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Ordered magnetic moments in (A,A$'$)Co_2Ge_2 systems

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Abstract

The relative orientation of ordered magnetic moments of f-atoms (A,A$'$) occupying randomly the same site, has been studied by powder neutron diffraction in the magnetically-ordered state of (A,A$'$)Co_2Ge_2 solid solutions. These materials crystallize in the $ThCr_2Si_2$-type structure and order antiferromagnetically in the AF-I structure, characterized by ferromagnetic (A,A$'$) basal planes stacked alternately ($+-+-$) along the tetragonal axis, with A and A$'$ moments aligned along this axis. The 'spin-charge' concept, which accounts for antiparallel orientation of light and heavy lanthanide moments in $(Nd_{1-x}Tb_x)Co_2Ge_2$, is found to apply also to uranium and terbium moments in $(U_{1-x}Tb_x)Co_2Ge_2$. The parallel orientation of uranium and neodymium moments, observed in $(U_{1-x}Nd_x)Co_2Ge_2$, also follows the 'spin-charge' concept. Uranium and terbium moment compensation (in basal planes of zero total moment) is anticipated for a $(U_{1-x}Tb_x)Co_2Ge_2$ solid solution with $x\approx 0.15$. © 1998 Elsevier Science S.A.

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1. Magnetic-moment orientation in the lanthanides

In the lanthanide (Ln) series the 4f electronic shell is spatially small and energetically deep, and is well screened by the outer shells. The total angular momentum J of the atom is determined by the Russell-Saunders (RS) scheme, and the associated magnetic moment is localized. In the RS scheme $\boldsymbol{J}$ depends on the total orbital ($\boldsymbol{L}$) and spin ($\boldsymbol{S}$) angular momenta via the vector relation

$$\boldsymbol{L} + g_o\boldsymbol{S} = g\boldsymbol{J} \tag{1}$$

where g is the Landé factor, and g_o the electron gyromagnetic ratio.

Assuming $g_o = 2$ in Eq. (1) leads to the vector relation

$$\boldsymbol{L} + 2\boldsymbol{S} = (\boldsymbol{L} + \boldsymbol{S}) + \boldsymbol{S} = \boldsymbol{J} + \boldsymbol{S} = g\boldsymbol{J} \tag{2}$$

and subsequently to

$$\boldsymbol{S} = (g - 1)\boldsymbol{J} \tag{3}$$

$(g-1)$ is the 'spin charge' [1], defined as

$$g - 1 = [J(J+1) + S(S+1) - L(L+1)]/[2J(J+1)] \tag{4}$$

which is positive for the heavy lanthanides (where $J=L+S$) and negative for the light lanthanides (where $J=L-S$).

The ordered magnetic moment is given by [1]

$$\boldsymbol{m} = -\mu_B g\boldsymbol{J} \tag{5}$$

and is antiparallel to $\boldsymbol{J}$. Using Eq. (3) in this definition we obtain

$$\boldsymbol{m} = -\mu_B[g/(g-1)]\boldsymbol{S} \tag{6}$$

and conclude that $\boldsymbol{m}$ is parallel to $\boldsymbol{S}$ in light lanthanides $[(g-1)<0]$ and antiparallel to $\boldsymbol{S}$ in heavy lanthanides $[(g-1)>0]$.

The validity of this statement was checked on lanthanide-containing systems of parallel lanthanide spins. Appropriate systems for this purpose are either ferromagnetic materials or ferromagnetic planes stacked in antiferromagnetic materials. If the magnetic sites in these materials contain one type of Ln atoms, light or heavy, all the ordered magnetic moments are aligned parallel to each other in the ferromagnetic environments. Examples are neodymium moments in ferromagnetic NdCd [2], and terbium moments in ferromagnetic TbCd [2] and in the ferromagnetic basal planes of antiferromagnetic (AF-I structure) $TbCo_2Ge_2$ [3,4]. However, if the magnetic site is randomly occupied by two types of Ln atoms, two situations may happen. The first one concerns two different light Ln atoms or two different heavy Ln atoms, and is similar to the one-type-atom case. The second one concerns light and heavy Ln atoms, randomly distributed in the same site. According to Eq. (6) these moments are antiparallel, and the total moment of the system depends on the difference of the moments of the individual Ln

