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Magnetic Investigations on AlB_2 Type Structures*

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Magnetic measurements over a temperature interval 6°–630°K show that the effective paramagnetic moments in Gd_3Si_5, Dy_3Si_5, and Tb_3Si_5 are those of the tripositive rare-earth ions, and these materials are either antiferromagnets or have spiral configurations. In $NdSi_{1.6}Ni_{0.4}$ the effective magnetic moment is due to Nd^{+3} only. $NdSi_{1.6}Fe_{0.4}$ shows a complex magnetic structure. $LaSi_{1.6}Ni_{0.4}$ and $LaSi_{1.6}Fe_{0.4}$ are Pauli paramagnets.

Introduction

Rare-earth disilicides, $LnSi_2$, crystallize in the tetragonal $ThSi_2$ type structure (*1–3*) and $GdSi_2$ has been observed to have a low-temperature orthorhombic form and a high-temperature tetragonal form (*4*). Lundin (*5*) reported that the true stoichiometry of Gd, Y, Dy, Er, and Lu "disilicides" is Ln_3Si_5 ($LnSi_{1.67}$) and that they crystallize with the hexagonal AlB_2 type structure. He also observed the low-temperature orthorhombic modification for Gd, Y, and Dy silicides but reports their stoichiometry as Ln_3Si_5 rather than $LnSi_2$. Lundin could not determine a transition temperature and speculates that the stability of a polymorph may be dependent on the composition. He also indicates that the transformation temperature may depend on atomic number and may occur at room temperature between the Dy and Er compounds. The lighter rare earths do not form this stoichiometry or the AlB_2 structure, but if part of Si is replaced by Al, Ni, Fe, or Co then the structure is produced (*6, 7*). We have investigated the magnetic behavior of Gd_3Si_5, Tb_3Si_5, Dy_3Si_5, $NdSi_{1.6}Ni_{0.4}$, $NdSi_{1.6}Fe_{0.4}$, $LaSi_{1.6}Ni_{0.4}$, and $LaSi_{1.6}Fe_{0.4}$ to study the effect of the rare-earth radius, $4f$ electron population and composition on the magnetic properties.

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Experimental

Gd, Tb, Dy, La and Nd were nominally 99.9% pure; Ni, Fe, and Si had a stated purity of 99.999%. All compounds were formed at 1500°C in an alumina crucible under partial pressure of argon in an induction furnace. After reaction the samples were annealed in evacuated Vycor tubing at a temperature of 850°C for 1 week. All preparations were examined metallographically and by X-ray powder diffraction methods and were found to be single phase. X-ray diffraction patterns were obtained by using Ni-filtered Cu radiation. Lattice constants were determined by a least-squares refinement employing 2θ values measured with Ni filtered Cu$K\alpha$ radiation and are shown in Table I. They agree very well with previously reported values (*5, 7*). We did not observe any evidence of the formation of an orthorhombic phase.

Magnetic measurements were carried out with a Faraday balance from liquid N_2 temperature to about 630°K and a vibrating sample magnetometer was used for temperatures below liquid N_2.

TABLE I

MAGNETIC AND CRYSTALLOGRAPHIC PARAMETERS FOR Ln_3Si_5

Compound	Effective Moment Paramagnetic B.M./metal atom	Weiss Temperature °K	Neel Temperature °K	Lattice Constants[a]	
				a Å	c Å
Gd_3Si_5	7.58	−85	41	3.873 (5)	4.183 (3)
Tb_3Si_5	9.79	−42	38	3.864 (8)	4.154 (4)
Dy_3Si_5	10.45	+2	7	3.835 (6)	4.131 (3)
$NdSi_{1.6}Ni_{0.4}$	3.83	−9.4		4.01 (2)	4.25 (1)
$NdSi_{1.6}Fe_{0.4}$	2.61	+58.5		4.03 (2)	4.19 (1)
$LaSi_{1.6}Ni_{0.4}$				4.06 (1)	4.40 (1)
$LaSi_{1.6}Fe_{0.4}$				4.09 (1)	4.37 (2)

[a] Numbers in parentheses are standard deviations in the last significant digit.

