FERROMAGNETISM OF CERIUM AND NEODYMIUM CHALCOGENIDES WITH A Th_3P_4 *STRUCTURE*

A. T. STAROVOĬTOV, V. I. OZHOGIN, G. M. LOGINOV, and V. M. SERGEEVA

Submitted April 20, 1969

Zh. Eksp. Teor. Fiz. 57, 791–793 (September, 1969)

The magnetization of the Ce_3Se_4, Pr_3S_4, and Nd_3S_4 chalcogenides is investigated in a pulsed magnetic field with an amplitude of 230 kOe and at temperatures of 4.2 or 1.6°K. Ferromagnetic ordering in fields stronger than 10 kOe is found in cerium and neodymium chalcogenides. The shape of the magnetization curves can be explained by taking into account the effect of the crystal field.

AN example of a ferromagnetic compound Gd_3Se_4 (T_C = 82°K) with a structure of the Th_3P_4 type is known among the chalcogenides of the rare-earth elements.[1,2] We thought it interesting to carry out investigations of the magnetic properties of the chalcogenides of the rare-earth elements cerium, praseodymium, and neodymium (of the Th_3P_4 type); this was reinforced by the fact that in investigating the monochalcogenides of these elements indirect indications of the possibility of the existence of ferromagnetic phases were obtained.[3] The investigated compounds were prepared by means of direct reaction between the elements.[4] X-ray analysis showed that compounds with the Th_3P_4 structure had formed.

Measurements of the static magnetic susceptibility in fields up to 15 kOe in the 300–80°K temperature range carried out on a magnetic balance[5] showed that the susceptibility of all the investigated compounds follows the Curie-Weiss law $\chi = C/(T - \Theta)$ (Fig. 1). In the Table we present experimental and theoretical values (calculated for a free rare-earth ion) of the effective magnetic moment n_{eff}, as well as values of the paramagnetic Curie temperature Θ and of the magnetic ordering temperature T_C. The positive value of Θ for Nd_3S_4 attests to the possible presence of ferromagnetic ordering below 50–40°K.

Investigations of the magnetization in pulsed fields up to 230 kOe at temperatures of 4.2 and 1.6°K were carried out by the induction method.[6] The field was calibrated with the antiferromagnetic resonance signal in hematite at a wavelength of 8 mm at T = 77°K. Electrolytically pure nickel [σ(77°K) = 57.2 gauss-cm³/g] was used to calibrate the measuring system. The magnetic moment sensitivity of the system amounted to 0.15 gauss-cm³. The error in measuring the magnetization did not exceed 5 percent.

Figure 2 shows the magnetization curves at T = 4.2 and 1.6°K. It is seen (see also the Table) that Nd_3S_4 and Ce_3Se_4 have rather large spontaneous magnetic moments n_0 and considerable differential susceptibilities χ_d in the region of strong fields. The hysteresis loop obtained at T = 4.2°K (Fig. 3) for Nd_3S_4 attests to the fact that the compound is magnetically hard, the coercive force H_c = 8.35 kOe, and $(BH)_{max} = 2 \times 10^6$ gauss-Oe. The value of the spontaneous magnetic moment at 1.6°K exceeds that at 4.2°K by 1 percent; this is in agreement with the rather high $T_C \sim 50$°K. In Ce_3Se_4 the hysteresis loop is considerably narrower and $H_c < 1$ kOe. However, the value of the spontaneous magnetic moment at 1.6°K exceeds its value at 4.2°K by 20 percent. The latter fact can be explained if one bears in mind the considerably lower temperature $T_C \sim 10$°K compared with Nd_3S_4. It is characteristic that the spontaneous magnetic moments are considerably lower than the magnetic moments ($gJ\mu_B$) calculated for the free ions Ce^{3+} and Nd^{3+}; thus, instead of 2.14 μ_B for Ce^{3+} and 3.28 μ_B for Nd^{3+} we have 0.67 and 1.27 μ_B respectively.

At the present stage of the investigation we are inclined to assume in the case of the neodymium and cerium chalcogenides the existence of ferromagnetic ordering in fields above 10 kOe. One can then explain the low spontaneous moments, as well as the course of the magnetization curves in the region of strong fields, if one takes into account the effect of the crystal field.