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atoms. At a certain ratio between the light and heavy Ln atoms (certain composition in the system) a compensation point occurs, where the total moment is zero. Such a compensation point is observed for the ferromagnetic pseudobinary (Nd,Tb)Cd system [2] by magnetization measurements, implying also the antiparallel character. This character and the compensation point are observed directly by neutron diffraction for the ferromagnetic planes stacked alternately in the AF-I pseudoternary (Nd,Tb)Co_2Ge_2 system [3].

2. Extension to the light actinides: uranium

Unlike the lanthanide series, in the actinide (An) series the 5f shell is spatially much more extended, and its energy is closer to the Fermi level or even coincides with it. Nevertheless, in the second half of the series from curium and on, the heavy actinides, the 5f electrons are quite localized and obey the RS scheme, with $J=L+S$. However, in the light actinides, notably in uranium, the RS scheme is not valid, since J is not a good quantum number, due to partial quenching (by the crystalline electric field) of the orbital momentum L. Hence, the above treatment is only a zero approximation and the actual situation should be tested experimentally, as we do here for uranium.

The large family of ternary AM_2X_2 compounds [4–6] and pseudoternary $(A,A')M_2X_2$ solid solutions (A and A' = f-elements; M = d-transition elements; X = Si or Ge) [3,7,8] is one of only a few systems that accommodate equally the various f-atoms. It crystallizes predominantly with the body-centered tetragonal $ThCr_2Si_2$-type structure, with close lattice parameters. This family contains several subfamilies with identical magnetic structures, of which the system of $(A,A')Co_2Ge_2$ solid solutions orders in the antiferromagnetic AF-I structure [7,8]. It turns out to be an appropriate system for testing the validity of the ‘spin charge’ concept for uranium.

3. Experimental details

Polycrystalline samples of $(U_{1-x}Tb_x)Co_2Ge_2$ and $(U_{1-x}Nd_x)Co_2Ge_2$ solid solutions with $x=0.25$, 0.50 and 0.75 were prepared by arc-melting stoichiometric amounts of the constituents in an argon atmosphere, followed by vacuum-annealing at 1023 K for 120 h. They were subsequently characterized by X-ray diffraction at room temperature (RT = 295 K).

Neutron-diffraction measurements on 20-g samples of the above solid solutions were done at the IRR-2 reactor (in cylindrical aluminum containers), using the diffractometers KANDI-II and KANDI-III (with $\lambda=240$–245 pm). A DISPLEX (brand name of a closed-cycle helium cooler made by Air Products Inc.) was used for the measurements, at RT and down to low temperature (LT = 12 K).

4. Results and analyses

The RT neutron diffractograms of the six $(U,Ln)Co_2Ge_2$ solid solutions depict nuclear $\{hk\ell\}$ reflections with $h+k+\ell=$ even, in positions consistent with the space group $I4/mmm$. The intensities are consistent with the body-centered tetragonal $ThCr_2Si_2$-type structure of the end compounds (UCo_2Ge_2, $TbCo_2Ge_2$, and $NdCo_2Ge_2$). The U and Ln atoms are randomly distributed in the basal planes. The RT lattice parameters of these materials show small overall variation (≈1% in a, 399–404 pm, and ≈3% in c, 987–1017 pm) across these systems.

The LT neutron diffractograms of the six $(U,Ln)Co_2Ge_2$ solid solutions, depict the above nuclear reflections, as well as a set of magnetic $\{hk\ell\}$ reflections with $h+k+\ell=$ odd. These reflections are consistent with an antiferromagnetic order of at least the (U,Ln) sublattice in the AF-I structure, characterized by a wavevector $\boldsymbol{k}=(0,0,1)$, i.e. by ferromagnetic (U,Ln) basal planes stacked alternately $(+-+-)$ along the tetragonal axis. The absence of $\{00\ell\}$ reflections with odd ℓ, notably {001}, indicates that the U and Ln ordered moments are aligned along this axis. The ordered magnetic moment on the cobalt sublattice is negligible.