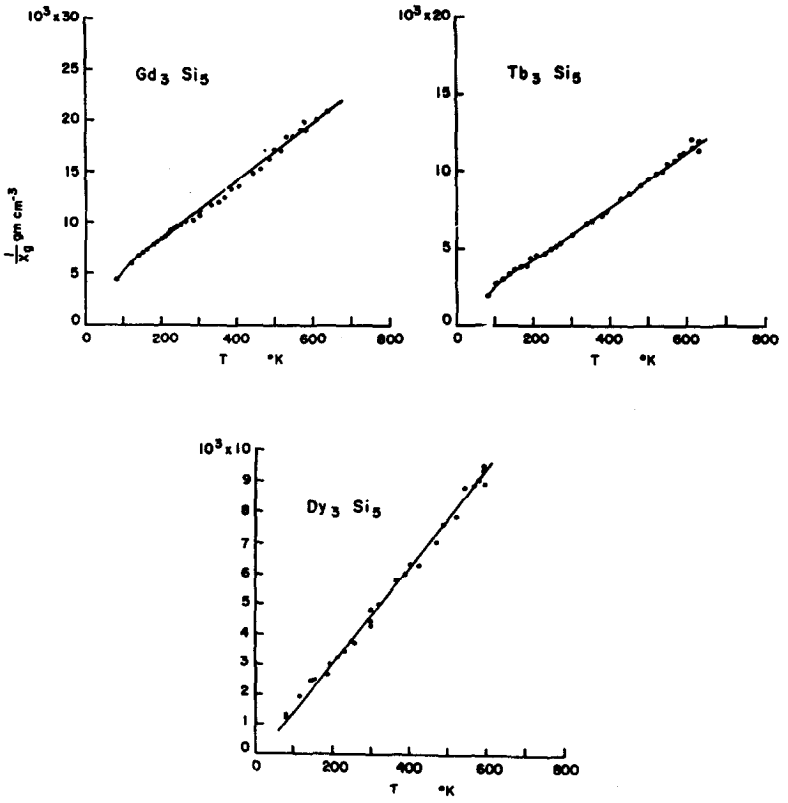

FIG. 1. Reciprocal paramagnetic susceptibility as a function of temperature for Gd_3Si_5, Tb_3Si_5, and Dy_3Si_5.

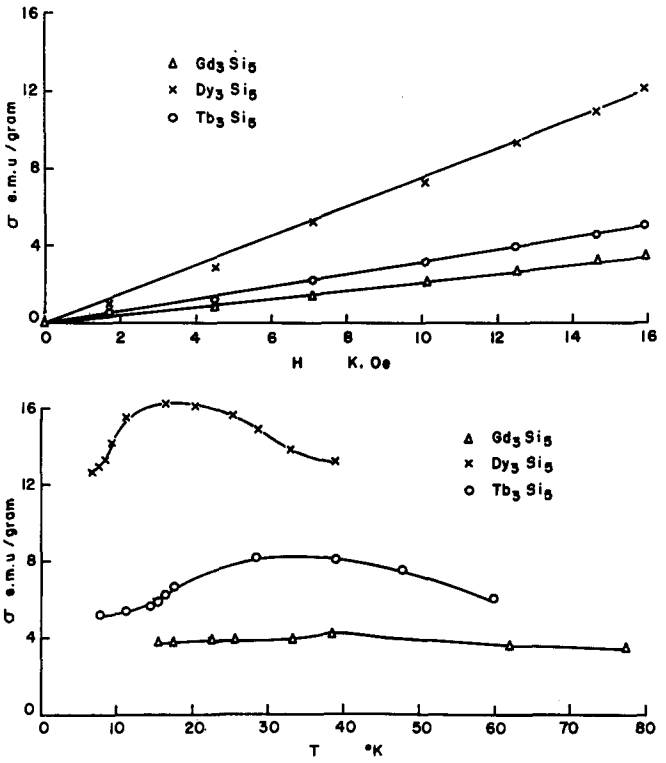

FIG. 2. Magnetization versus magnetic field and temperature for Gd_3Si_5, Tb_3Si_5, and Dy_3Si_5.

