glass,[1] however two stoichiometric compounds [URh_2Ge_2 (Ref. 2) and $PrAu_2Si_2$ (Refs. 3–5)] have been proposed as potential exceptions. In both cases, some form of site disorder has been invoked to provide the randomness essential for the formation of a spin glass. Unfortunately, while the concept of "spin glass" is well defined, and the minimum requirements for such ordering to be possible are clear, demonstrating that a spin glass state does indeed occur in a given material is not trivial.

The $PrAu_2(Ge_xSi_{1-x})_2$ alloy system provides an excellent place to investigate the possibility that a spin glass can form in a chemically ordered compound: the changes in magnetic properties from antiferromagnetic (AF) to spin glass (SG) can be followed at constant structure as the alloy composition is changed. A neutron diffraction and susceptibility study[3] showed that the simple AF-I-type ordering of the germanide[3,6] observed below $T_N \sim 12$ K at $x=1$ was lost for $x < 0.2$, while a susceptibility cusp persisted to $x=0$.[3,7] Given the smooth evolution in characteristic temperatures (derived from susceptibility data) and the absence of additional magnetic reflections in the neutron diffraction patterns for $x < 0.2$, it was natural to propose that the stoichiometric compound, $PrAu_2Si_2$, exhibits spin-glass ordering below $T_f \sim 3.2$ K.[3] However, it was recognized that some form of disorder was essential to this argument. It is clear that the body centered tetragonal ($ThCr_2Si_2$-type $I4/mmm$) crystal structure supports AF order (at $x=1$) and that this structure does not change with x. Analysis of the intensities of two low-order peaks in the neutron scattering patterns led to the suggestion that about 10% Au/(Si,Ge) site disorder was present in all samples and that while it did not destroy the AF order in the Ge-rich alloys, it did provide sufficient frustration in the Si-rich alloys to lead to the spin-glass ordering.

There are two problems with this solution to the frustration problem. First, it is not clear that 10% site disorder could yield sufficient frustration to lead to SG ordering as the thresholds for both bond[8] and site[1,9] frustration are ~25%. Second, the observed phase diagram for this system[3] is not consistent with the effects of steadily increasing frustration. Neither bond nor site frustration leads to an abrupt loss of long-ranged order. A second transition appears in both cases before the spin glass is reached.[10] A more recent muon spin relaxation (μSR) study of the same materials offers an intriguing solution to the problem. Noakes *et al.* found no evidence for *static* order down to 40 mK in $PrAu_2Si_2$, suggesting that the Pr moments remained dynamic at temperatures well below $T_f \sim 3.2$ K.[11]

We have used ^{197}Au Mössbauer spectroscopy and revisited the x-ray and neutron diffraction data on this system in order to address two key questions: (i) what, if any, is the nature of the Pr ordering? (ii) what level of chemical disorder is present in $PrAu_2Si_2$?

The samples of $PrAu_2(Ge_xSi_{1-x})_2$ ($x=0$, 1) used here are those previously prepared and studied by Krimmel *et al.*[3] Basic magnetic characterization was carried out using a Quantum Design PPMS magnetometer with a 9 T magnet operating between 1.8 and 300 K. Our results are fully consistent with those previously published on the same samples.[3] X-ray diffraction data were obtained on powder samples with a conventional Cu K_α diffractometer. Neutron diffraction measurements were made using the C2 multiwire powder diffractometer on NRU at the Chalk River Laboratories, Ontario. Temperatures down to 3.6 K were obtained using a closed-cycle refrigerator. Both x-ray and neutron diffraction data sets were fitted using the GSAS/EXPGUI package.[12] ^{197}Au Mössbauer sources were prepared by neutron activation of ^{196}Pt foils in the SLOWPOKE reactor at Ecole Polytechnique, Montréal to yield about 1 GBq of the 19 h ^{197}Pt. The spectrometer was operated vertically with

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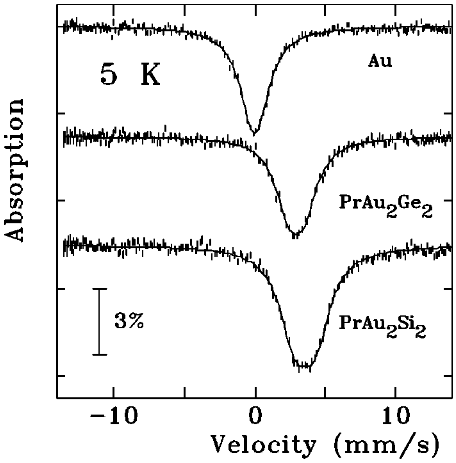

FIG. 1. ^{197}Au Mössbauer spectra of Au metal, $PrAu_2Ge_2$, and $PrAu_2Si_2$ measured at 5 K.

