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Influence of transition metals on magnetic properties of GdT_2X_2

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Abstract

The compounds GdT_2X_2 with X = Sn or Sb are anti-ferromagnets, but their magnetic structure is not simple and magnetic interaction between gadolinium magnetic moments are frustrated. The resistivity dependence on temperature is remarkably influenced by non s-type conduction electrons. From the comparison of these results with the data for compounds with X = Si or Ge and from the analysis of ESR data, it can be concluded that magnetic and transport properties depend on the density of electron states at the Fermi level $\eta(E_F)$. This value depends mainly on T metal: $\eta(E_F)$ increases from the Cu (Ag)-containing compounds to the Ni and Co (Pd, Rh, Ru) compounds. Changes are caused by an increase in the density of d-states at the Fermi level. For two compounds the estimation of the $\eta(E_F)$ values was obtained from ESR study of bottleneck effect: $\eta(E_F) = 0.15$ states/(eV spin atom) for $GdCu_2Si_2$ and $\eta(E_F) = 0.3$ states/(eV spin atom) for $GdNi_2Si_2$. © 1997 Elsevier Science S.A.

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1. Introduction

The compounds GdT_2X_2 (T = transition metal and X = (s,p)-type element) crystallize with the body-centered tetragonal structure of the $ThCr_2Si_2$ type for X = Si or Ge [1] or with the primitive tetragonal $CaBe_2Ge_2$ type structure for X = Sn or Sb [2]. The magnetic moment of the transition metal is zero (except for Mn). The gadolinium sublattice orders antiferromagnetically at low temperatures. All these compounds are metallic conductors. The magnetic properties are mainly determined by the conduction-electron mediated exchange interaction between the gadolinium moments (RKKY type), because the effects of the crystalline electric field (CEF) acting on the 4f electrons can be neglected for the S-state ion Gd^{3+}. Thus, changes of the conduction electron character and filling of the conduction electron (CE) bands influence the Gd–Gd exchange interactions.

Most of the previous experimental studies of GdT_2X_2 compounds were devoted to silicides. From investigations of crystallographic structure, magnetic susceptibility, resistivity and Mössbauer effect for different 3d, 4d and 5d metals [1,3–7], it follows that physical properties depend on the number of d electrons (n_d) of the transition element. The dependence of the Néel temperature T_N on n_d shows similar trends for the three transition-metal rows with a maximum for the compounds with T = Co, Rh or Ir. For compounds with the largest T_N, the lattice parameter a is the smallest. The results for ger-

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manides are more scarce, but their behaviour is similar to compounds with X = Si [1,8–10]. Recent investigations of compounds with T = Cu, Ni and X = Sn, Sb [2,11] allow us to see how the properties change with the X element.

Some of the data were discussed in terms of the simple, isotropic RKKY model, assuming s-type conduction electrons and a spherical Fermi surface. It was estimated that for GdT_2Si_2 with T = 3d, the effective CE-4f exchange interaction constant J_{sf} is positive [1]. However, investigations of Mössbauer effect, X-ray absorption spectroscopy or electron spin resonance (ESR) [3,7,12–16] indicate an important weight of d electron states near the Fermi level. Therefore observed changes of properties, when T or X changes, should be described by changes of more realistic electronic structure. There are no theoretical calculations of the density of electron states for these compounds. Nevertheless, some information on the electronic structure and on the interaction between the magnetic Gd^{3+} spins and the conduction electrons can be obtained by investigation with ESR.

2. Magnetic properties and resistivity of the compounds $GdCu_2X_2$ and $GdNi_2X_2$

As was mentioned above, for GdT_2X_2 compounds, changes in magnetic properties (susceptibility, Néel temperature, magnetic structure, ESR), as well as in resistivity, have been observed when the T or X component was changed [1–16]. Let us follow the evolution of two transition metals: Cu ($n_d = 10$) and Ni ($n_d = 8$) for X = Si, Ge, Sn, Sb. Experimental data are collected in Table 1.