Results and Discussion

The variation of inverse magnetic susceptibility versus T of Gd_3Si_5, Tb_3Si_5, and Dy_3Si_5 is shown in Fig. 1, and the magnetization as a function of H and T for these compounds is shown in Fig. 2. Effective paramagnetic moments were calculated by means of a least-squares fit to the Curie–Weiss law using the high-temperature data, and they, together with Weiss constants, are shown in Table I. The effective moments for the Gd, Tb, and Dy alloys indicate that the rare-earth element is in the trivalent state. The magnetization versus T curves go through broad maxima, and at 6°K the magnetization increases linearly with applied field and the moments are small. The behavior suggests that these three compounds are antiferromagnetic or have a spiral structure. The broad maxima may indicate the latter possibility.

The substitution of Ni and Fe for Si is expected to modify the magnetic properties of these compounds and $LaSi_{1.6}Fe_{0.4}$ and $LaSi_{1.6}Ni_{0.4}$ were prepared to study this effect when the rare-earth contribution is absent. Both compounds show a temperature-independent Pauli paramagnetism with susceptibilities of the order of 3×10^{-6} emu/g. Since Fe and Ni are the sole components expected to contribute to a moment the observation suggests that the $3d$ bands of the transition metals are filled by the valence electrons of La and Si. If this is the only effect the replacement of La by another trivalent rare-earth ion should produce a material which in the paramagnetic region should have a moment due to the tripositive ion only. An effective magnetic moment of 3.83 μ_B for $NdSi_{1.6}Ni_{0.4}$ is obtained by a least-squares fit to the data of inverse susceptibility versus T between 40° and 250°K (Fig. 3), in agreement with expected values for Nd^{3+}. No contribution from Ni is observed and the conclusion that Ni has a filled $3d$ band seems to hold for this compound.

The magnetization versus field dependence

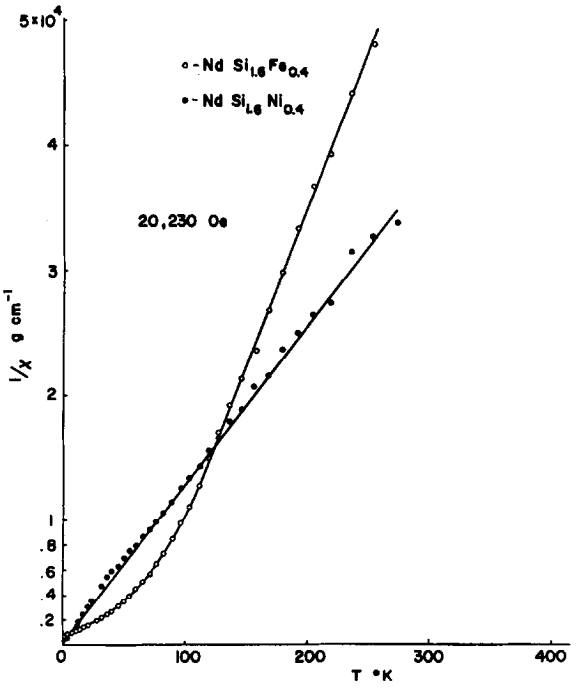

FIG. 3. Inverse magnetic susceptibility versus temperature for $NdSi_{1.6}Ni_{0.4}$ and $NdSi_{1.6}Fe_{0.4}$ measured at 20 kOe.

at 4.2°K (Fig. 4) is not typical of a paramagnet. The slope of the curve decreases with increasing field strength similar to the behavior of canted spin structures, and this compound may possibly have a transition to such a structure at lower temperatures.