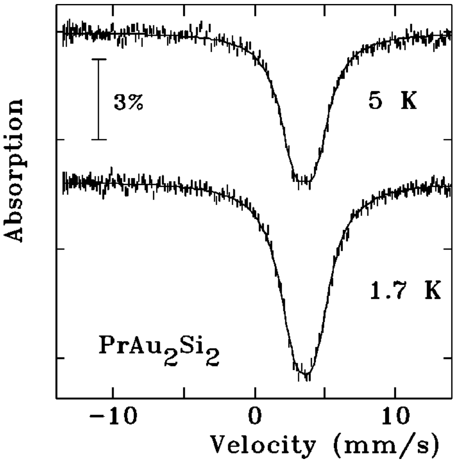

FIG. 2. ^{197}Au Mössbauer spectra of $PrAu_2Si_2$ measured on cooling from 5 to 1.7 K showing no change in spectral shape that could be attributed to magnetic ordering.

both source and sample cooled in a helium-flow cryostat. A He/Ne laser interferometer was used to provide simultaneous calibration of all spectra. Calibration was checked using a ^{57}Co/Rh source and α-Fe in the same geometry at room temperature. Spectra were fitted using a conventional nonlinear least-squares minimization routine.

The ^{197}Au Mössbauer spectra of $PrAu_2Ge_2$ and $PrAu_2Si_2$ at 5 K, shown in Fig. 1, exhibit a small positive isomer shift relative to Au metal at 5 K that increases from Ge to Si. There is also a small, unresolved, quadrupole splitting [1.09(8) mm/s for the germanide, 1.43(4) mm/s for the silicide] that is essentially temperature independent, changing by about 2% in both alloys over the narrow temperature range considered here (1.7–20 K). Simple point-charge calculations suggest that Au on the Ge-4-*e* site should exhibit a significantly larger quadrupole splitting than Au on its proper 4-*d* site, so that two components should be observed if there were Au–Ge site disorder. However, the spectra can be fitted using a single Au site, with no evidence (less than 1.5%) for a second, a wider split, component which could be attributed to Au on the Ge-4-*e* site. The uncertainties on the electrostatic environments of the two possible sites are quite large, so that eliminating significant site disorder on this basis is not conclusive. However, the AF-I ordering below T_N makes the *magnetic* environments of the two sites completely different. The 4-*d* site normally occupied by Au in these compounds is equidistant from four Pr atoms. In the germanide, these Pr moments order in a 2-"up":2-"down" configuration and their transferred fields cancel at the Au site. By contrast, the Pr neighbours of the 4-*e* site (normally occupied by Ge) all order parallel and a significant transferred hyperfine field is expected at a gold nucleus on the 4-*e* position. Therefore, in the presence of site disorder, and independent of any differences in electric field gradients, we would expect a two-component spectrum to develop below T_N as Au atoms on the 4-*e* site start to experience a transferred magnetic field. The absence of any spectral changes on cooling $PrAu_2Ge_2$ through T_N is therefore consistent with the AF-I magnetic structure deduced previously from neutron diffraction[3] and allows us to rule out significant Au–Ge site disorder ($<1\%$) in the germanide. Analysis of ^{193}Ir Mössbauer data for the isostructural $DyIr_2Si_2$ which also exhibits AF-I ordering led to similar conclusions,[13] while AF-II order in $PrFe_2Ge_2$ splits the Fe-4-*d* sites into two equal populations, one with a transferred field, the other at which the field cancels.[14]