For all $GdCu_2X_2$ compounds the T_N values are almost the same: 11 ÷ 12 K. The Ni-containing compounds have higher T_N than the Cu compounds for the silicides and germanides, but smaller for X = Sn and Sb. These low Néel temperatures for the latter compounds are accompanied by a strongly negative Curie paramagnetic temperature and the $T_N/|\theta_P|$ ratio is the lowest (approx. 0.2) for the $GdNi_2Sb_2$ compound. Compounds with X = Si, Ge, Sn are isoelectronic, but the bonding changes from covalent to more metallic. This is followed by an increase of the global interactions and of the magnitude of θ_P. For more metallic bonding, the range of interactions may increase. Longer range of interactions for RKKY oscillatory behaviour can give rise to some cancellation of magnetic interactions, leading to frustration and to a lowering of the Néel temperature. It may explain the small value of $T_N/|\theta_P|$ for Sn-containing compounds, whereas $T_N \approx -\theta_P$ for Si. Above T_N the short-range-order phenomena are seen in the reciprocal susceptibility $1/\chi(T)$ and resistivity $\rho(T)$ dependencies due to the quasi two-dimensional interactions [2,5,11]. Frustration of magnetic interactions is expected to be the largest for $GdNi_2Sb_2$.

The huge cross-section of natural gadolinium at thermal neutron wavelengths creates severe problems for magnetic structure studies by neutron diffraction in Gd based compounds. This is a reason why magnetic structures were solved for a few GdT_2X_2 compounds only. $GdCu_2Si_2$ has a simple anti-ferromagnetic structure [5,6] with the propagation vector Q = (1/2, 0, 1/2) and magnetic moment direction along [0 1 0]. $GdNi_2Si_2$ has an amplitude modulate (AM) structure [5,6] with Q = (0.27, 0, 0.903) and a moment order along [0 1 0]. $GdNi_2Sn_2$ (Fig. 1) also has a modulated structure with magnetic moments along [1 0 0] and the propagation vector Q = (0.3, 1/2, 1/2). From neutron diffraction and specific heat (C_{mag}) measurements it was found that $GdNi_2Sb_2$ and $GdCu_2Sb_2$ have a modulated structure also, but because of the poor resolution of the diffractometer at short wavelength ($\lambda = 0.56$ Å), it is very difficult to find propagation vectors and direction of magnetic moments [17]. For the latter three compounds the additional anomalies in $\chi(T)$, $\rho(T)$ and $C_{mag}(T)$ dependencies observed below T_N [2,11,17] are attributed to the change of magnetic structure from amplitude modulated towards an equal moment structure.

Below T_N the metamagnetic transitions are observed also in field dependencies of magnetization

Table 1
Magnetic properties of $GdNi_2X_2$ and $GdCu_2X_2$

	T_N (K)	Θ_p (K)	μ_{eff} (μ_B)	ΔC_{mag} (J K^{-1} mol^{-1})	Magnetic structure
$GdNi_2Si_2$	14.5	−7	8.05 [5]	10.9 [6]	M [5,6]
$GdCu_2Si_2$	12.5	−16	8.01 [5]	18 [6]	Simple AF [5,6]
$GdNi_2Ge_2$	22	−19	8.2 [8]	—	—
$GdCu_2Ge_2$	12	−30	7.8 [9]	—	—
$GdNi_2Sn_2$	7	−15	8.02 [11]	14 [17]	M [17]
$GdCu_2Sn_2$	11	−57	8.2 [11]	—	—
$GdNi_2Sb_2$	5.8	−28	8.21 [2]	12.5 [17]	M [17]
$GdCu_2Sb_2$	11	−27	8.12 [2]	14.5 [17]	M [17]

