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Magnetic phase transitions from the point of view of macroscopic and microscopic methods

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Magnetic phase transitions in some rare earth compounds are discussed from the point of view of different experimental methods. The discussion concentrates on the determination of phase transitions in magnetically ordered states. The data presented in this work suggest that the "classical" method, namely the specific heat method, does not yield information on phase transitions between commensurate and incommensurate magnetic structures.

Key words: *magnetic phase transition; rare earth intermetallics; specific heat; electrical resistivity; neutron diffraction*

1. Introduction

One of the important problems of solid state physics are investigations of phase transitions in crystals. The methods used to investigate the magnetic phase transitions could be divided into macroscopic and microscopic ones. Temperature dependences of magnetization, magnetic susceptibility and specific heat measurements belong to the former group while neutron diffraction and the Mössbauer effect to the latter one.

Below characteristic temperatures of magnetic materials, i.e. the Curie temperature (T_C) for ferromagnets and the Néel temperature (T_N) for antiferromagnets, the magnetic moments of atoms order. The transition from the paramagnetic to the magnetically ordered phase is the second order phase transition and a characteristic maximum in the temperature dependence of specific heat is observed [1]. Neutron diffraction methods provide information on the symmetry of the magnetic structure from the intensities of the magnetic peaks. Thermal dependence of the intensities of magnetic peaks gives us information on the critical temperature of the magnetic ordering (T_C or T_N), as well as of the magnetic phase transitions (i.e., changes in the magnetic structure) [2]. Very quick development of these methods in recent years, in particular the

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neutron diffraction measurements with multidetectors, allows us to obtain new interesting information on phase transitions. However, information from different experimental data does not always give similar results.

In this work, results for some rare earth intermetallic compounds are discussed. The data presented concern the RT_2X_2 compounds (R is a rare earth element, T is a transition nd-element and X is Si or Ge). These compounds crystallize in a simple tetragonal structure of $ThCr_2Si_2$ type (space group *I*4/*mmm*). R atoms with localized magnetic moment occupy only one sublattice (2*a* positions). The information on the magnetic phase transitions in the ternary rare earth compounds is summarized in two papers [3, 4]. The paper focuses on some examples chosen to illustrate the large variety of behaviours in magnetic phase transition regions but its aim is not to give a complete review of these phenomena.