The ^{197}Au Mössbauer spectra of $PrAu_2Si_2$ at 5 K (i.e., above T_f) (Fig. 1) also shows no evidence (less than 2%) for a second component. Furthermore, cooling $PrAu_2Si_2$ through $T_f \sim 3.2$ K leads to no change in the observed Mössbauer spectrum (Fig. 2) beyond that associated with the expected increase in f-factor. As noted earlier, the simple form of the spectrum above T_f strongly suggests that there is little or no site disorder in this alloy, however, it is the absence of any changes on cooling through T_f that is more significant. While the simple AF-I structure, seen for $x \geqslant 0.2$, leads to a cancellation of the transferred field at the 4-*d* site, SG ordering in $PrAu_2Si_2$ could not cause a complete cancellation at every Au site and we would expect a wide distribution of transferred hyperfine fields [see for example the ^{119}Sn Mössbauer spectrum of the spin glass *a*-$(Fe_{0.55}Mn_{0.45})_{78}Sn_2Si_6B_{14}$ (Ref. 15)]. If the Pr moments order, some spectral broadening must occur no matter which site the Au atoms occupy. We observe none. Neutron diffraction rules out long-ranged AF order,[3] our Mössbauer data are inconsistent with SG order. Both data sets are however in full accord with the recent μSR study which found no static order in $PrAu_2Si_2$ down to 40 mK.[11]

We turn now to the diffraction data, and concentrate on $PrAu_2Si_2$ as it is here that the presence or absence of Au/Si substitution is critical, and also the Au–Si scattering length contrast is superior to that of Au–Ge in both x rays ($Z_{Si}=14$, $Z_{Ge}=32$, $Z_{Au}=79$) and neutrons [$b_c=4.15$(Si), 8.18(Ge), 7.90(Au) fm]. Figure 3 shows x-ray and neutron diffraction data for $PrAu_2Si_2$. The x-ray pattern was taken in three banks with increasing counting time used at higher angles to compensate for the fall off in form factor. The fits shown through both data sets are calculated with no Au/Si site disorder. Permitting Au–Si site exchange leads neither to a visual improvement in the fits nor to a significant change in the goodness of fit parameters. Forcing a 10% site exchange between

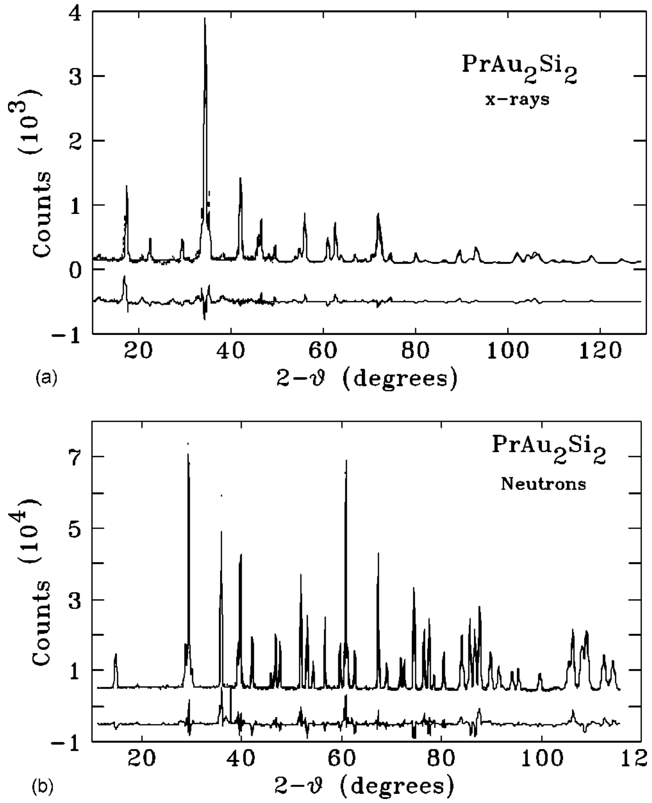

FIG. 3. Powder diffraction patterns for $PrAu_2Si_2$. Top: Cu K_α x-ray data taken at room temperature. Bottom: 1.33 Å neutron data taken at 20 K. Fits obtained assuming no Au–Si site disorder are shown as solid lines. Residuals are shown below each fitted data set.

Au and Si leads to both a visual degradation of the fit (several peak intensities are wrong) and a significant increase in χ^2. The best fits to the two data sets yield gold occupation levels for the Au-4*d* site of: 1.003 ± 0.010 (neutrons) and 1.011 ± 0.012 (x rays). This is consistent with $PrAu_2Si_2$ being a fully ordered compound.

In conclusion, we find no evidence for static spin-glass ordering of Pr moments in $PrAu_2Si_2$, or of Au/Si site disorder that might lead to frustration. The Pr moments likely remain dynamic well below the 3.2 K maximum in the susceptibility.

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