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Letter

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^{155}Gd Mössbauer effect and magnetic properties of $GdMn_6Sn_6$

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The crystal structure of the compound $HfFe_6Ge_6$ is relatively simple. It is based on the $CaCu_5$ type and its unit cell comprises only a single hafnium site and a single 3d site [1]. Recently, it was discovered by Malaman *et al.* [2] that ternary rare-earth compounds of the type RMn_6Sn_6 adopt the same crystal structure. Furthermore, the compounds RMn_6Sn_6 give rise to magnetic ordering temperatures well above room temperature. In view of the relatively weak magnetic coupling between rare-earth moments, this suggests that the manganese atoms carry a magnetic moment, and are primarily responsible for the relatively high magnetic ordering temperature.

In the present investigation, we have focused our attention on the magnetocrystalline anisotropy of these materials. As in several previous investigations, we have used ^{155}Gd Mössbauer spectroscopy to obtain an indication of the strength of the crystal-field-induced rare-earth-sublattice anisotropy [3].

The $GdMn_6Sn_6$ sample was prepared by arc-melting starting materials of at least 99.9% purity. After arc-melting, the sample was wrapped into tantalum foil and sealed into an evacuated quartz tube. Vacuum annealing was performed at 700 °C for more than 4 weeks. After this treatment, the sample was analyzed by X-ray diffraction and found to be approximately single-phase. In order to determine the easy magnetization direction in $GdMn_6Sn_6$, X-ray diagrams were also taken from magnetically aligned powder. Conclusive evidence was obtained that the easy magnetization direction in $GdMn_6Sn_6$ is perpendicular to the *c*-axis.

Magnetic measurements were made on a SQUID magnetometer. The results made in a field of 2 T are shown in Fig. 1. They agree closely with the data published by Malaman *et al.* [2].

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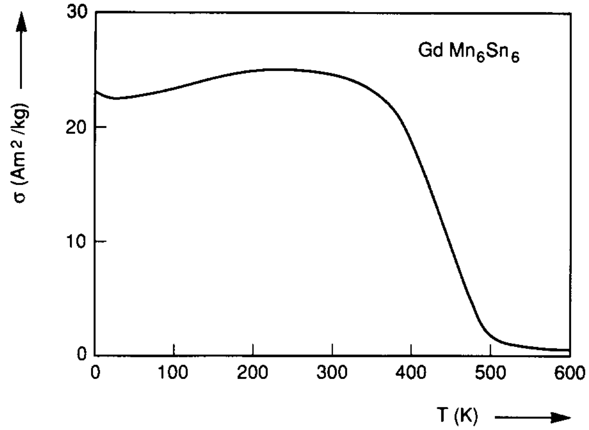

Fig. 1. Temperature dependence of the magnetization in $GdMn_6Sn_6$ measured in a field of 2 T.

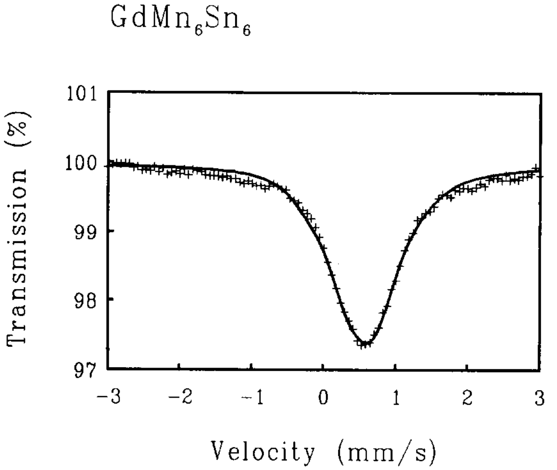

Fig. 2. ^{155}Gd Mössbauer spectrum of $GdMn_6Sn_6$. The solid curve through the data points represents a fit.

The Mössbauer spectrum of $GdMn_6Sn_6$ was taken using the 86.5 keV resonance of ^{155}Gd. The source was neutron-irradiated $SmPd_3$ using samarium enriched to 98% in ^{154}Sm. Details of the spectrometer are given elsewhere [3]. The spectrum obtained is shown in Fig. 2.

The spectrum has been analyzed by means of a least-squares fitting procedure involving the diagonalization of the full nuclear Hamiltonian and using a transmission integral. The independently refined variables consisted of the isomer shift (IS), the effective hyperfine field (H_{eff}), and the quadrupole splitting (QS) (or the electric field gradient tensor element V_{zz}, obtained via the relation $QS = \frac{1}{4}eQV_{zz}$ $(3\cos^2\theta - 1)$, using the value $Q = 1.30 \times 10^{-28}$ m^2 given by Tanaka *et al.* [4]. The fitting procedure has furthermore been performed with the constraint that the angle θ between H_{eff} and the c-axis be 90° as was derived from X-ray diffraction on magnetically aligned $GdMn_6Sn_6$ powder. The absorber and source linewidths were constrained to 0.25 and 0.36 mm s^{-1} for the transmission integral. The hyperfine parameters corresponding to the best fit are as follows:

$V_{zz} = -(2.0 \pm 0.3) \times 10^{21}$ V m^{-2}

$|H_{eff}| = (11.6 \pm 0.9)$ T

IS $= (0.55 \pm 0.01)$ mm s^{-1}

We will first compare the value of the electric field gradient with that obtained previously in $GdCo_3B_2$ [5]. The latter compound has the $CeCo_3B_2$ structure which can be regarded as one of the building blocks of the $HfFe_6Ge_6$ structure. In fact, following Parthé and Chabot [1], it can be shown that the $GdMn_6Sn_6$ structure can be considered as consisting of slabs of $CeCo_3B_2$-type $GdMn_3Sn_2$, intergrown with slabs of Zr_4Al_3-type Mn_3Sn_4. The electric field gradient determined by ^{155}Gd Mössbauer spectroscopy at the site of the gadolinium nucleus in $GdCo_3B_2$, corresponds to one of the highest V_{zz} values found in gadolinium compounds and is equal to 31.2×10^{21} V m^{-2} when using the Q value of Tanaka mentioned above. Not only does this V_{zz} have the opposite sign, its absolute value is more than 15 times larger than that found for $GdMn_6Sn_6$ in the course of the present investigation. This enormous difference will be discussed below in terms of the recently obtained insight from electronic band-structure calculations, that the field gradient in intermetallic compounds is mainly caused by the asphericities in charge distribution of the 6p and 5d valence electrons of the rare-earth atom [6, 7].

In Fig. 3, a schematic representation of the coordination shell of the gadolinium atoms in $GdMn_6Sn_6$ has been given. The gadolinium atoms in the center are surrounded in the equatorial plane by a hexagon of six s,p

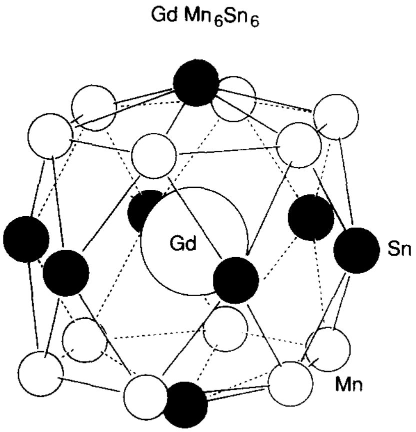

Fig. 3. Schematic representation of the gadolinium atom coordination in $GdMn_6Sn_6$. The sp atoms (tin) are indicated by filled circles, the 3d atoms (manganese) by open circles. The large central open circle represents gadolinium.

atoms while in the planes below and above the equatorial plane one may discern hexagons consisting of transition-metal atoms. This type of coordination is common to the gadolinium atoms in $GdMn_6Sn_6$ and $GdCo_3B_2$. Apparently, in the latter compound this situation is able to produce large asphericities of the 6p and 5d valence electrons responsible for a large field gradient at the nuclear site of the gadolinium atoms. The main difference in coordination between these two structures occurs along the c direction. In $GdCo_3B_2$, the neighbour atoms along this direction are two gadolinium atoms. However, owing to the intergrown Mn_3Sn_4 slabs, the neighbouring atoms in $GdMn_6Sn_6$ in the same direction are two s,p atoms, as may be seen from Fig. 3. Moreover, these two atoms are the nearest neighbours to the gadolinium atoms in $GdMn_6Sn_6$ so that they can be expected to have a large influence on the field gradient. It is clear from Fig. 3 that the presence of these two s,p atoms will have a detrimental influence on the asphericity of the gadolinium valence-electron charge distribution since they make the coordination of the s,p atoms more uniform in the main crystallographic directions. The large difference in V_{zz} between $GdCo_3B_2$ and $GdMn_6Sn_6$ can therefore be understood qualitatively from the significant differences in gadolinium-atom coordination.

The main purpose of the present ^{155}Gd Mössbauer study of $GdMn_6Sn_6$ was to obtain experimental information on the second-order crystal-field parameter $A_2{}^0$ associated with the R atoms in RMn_6Sn_6 compounds. In previous investigations it was often assumed that the electric field gradient V_{zz} at the nucleus, as well as the effective crystal field experienced by the 4f electrons (represented by the $A_2{}^0$ parameter), are basically the result of the same electrostatic potential surrounding the R atoms. This led to the following relation between these two quantities $A_2{}^0$ and V_{zz}:

$$A_2{}^0 = -\frac{(1-\sigma_2)}{4(1-\gamma_\infty)} V_{zz} \qquad (1)$$

where the screening factor σ_2 has a value close to 0.5 and the Sternheimer antishielding factor a value of -92 [5].

Recent band-structure calculations have shown that, contrary to what is expected from the point-charge model, no general proportionality relation between V_{zz} and $A_2{}^0$ exists [6, 7]. The reason is that V_{zz} is determined mainly by the asphericity of the 6p shell, whose density near the nucleus is much larger than that of the 5d shell, whereas $A_2{}^0$ is determined by the asphericity of both shells. Nevertheless, it was found that there is a fairly good correlation between the experimental values of V_{zz} and $A_2{}^0$ in several series of related intermetallic compounds. This latter correlation may justify then to some extent that the values of V_{zz} can be used to make predictions regarding the magnetocrystalline anisotropy.

When using eqn. (1) one finds that $A_2{}^0$ in RMn_6Sn_6 equals about $+92$ $K/a_0{}^2$. This is a fairly low value compared with the $A_2{}^0$ values found in the same manner for highly anisotropic materials such as $R_2Fe_{14}B$, RCo_5 and $R_2Fe_{17}N_x$. This low $A_2{}^0$ value suggests that the anisotropic behaviour of the

RMn_6Sn_6 compounds will be determined only to a limited extent by the second-order parameter, leaving an important role for the parameters of higher order than A_2^0. A similar situation occurs in the many ternary rare-earth compounds with the $ThMn_{12}$ structure [9], where it proved impossible to predict the easy magnetization direction exclusively on the basis of the sign of the second-order Stevens' factor.

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