The LT neutron diffractograms of $(U_{0.75}Tb_{0.25})Co_2Ge_2$, UCo_2Ge_2, and $(U_{0.75}Nd_{0.25})Co_2Ge_2$ are shown in Fig. 1. While the nuclear reflections from these materials are similar, the intensity of the magnetic reflections from them increase in the given order. The average (U,Ln) ordered magnetic moment is determined from the LT diffractograms, using the modified Rietveld profile analysis [9] and exponential magnetic form factors [4–8]. The moments deduced from the diffractograms of Fig. 1 are $1.3\pm0.1\ \mu_B$, $1.9\pm0.2\ \mu_B$ and $2.3\pm0.1\ \mu_B$, respectively. Analysis of these moments, and of the ordered moments deduced from the LT diffractograms of the other four solid solutions is based on the assumption that the lanthanide ordered moments are equal or near their free-Ln^{3+}-ion values (gJ), 3.27 μ_B for neodymium ($4f^3$ configuration) and 9.0 μ_B for terbium ($4f^8$ configuration). The uranium ordered moment is lower than that of any of the possible electronic configurations, $5f^1$ to $5f^4$, 2.15–3.27 μ_B, due to the mentioned partial quenching of the orbital angular momentum. In UCo_2Ge_2, it is $m_U=1.9\pm0.2\ \mu_B$ [6–8]. Since all magnetic moments are aligned along the tetragonal axis, they should be presented as combinations of the individual moments:

