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^{155}Gd Mössbauer effect in several BaNiSn_3 -type compounds

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Received 5 April 1994

Abstract

We have investigated the magnetic properties and the ^{155}Gd Mössbauer spectra of several BaNiSn_3 -type rare earth compounds comprising GdCoSi_3 , GdNiGa_3 , GdCuGa_3 and GdCuAl_3 . All four compounds were found to order antiferromagnetically at low temperatures. From the quadrupole splitting obtained from fitting the ^{155}Gd Mössbauer spectra, we derived values for the electric field gradient V_{zz} at the nuclear Gd site. The values of V_{zz} were found to be positive and to increase in the sequence mentioned above. This behaviour is discussed in terms of on-site valence electron asphericity contributions to V_{zz} .

Keywords: Mössbauer spectroscopy; Antiferromagnetism; Quadrupole splitting

1. Introduction

In several previous investigations we have studied numerous compounds of the type GdT_2X_2 ($T \equiv 3d, 4d, 5d$; $X \equiv \text{Si, Ge, Sn, Sb}$) by means of ^{155}Gd Mössbauer spectroscopy [1,2,3]. From the quadrupole splitting of these spectra we derived values of the electric field gradient V_{zz} at the nuclear site. The systematic behaviour of V_{zz} within the various transition metal series (T) was successfully described on the basis of band structure calculations [1]. These calculations made it clear that V_{zz} is dominated by the asphericities of the on-site valence electrons of the Gd atoms. These asphericities are due to the hybridization between the Gd valence states and the d-states of the T atoms, which causes the formation of bonding orbitals with large charge densities between the Gd and T atoms. In the present study we have extended our investigation to Gd compounds crystallizing in the tetragonal BaNiSn_3 -type structure. This structure is closely related to the ThCr_2Si_2 -type structure adopted by the GdT_2Si_2 -type compounds studied earlier.

2. Experimental details

The ternary Gd compounds studied in this investigation were prepared by arc melting starting materials of at least 99.9% purity. Subsequently the ingots were vacuum annealed at 800 °C for several weeks. After vacuum annealing, the samples were examined by X-

ray diffraction to check whether single-phase compounds had formed. The BaNiSn_3 -type structure was observed for all compounds studied. The formula compositions and structure types of all these materials agree with those reported before [4,5].

The magnetic properties of the compounds were studied in the temperature range 4.2–250 K with a superconducting quantum interference device (SQUID) magnetometer using a field strength of 0.1 T.

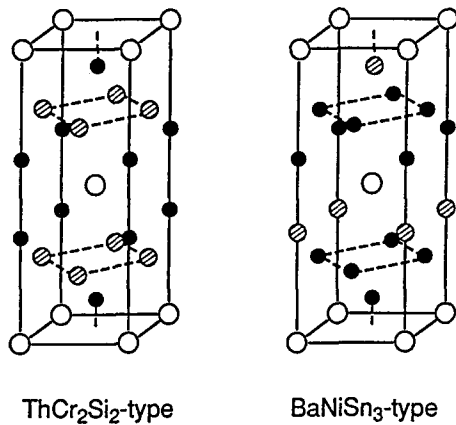
Mössbauer spectra of the various compounds were taken at 4.2 K by using the 86.5 keV resonance of ^{155}Gd . Neutron-irradiated SmPd_3 , prepared from samarium enriched to 98% in ^{154}Sm , was used as source material. Details of the spectrometer have been described elsewhere [6].

The spectra of the four compounds studied have been analysed by means of a least-squares fitting procedure that included diagonalization of the full nuclear hamiltonian and use of a transmission integral. The independently refined hyperfine parameters consisted of the isomer shift (IS), the effective hyperfine field (H_{eff}) and the quadrupole splitting (QS). From the latter quantity the electric field gradient tensor element V_{zz} was obtained via the relation $\text{QS} = \frac{1}{4}eQV_{zz}(3 \cos^2\theta - 1)$ using the value $Q = 1.30 \times 10^{-28} \text{ m}^2$ given by Tanaka et al. [7]. The angle θ between H_{eff} and the c axis was kept as an adjustable parameter. The linewidth of absorber and source were constrained to 0.25 and 0.36 mm s^{-1} respectively for the transmission integral.