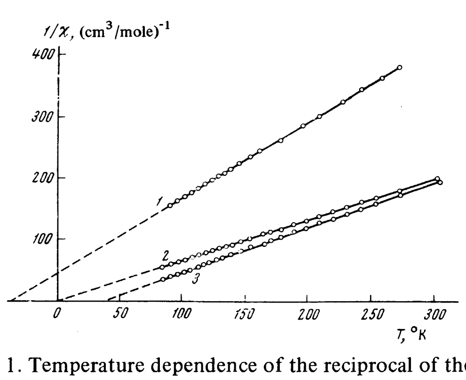

FIG. 1. Temperature dependence of the reciprocal of the magnetic susceptibility (per formula $ReX_{1.33}$): 1 – Ce_3Se_4, 2 – Pr_3S_4, 3 – Nd_3S_4.

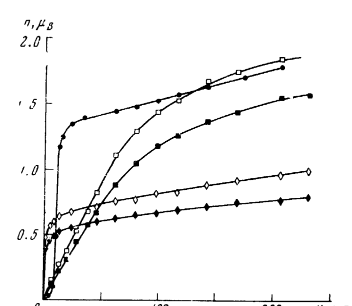

FIG. 2

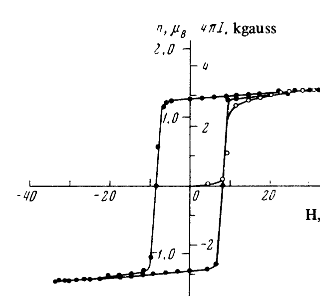

FIG. 3

FIG. 2. Dependence of the magnetization of Re_3X_4 chalcogenides (calculated per Re^{3+} ion) on the magnetic field: ◇, ♦ – Ce_3Se_4, □, ■ – Pr_3S_4, ● – Nd_3S_4. Black points – T = 4.2°K, light points – T = 1.6°K.

FIG. 3. Hysteresis loop for Nd_3S_4 at T = 4.2°K.

Re_3X_4	a, Å	Ground state of Re^{3+}	n_{eff}, μ_B		Θ, °K	T_C, °K	n_0, μ_B	$\langle A\|M\|A\rangle$, μ_B	$\chi_d \cdot 10^4$, μ_B/kOe
			$g\sqrt{J(J+1)}$	experiment					
Ce_3Se_4	8.97	$^2F_{5/2}$	2.54	2.56	−30	10	0.67	0.71	15
Pr_3S_4	8.59	$^3H_4$	3.58	3.50	0	—	0	0	
Nd_3S_4	8.48	$^4I_{9/2}$	3.62	3.35	40	50	1.27	1.33	27

The values of n_0 and χ_d are given for T = 1.6°K.

For Ce^{3+} and Nd^{3+} which are located in a cubic crystal field the lower energy levels are either A doublets (Γ_7 and Γ_6 respectively) or Γ_8 quartets.[7] The calculated values of the spontaneous magnetic moments $\langle A|M|A\rangle$ for the $\Gamma_7(Ce^{3+})$ and $\Gamma_6(Nd^{3+})$ levels[8] are close to the experimental values (see the Table). The differential susceptibility observed for Ce_3Se_4 and Nd_3S_4 is explained within the framework of our model by the mixing of excited states.

No spontaneous magnetic moment is observed for Pr_3S_4; we assume that this is connected with the absence of magnetic ordering at low temperatures. The latter can, for instance, be due to the fact that the lowest energy level of Pr^{3+} in the crystal field is a Γ_1 singlet. In order to explain the course of the magnetization curves, one must apparently take into account the polarization of the lowest energy level in the magnetic field.

The obtained data allow one to hope that the Re_3X_1 chalcogenides with the Th_3P_4 structure constitute a new and interesting class of ferromagnetic substances.

In conclusion the authors express their gratitude to I. K. Kikoin, V. P. Zhuze, and G. A. Smolenskiĭ for interest in the work.

[1] F. Holtzberg, T. R. McCuire, S. Methfessel, and J. S. Suits, J. Appl. Phys. 35, No. 3 (Part 2) 1033 (1964).

[2] S. Methfessel, Z. Angew. Phys. 18, 414 (1965).

[3] G. A. Smolenskii, V. P. Zhuze, V. E. Adamjan, and G. M. Loginov, Phys. Stat. Sol. 18, 873 (1966).

[4] A. V. Golubkov, T. B. Zhukova, and V. M. Sergeeva, Neorgan. Materialy 2, 77 (1966).

[5] V. E. Adamyan, A. V. Golubkov, G. M. Loginov, and V. N. Fedorov, Fiz. Tverd. Tela 7, 3372 (1965) [Sov. Phys.-Solid State 7, 2715 (1966)].

[6] J. S. Jacobs and P. E. Lawrence, Rev. Sci. Instr. 29, 713 (1958).

[7] K. R. Lea, M. J. Leask, W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).

[8] B. Bleaney, Proc. Roy. Soc. A276, 28 (1963).

Translated by Z. Barnea
90