$$m(U_{0.75}Tb_{0.25}) = (0.25\times9.00)\mu_B \pm 0.75 m_{U(Tb)} = 1.3\mu_B$$

$$m(U_{0.75}Nd_{0.25}) = (0.25\times3.27)\mu_B \pm 0.75 m_{U(Nd)} = 2.3\mu_B$$

$m_{U(Tb)}$ and $m_{U(Nd)}$ are the uranium ordered magnetic

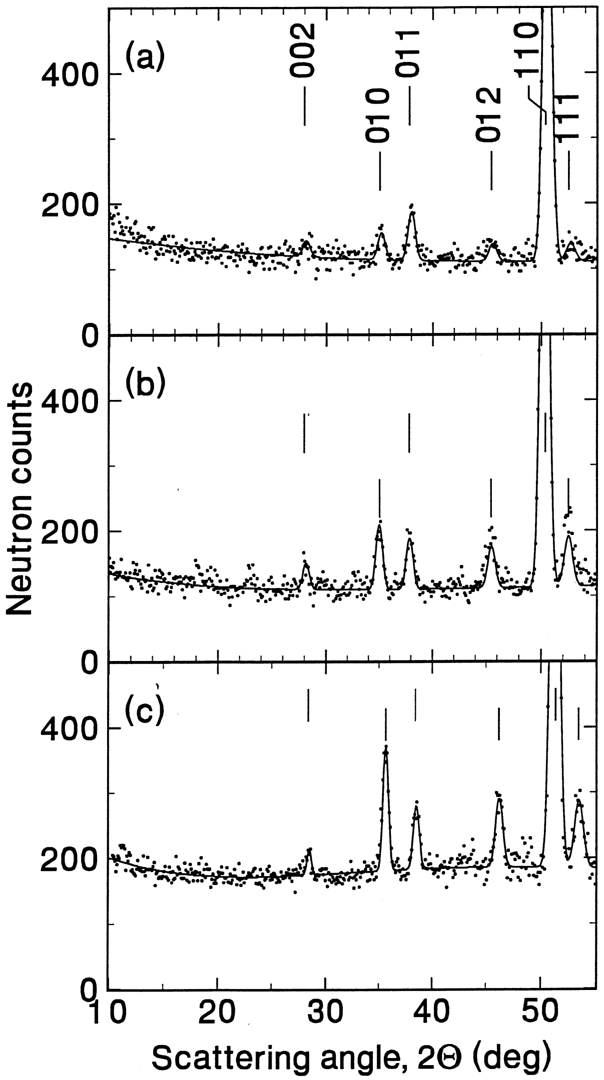

Fig. 1. LT neutron diffractograms of (U,Ln)Co_2Ge_2 materials, depicting nuclear reflections ($h+k+\ell=$even, space group *I*4/*mmm*), with intensities consistent with the $ThCr_2Si_2$-type crystal structure, as well as magnetic reflections ($h+k+\ell=$odd, AF-I structure): (a) $(U_{0.75}Tb_{0.25})Co_2Ge_2$; (b) UCo_2Ge_2; (c) $(U_{0.75}Nd_{0.25})Co_2Ge_2$. The $\{hk\ell\}$ indices, nuclear (upper) and magnetic (lower), in (a) are common to the three materials.

moments in the terbium and neodymium systems, respectively.

In order to satisfy these relations the magnetic moments of uranium (light An) should be antiparallel to the magnetic moments of terbium (heavy Ln) and parallel to the magnetic moments of neodymium (light Ln). Thus the 'spin-charge' concept applies also to uranium, in spite of the invalidity of the RS scheme. We can therefore rewrite the last relations:

$$m(U_{0.75}Tb_{0.25}) = 2.25\mu_B - 0.75m_{U(Tb)} = 1.3\mu_B$$

$$m(U_{0.75}Nd_{0.25}) = 0.82\mu_B + 0.75m_{U(Nd)} = 2.3\mu_B$$

A single value of the uranium moment cannot satisfy both relations, and $m_{U(Tb)}$ is smaller than $m_{U(Nd)}$. Furthermore, the moments deduced for the other four compositions exhibit the same features of moment orientation and size. $m_{U(Tb)}$, the uranium ordered moment in the $(U_{1-x}Tb_x)Co_2Ge_2$ system, is $\approx 1.1\ \mu_B$, lower than the moment in UCo_2Ge_2 [7]. $m_{U(Nd)}$, the uranium ordered moment in the $(U_{1-x}Nd_x)Co_2Ge_2$ system is $\approx 1.9\ \mu_B$, similar to the moment in UCo_2Ge_2 [8].

5. Conclusions and full magnetic compensation

The AF-I structure observed in the $(A,A')Co_2Ge_2$ systems, consisting of ferromagnetic basal planes stacked alternately, entails in-plane ferromagnetic exchange interactions between the f-atoms (A or A′), as known for the end compounds ACo_2Ge_2. This kind of plane requires that the U and Tb moments have antiparallel orientation in the system $(U_{1-x}Tb_x)Co_2Ge_2$, while the U and Nd moments have parallel orientation in the system $(U_{1-x}Nd_x)Co_2Ge_2$. In the system $(U_{1-x}Tb_x)Co_2Ge_2$, the magnetic planes are better described as ferrimagnetic, as do the magnetic planes in the lanthanide systems (Nd,Tb)Cd [2] and $(Nd,Tb)Co_2Ge_2$ [3].

These observations are in accordance with the concept of 'spin-charge' [1], $(g-1)$, which is negative for light f-atoms and positive for heavy ones. We conclude that in spite of the general invalidity of the Russell-Saunders scheme for uranium (*J* not being a good quantum number), the uranium moment orients like the moment of a light lanthanide (where *J* is a good quantum number).

The antiparallel case can lead to a special situation in which the total ordered magnetic moment of the light f-element (e.g. uranium) is completely balanced by the total ordered magnetic moment of the heavy f-element (e.g. terbium). The moment arrangement in a representative basal plane of the $(U_{1-x}Tb_x)Co_2Ge_2$ solid solution, with a composition resulting in magnetic compensation ($x \approx 0.15$, where the total magnetic moment of the plane is zero) is illustrated in Fig. 2. Also shown, for comparison, are arrangements of the magnetic moments in the basal planes of the neighbouring compositions with $x=0.05$ and 0.25.