The least-squares fit of a straight line to the $1/x$ versus T data obtained at 20 kOe for $NdSi_{1.6}Fe_{0.4}$ above 80°K (Fig. 3) yields an effective moment of 2.61 μ_B. The susceptibility data measured at 6132 Oe yield an effective moment of about 2.2 μ_B. These values are considerably less than the approximately 3.8 μ_B value expected for Nd^{3+}. In Fig. 5 the magnetization versus T behavior at several field strengths shows a sharp rise at low temperatures after an apparently antiferromagnetic-type behavior. The curve shown in Fig. 4 is reminiscent of the behavior of Tm(8) where a transition from a ferromagnetic state to a structure with a modulated moment occurs (*9*). Single crystal studies are clearly required for further elucidation of the magnetic structure of this phase.

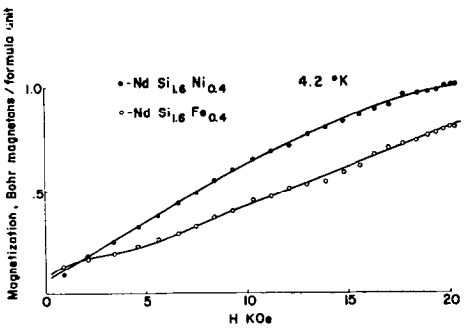

FIG. 4. Field dependence of magnetization for $NdSi_{1.6}Ni_{0.4}$ and $NdSi_{1.6}Fe_{0.4}$ at 4.2°K.

We have concluded that the 3*d* bands of the transition-metal atoms in the lanthanum compounds are probably filled, thus accounting for the observed Pauli paramagnetism. Also in $NdSi_{1.6}Ni_{0.4}$ the *d* band of Ni is filled and only the Nd^{3+} contribution to the susceptibility is observed. $NdSi_{1.6}Fe_{0.4}$ has a

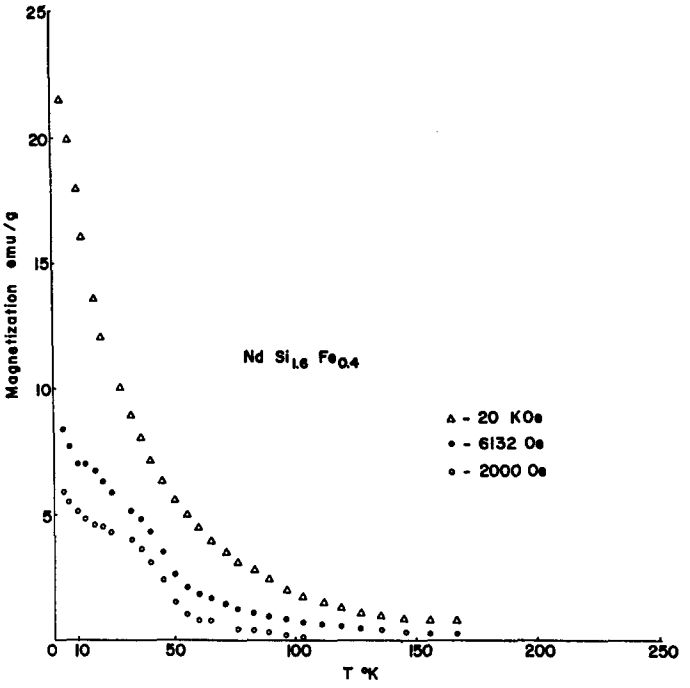

FIG. 5. Magnetization versus temperature for $NdSi_{1.6}Fe_{0.4}$ at field strengths of about 2, 6, and 20 kOe.

complicated spin structure and it is not possible to state with certainty that the *d* band of iron is filled and that Fe makes no contribution to the spin lattice. The difference in the magnetic behavior of $NdSi_{1.6}Ni_{0.4}$ and $NdSi_{1.6}Fe_{0.4}$ could be related to the difference in the conduction electron concentration. Magnetic ordering in these compounds is mainly controlled by RKKY-type interactions and these are sensitive to the electron concentrations (*10*).

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