Table 1

Lattice constants and hyperfine parameters derived from fitting the ^{155}Gd Mössbauer spectra at 4.2 K for various BaNiSn_3 -type compounds

Compound	a (nm)	c (nm)	V_{zz} (10^{21} V m^{-2})	$\mu_0 H_{\text{eff}}$ (T)	IS (mm s^{-1})	θ ($^\circ$)	f (%)
GdCoSi_3	0.4068	0.951	3.9	25.6	0.57	90	100
GdNiGa_3	0.4165	0.994	6.2	28.5	0.59	52	100
GdCuGa_3	0.4135	1.043	7.6	28.7	0.62	52	100
GdCuAl_3	0.4159	1.064	8.5	18.5	0.57	90	51
			6.0	28.7	0.57	90	37
			1.8	14.5	0.57	90	12

Fig. 1. Schematic representation of the ThCr_2Si_2 and BaNiSn_3 structures.

3. Results and discussion

The lattice constants of the compounds investigated are listed in Table 1. These values are in satisfactory agreement with data reported earlier [4,5]. The unit cell of the BaNiSn_3 structure type is shown in Fig. 1, where it can be compared with the unit cell of the ThCr_2Si_2 structure. Examples of magnetic measurements are displayed in Fig. 2. The temperature dependence of the susceptibility of the compounds investigated gives rise to a cusp-type maximum indicative of antiferromagnetic ordering. The corresponding values of the Néel temperature T_N have been listed in Table 2. As shown in Fig. 2, the reciprocal susceptibility shows Curie–Weiss behaviour at temperatures well above T_N . The corresponding values of the effective moment μ_{eff} and the asymptotic Curie temperature Θ_p have been included in Table 2. Curie–Weiss behaviour in GdCuAl_3 is followed only above about 70 K. Very likely the discontinuity in the $\chi(T)$ curve at about 30 K is due to one or more impurity phases.

^{155}Gd Mössbauer spectra of the various compounds are shown in Fig. 3. At 4.2 K all spectra show Zeeman splitting as well as quadrupole splitting. The full curves through the data points represent fits to the spectra. The corresponding hyperfine parameters are listed in Table 2.