M-modulated structure

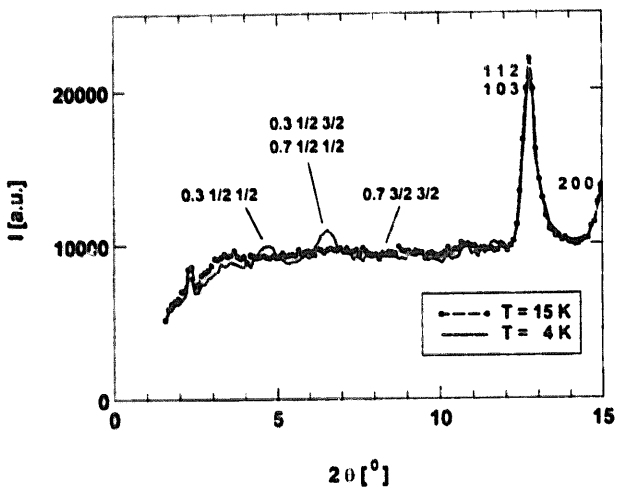

Fig. 1. Neutron diffraction patterns for $GdNi_2Sn_2$ at 15 K and 4 K.

M(H) for all compounds with Cu and Ni [2–4,8,11]. The effect is smaller for $GdCu_2X_2$ compounds than for $GdNi_2X_2$. These anomalies can be attributed either to a change in the magnetic structure, passing from modulated to commensurate, or to a manifestation of a small anisotropy via spin-flop phenomena.

The temperature dependence of resistivity $\rho(T)$ in the paramagnetic range of temperatures has a negative curvature [2–4,11]. The temperature coefficient of resistivity is larger for Ni-containing compounds and can be attributed to the shape of the conduction band density of d-states and larger s–d scattering for $GdNi_2X_2$.

3. ESR of Gd^{3+} ions in GdT_2X_2

From ESR investigations of gadolinium compounds (with 3d-Co, Ni, Cu and 4d-Ru, Rh Pd, Ag transition metals) in the paramagnetic region [2,12,14,15 and this work], two ESR parameters have been obtained: the g-factor (Table 2) and the thermal broadening of the resonance line $b = dDH/dT$ (Fig. 2), where DH = line-width. These parameters depend mainly on the transition metal. The slope of line-width b increases when the number of electrons in the transition element decreases. The slope is very small; the largest value is equal to 4.6 Oe K^{-1} for $GdCo_2Ge_2$. The smallest value, equal to zero (within the limits of experimental error), was found in compounds with T = Cu, Ag. The g-factor is different from that for spins in the non-metallic host (g-shift: $\Delta g = g_{metal} - g_{insul}$; $g_{insul} = 1.993$ for Gd^{3+}) and the g-shifts are small and positive. The Δg is negative only for $GdAg_2Sn_2$ and $GdRu_2Sn_2$. The values of ESR parameters change when the concentration of gadolinium in compounds decreases [11,14,16]. It indicates that these ternary compounds are bottlenecked [18,19]. The bottleneck effect is the strongest for the Cu- and Ag-containing compounds and is partially removed when Cu atoms are replaced by Ni and Co atoms or Ag atoms are replaced by Pd, Rh and Ru. Replacement of the X element in a compounds by another one does not influence significantly this behaviour.

This increase of the b value (Fig. 2) and opening of the bottleneck by replacement of Cu (Ag) atoms can be explained in the following way. In a bottleneck regime, the slope of the line-width depends on the bottleneck parameter $A = \delta_{eL}/\delta_{eS}$, where δ_{eL} = the conduction electron–lattice relaxation rate; δ_{eS} = the CE–Gd spin relaxation rate (Overhauser rate) [18]:

$$b = b_0 A/(1 + A) \qquad (1)$$

The Overhauser relaxation rate is given by the relation

$$\delta_{eS}(c) = (16\pi^2/3h) c S(S + 1) \eta J_{Se}^2 \qquad (2)$$

with: $\eta(E_F)$ = the density of the electron states at the Fermi level, J_{Se} = the exchange coupling constant between gadolinium spin S and CE, $S = 7/2$ for the Gd^{+3} spin and c = the atomic concentration of Gd.