Unlike several magnetic systems with magnetically frustrated sites or planes, that do not contain magnetic moments which may eventually order magnetically, the magnetically-balanced situation (of basal planes with zero total moment) is an ordered magnetic state with compensated moments. This is the situation in a solid solution $(U_{1-x}Tb_x)Co_2Ge_2$ with $x \approx 0.15$, and a solid solution $(Nd_{1-x}Tb_x)Co_2Ge_2$ with $x \approx 0.27$ [3]. The planes with zero total moment are assumed to be stacked antiferromagnetically (in the AF-I structure) with respect to each type of compensated moments, as obtained by interpolation of the moment stacking in neighbouring compositions.

The LT diffractogram of the $(Nd_{0.75}Tb_{0.25})Co_2Ge_2$ solid

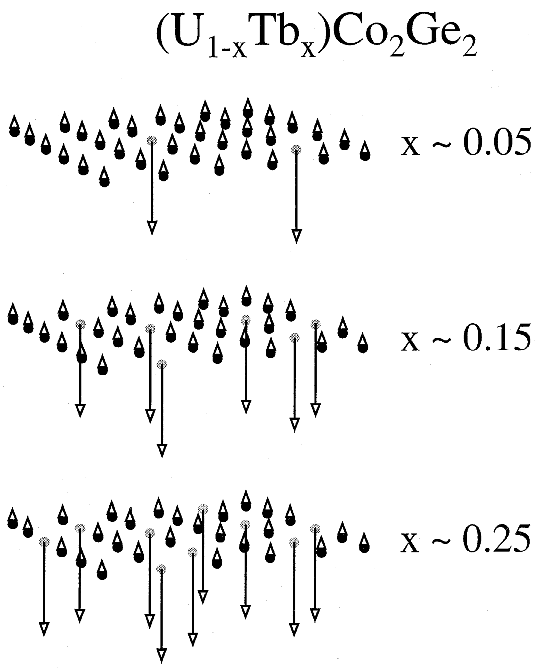

Fig. 2. Schematic arrangement of random antiparallel moments of uranium (short arrows, upwards) and terbium (long arrows, downwards) in a basal plane of the solid solution $(U_{1-x}Tb_x)Co_2Ge_2$ with $x \approx 0.15$, where the total magnetic moment is zero (full magnetic compensation). The arrangement in the basal planes of the neighbouring compositions $x = 0.05$ and 0.25, with average moments of $\approx 0.7\ \mu_B$ (upwards) and $\approx 1.3\ \mu_B$ (downwards), respectively, is shown for comparison.

solution, close to the composition ($x \approx 0.27$) of full magnetic compensation, does not depict any magnetic reflections [3]. The ordering temperature T_N of this material, is detected by ac magnetic susceptibility measurements. The magnetic ordering in solid solutions with full magnetic compensation, $(Nd_{1-x}Tb_x)Co_2Ge_2$ with $x \approx 0.27$ and $(U_{1-x}Tb_x)Co_2Ge_2$ with $x \approx 0.15$, can therefore be detected by ac magnetic susceptibility. Above T_N a paramagnetic state occurs, with two types of paramagnetic moments of f-elements, as well as paramagnetic moments of cobalt [10], all contributing to the total magnetic susceptibility (Curie-Weiss type) of the material.

A polycrystalline material with 'full magnetic compensation in the ordered state', is not expected to contribute magnetic reflections to the LT neutron diffractogram. This is indeed the case of the solid solution $(Nd_{0.75}Tb_{0.25})Co_2Ge_2$ [3]. However, if the magnetic form factors of the compensating atoms are different, magnetic reflections may be detected at high scattering angles, using better resolution. Neutron investigation of single crystals of such materials may detect such reflections, and perhaps elucidate the intrinsic sequence of the antiparallel moments.

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