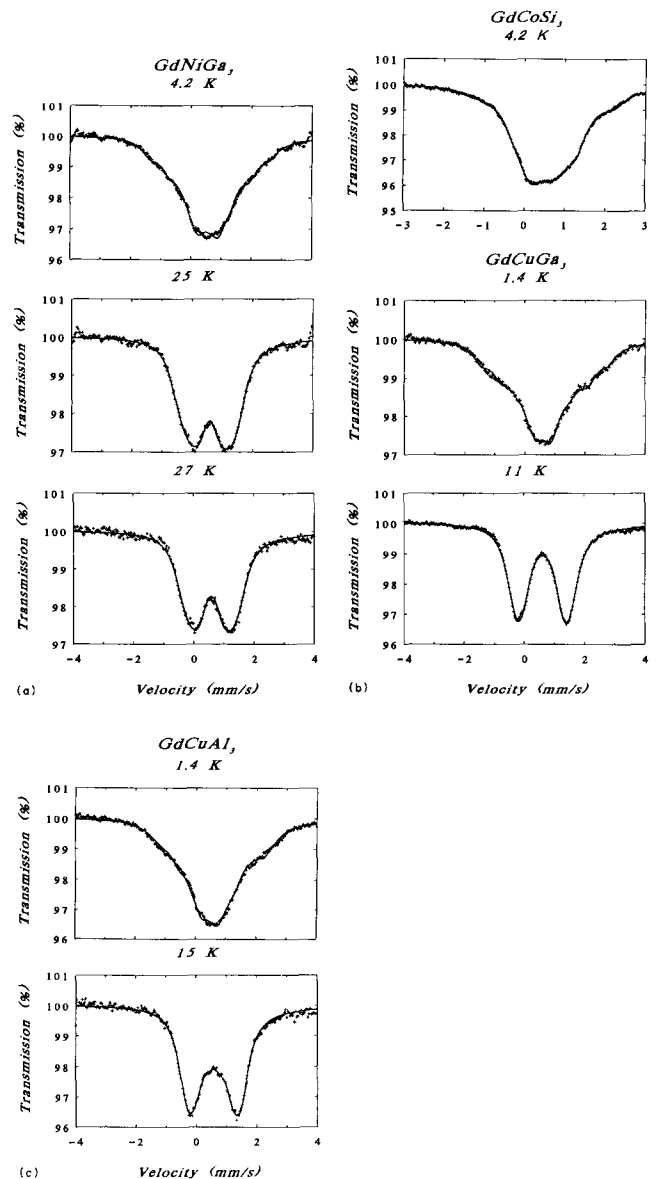


Fig. 2. (a) ^{155}Gd Mössbauer spectra of GdNiGa_3 at three different temperatures. (b) ^{155}Gd Mössbauer spectra of GdCoSi_3 and GdCuGa_3 . (c) ^{155}Gd Mössbauer spectra of GdCuAl_3 .

The data of the compounds GdCoSi_3 , GdNiGa_3 and GdCuGa_3 were fitted with only one spectrum, whereas three subspectra were required for fitting the data of

Table 2
Magnetic characteristics of several ternary Gd compounds with BaNiSn₃-type structure: Θ_p , asymptotic Curie temperature; T_N , Néel temperature; μ_{eff} , effective moment per formula unit

Compound	Θ_p (K)	T_N (K)	μ_{eff} (μ_B)
GdCoSi ₃	−19.7	9.6	7.76
GdNiGa ₃	−20.6	14.5	7.62
GdCuGa ₃	−13.3	10.1	7.97
GdCuAl ₃	≈ 2	10.0	7.95

Since these impurity phases hardly showed up in the X-ray data, it is conceivable that the crystal structure of GdCuAl₃ does not have the strict site occupation of Al and Cu as shown in Fig. 1. Some disordering of the Al and Cu atoms may give rise to concentration fluctuations that can cause the deviating behaviour mentioned above.

In previous investigations it was shown that the electric field gradient at the nuclear site of the Gd atoms in Gd metal and in several types of intermetallic compounds is mainly determined by the aspherical charge distribution of the on-site 5d and 6p valence electrons [1,8,9]. It is reasonable therefore to assume that the field gradient in the compounds studied in the course of the present investigation has a similar origin. In order to facilitate the comparison of the V_{zz} values found in the different compounds, we have listed these compounds in Table 1 in order of increasing V_{zz} , neglecting the minority subspectra due to the impurity phases in GdCuAl₃.