The b_0 is the b value at the unbottlenecked limit:

$$b_0 = (\eta J_{Se})^2 4\pi k_B/(g\mu_B) \qquad (3)$$

Table 2
The g factors for GdT_2X_2 compounds

T	X Si	 Ge	 Sn	 Sb
Co	1.995 ± 0.01 [14]	2.02 ± 0.01 [15]	—	2.00 ± 0.01
Ni	2.01 ± 0.01 [14]	2.02 ± 0.01 [15]	2.00 ± 0.01 [12]	1.99 ± 0.01 [2]
Cu	2.00 ± 0.01 [14]	2.01 ± 0.01 [15]	1.99 ± 0.005 [12]	1.99 ± 0.005 [2]
Ru	1.99 ± 0.01 [14]	—	1.97 ± 0.01 [12]	—
Rh	1.995 ± 0.01 [14]	—	—	—
Pd	1.992 ± 0.01 [14]	2.01 ± 0.01 [15]	1.995 ± 0.005 [12]	2.00 ± 0.005
Ag	1.992 ± 0.01	2.005 ± 0.005 [15]	1.98 ± 0.01 [12]	1.988 ± 0.005

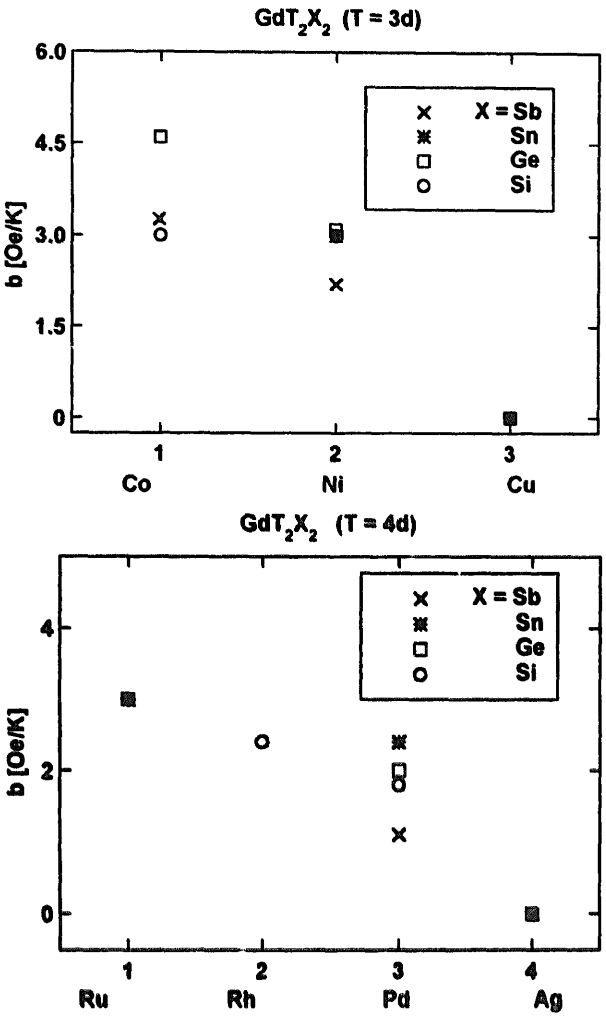

Fig. 2. The dependence of the b parameters on transition metal T and element X for GdT_2X_2.

A stronger bottleneck effect means that the A parameter ($A \ll 1$) is smaller. When the bottleneck is partially opened, the parameter A increases.

For a quantitative description of this process, the unbottlenecked b_0 value has to be known. The unbottlenecked limit has been reached for two compounds only: $GdCu_2Si_2$ ($b_0 = 5.2$ Oe K^{-1}) and $GdNi_2Si_2$ ($b_0 = 20$ Oe K^{-1}), by replacement of magnetic Gd ions by non-magnetic La and Y [20,21]. From formula 3 one can estimate that the $\eta(E_F)J_{Se}$ products are equal to $(7.5 \pm 0.5) \times 10^{-3}$ and $(15 \pm 1) \times 10^{-3}$ for $GdCu_2Si_2$ and $GdNi_2Si_2$, respectively. Analysis of ESR data for three diluted system [20,21] on the basis of the theoretical calculations of the density of the electron states for the $LaCu_2Si_2$ compound [22,23] and XPS data for $GdCu_2Si_2$ and $GdNi_2Si_2$ [24] allowed estimation of the values of $\eta(E_F)$, J_{Se}, A, δ_{eS} and δ_{eL} (Table 3).