In view of the structural similarity of the BaNiSn₃ type and the ThCr₂Si₂ type (see Fig. 1), it seems appropriate to compare the trend of V_{zz} observed in the course of the present investigation for the former type of compounds with those observed in previous investigations for RT₂X₂ where T is a transition metal and X ≡ Si or Ge [1,2]. From band structure calculations it was derived that the shift of V_{zz} towards more positive values in the sequence T ≡ Co, Ni, Cu originates from a change in the hybridization of the Gd valence electron states (5d, 6p) with the 3d electron states [1]. This hybridization leads to the formation of bonding orbitals with large charge densities between the Gd and T atoms and this on-site valence electron asphericity is the main contributor to V_{zz} . The Gd orbitals taking part in the hybridization are primarily those with their charge cloud directed towards the 3d atoms. The development of strong 6p_z and 5d_{xz} (5d_{yz}) orbitals causes negative contributions to V_{zz} , the development of strong 6p_x (6p_y) and 5d_{xy} orbitals causing positive contributions. In the RT₂X₂ compounds with the ThCr₂Si₂ structure the shift towards more positive values of V_{zz} with increasing atomic number of the T component was shown to be primarily due to a decrease in the 6p_z contribution, combined with an increase in the 5d_{xy} contribution. If one assumes that the shift towards more positive V_{zz} values in the GdTX₃ compounds in the sequence T ≡ Co, Ni, Cu has a similar origin, one has to take account of the fact that the 3d atoms in the BaNiSn₃ structure are located more towards the equatorial plane and less in the *c* (or *z*) direction than in the ThCr₂Si₂ structure. Consequently, the negative contributions to V_{zz} are expected to be lower and the positive contributions larger in the BaNiSn₃ type than in the ThCr₂Si₂ type. This may explain why the V_{zz} values in the former compounds are all positive and

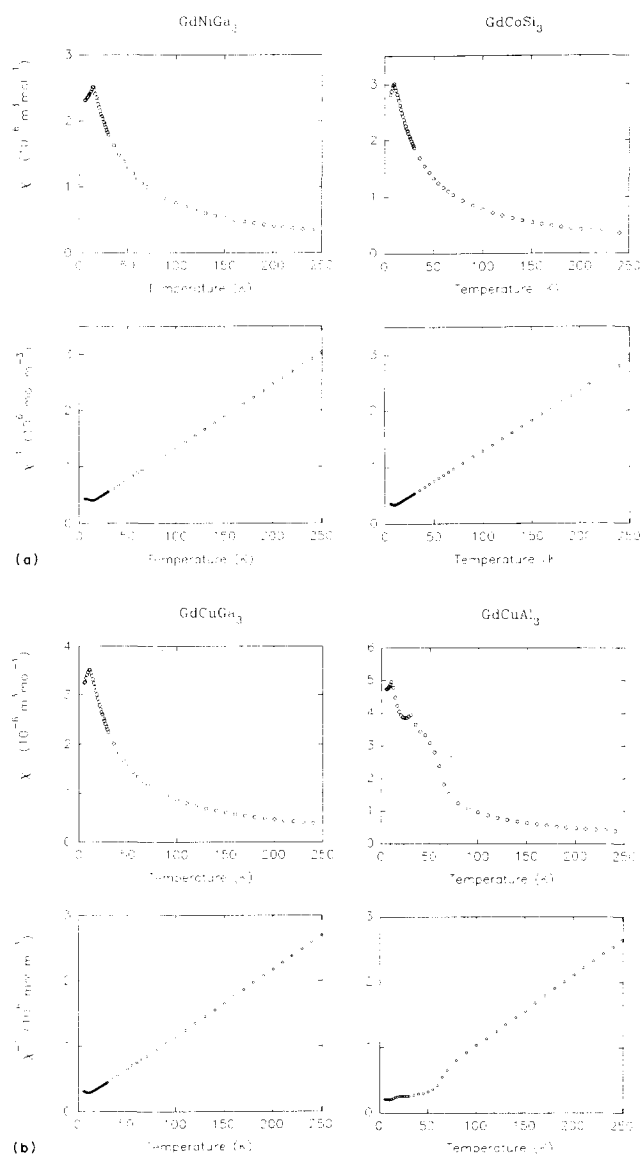


Fig. 3. (a) Temperature dependence of the susceptibility (top) and reciprocal susceptibility (bottom) of the compounds GdNiGa₃ and GdCoSi₃. (b) Temperature dependence of the susceptibility (top) and reciprocal susceptibility (bottom) of the compounds GdCuGa₃ and GdCuAl₃.

GdCuAl₃. Apparently the occurrence of more than one subspectrum is due to the presence of the impurity phases already noticed in the magnetic measurements.

do not involve a sign reversal from negative to positive as observed in the ThCr_2Si_2 -type compounds.

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