It can be seen that the bottleneck parameter A increases when we pass from the Cu- to Ni-containing compound, because the CE relaxation to the lattice increases more than the relaxation to the Gd spins subsystem. The larger density of states at the Fermi level for $GdNi_2Si_2$ leads to the larger relaxation (approximately two times) of the conduction electrons to the spin subsystem δ_{eS} and the Gd ions are more strongly coupled with CE than in $GdCu_2Si_2$. For $GdNi_2Si_2$ the relaxation rate δ_{eL} increases more than twenty times than that of $GdCu_2Si_2$ due to the increase in the d-states density at E_F and the correspondingly more rapid relaxation of the d-electrons with the lattice than is the case for the s or p electrons. As a result, the bottleneck is partially opened in $GdNi_2Si_2$.

Table 3
ESR parameters, relaxation rates and density of state for $GdCu_2Si_2$ and $GdNi_2Si_2$

	$GdCu_2Si_2$	$GdNi_2Si_2$		
b [Oe K^{-1}]	0.05	3		
b_0 [Oe K^{-1}]	5.2	20		
$\eta(E_F)$ [st./(eVat.sp.)]	0.15	0.3		0.45
δ_{eS} [s^{-1}]	1.5×10^{13}	3.0×10^{13}		1.96×10^{13}
δ_{eL}[s^{-1}]	1.5×10^{11}	52.8×10^{11}		34.5×10^{11}
A	0.01	0.176		

Above quantitative analysis are impossible for the others GdT_2X_2. However, the only reasonable explanation of the b variation with 3d and 4d transition metal (Fig. 2) is the same. The b value increases with the decreasing of the number of d electrons of T metal, because the density of state at the Fermi level increases, leading to the enlargement of the b_0 value and the δ_{eS} relaxation rate. The changes of $\eta(E_F)$ are mainly caused by an increase in the density of the d-states near the Fermi level. More orbital character of conduction electrons causes an augmentation of the δ_{eL} relaxation rate. So, when Cu (Ag) is replaced by Ni, Co (Pd, Ru, Rh) both δ_{eS} and δ_{eL} increase, but the latter increase is larger and as a result, the bottleneck parameter A increases and bottleneck effect becomes weaker.

For almost all compounds the g-factor shifts are positive and the Δg value increases with decreasing concentration of Gd. From the theoretical description of the g-shift in the bottleneck limit [19], it can be concluded that the exchange constant J_{Se} is positive. The negative g-shift observed for some compounds with 4d metals can be caused by negative J_{Se} or by the splitting of the conduction electron d-band.

4. Conclusions

Magnetic and transport properties of GdT_2X_2 compounds depend on the density of the electron states at the Fermi level $\eta(E_F)$.

From ESR results it can be concluded that the

$\eta(E_F)$ value increases from Cu (Ag)-containing compounds to the Ni and Co (Pd, Rh, Ru) compounds. It leads to the increase of the CE-Gd spin relaxation rate δ_{eS} and may enlarge interaction between the Gd magnetic moments. In addition, the conduction electron character changes to a more d-type.

The estimation of the density of states was obtained from the ESR study of bottleneck effect for two compounds: $\eta(E_F) = 0.15$ states/(eV spin atom) for $GdCu_2Si_2$ and $\eta(E_F) = 0.3$ states/(eV spin atom) for $GdNi_2Si_2$ (with $J_{Se} = 0.05$ eV).

The effective exchange coupling constant J_{Se} between localized spins and conduction electrons is positive for all investigated compounds, except for $GdRu_2Sn_2$ and $GdAg_2Sn_2$.

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