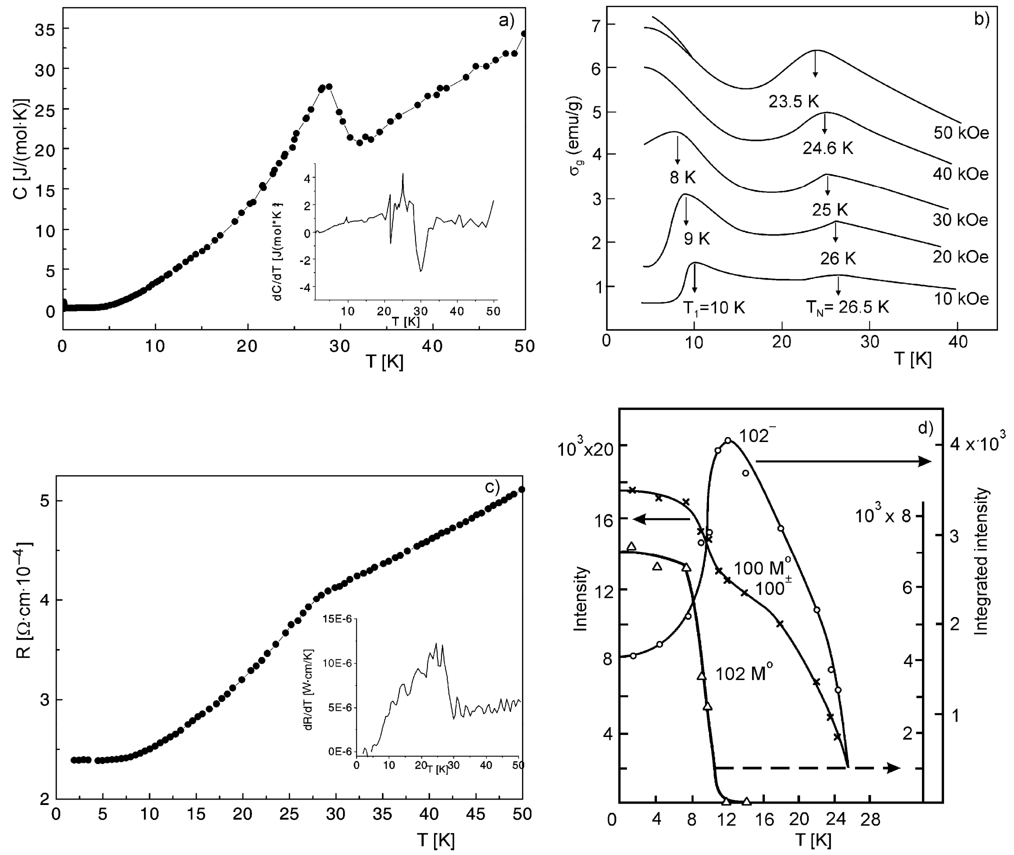
2. Results

2.1. $NdCo_2Ge_2$ compound

In Figure 1, the temperature dependences of magnetization, specific heat, electrical resistivity and plots of neutron diffraction data (the dependence of integrated intensities of some magnetic peaks and the k_z-component of the propagation vector) of $NdCo_2Ge_2$ are presented. The magnetization shows a peak at about 10 K and a small maximum at about 26.5 K [5], while the specific heat and resistivity show only anomalies at 26.5 K [6]. Neutron diffraction data give the explanation of these differences. At 1.5 K two magnetic ordering modes coexist: a simple collinear antiferromagnetic AFI type, in which the Nd magnetic moment at the position (0, 0, 0) is antiparallel to the one at the position (1/2, 1/2, 1/2) and a sine-modulated magnetic structure with the propagation vector $\mathbf{k} = (0, 0, 1 - k_z)$, where $k_z = 0.261$ in the reduced unit cell. With increasing temperature, the intensities of the peaks corresponding to the simple collinear magnetic structure diminish and vanish at 12 K while the intensities of the peaks corresponding to the modulated structure increase up to 12 K and then decrease up to the Néel temperature equal to 26 K. The peak in the k_z value is connected with the transition at T_t (Fig. 1) [7].

2.2. $PrFe_2Ge_2$ and $NdFe_2Ge_2$ compounds

The results of the investigations concerning magnetic phase transitions in $PrFe_2Ge_2$ are summarized in Fig. 2. The temperature dependences of the dc magnetization and ac magnetic susceptibility have the maxima at $T_N = 13$ K and an additional maximum in the ac magnetic susceptibility at 8 K. The resistivity shows anomalies at 8.2 and 14.6 K [8] while the specific heat only at $T_N = 14.2$ K [8, 9]. The neutron diffraction data show the phase transition from simple collinear antiferromagnetic structure described by the propagation vector **k** = (0, 0, 1/2) to the sinusoidally-modulated structure with the propagation vector **k** = (0, 0, 0.476) at 9 K [10].



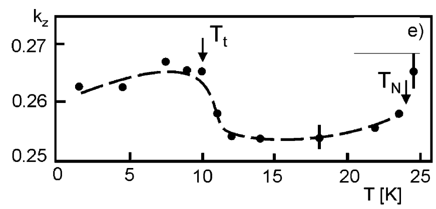


Fig. 1. Thermal dependences for $NdCo_2Ge_2$: a) specific heat, b) magnetization at various fields [5], c) resistivity [6], d) integrated magnetic intensities of some magnetic peaks, e) k_z-component of the propagation vector [7]

Temperature dependence of the ac magnetic susceptibility χ of $NdFe_2Ge_2$ exhibits a maximum at 16.7 K. Below the Néel temperature the maximum at T_t = 13.5 K in the temperature dependence of d χ'/dT indicates an additional phase transition [11]. These anomalies are visible also in the specific heat and resistivity measurements [8]. Neutron diffraction data indicate the phase transition between the collinear antiferromagnetic structure with the **k** = (0, 0, 1/2) below T_t and **k** = (0, 0, 0.46(1)) above T_t [11].

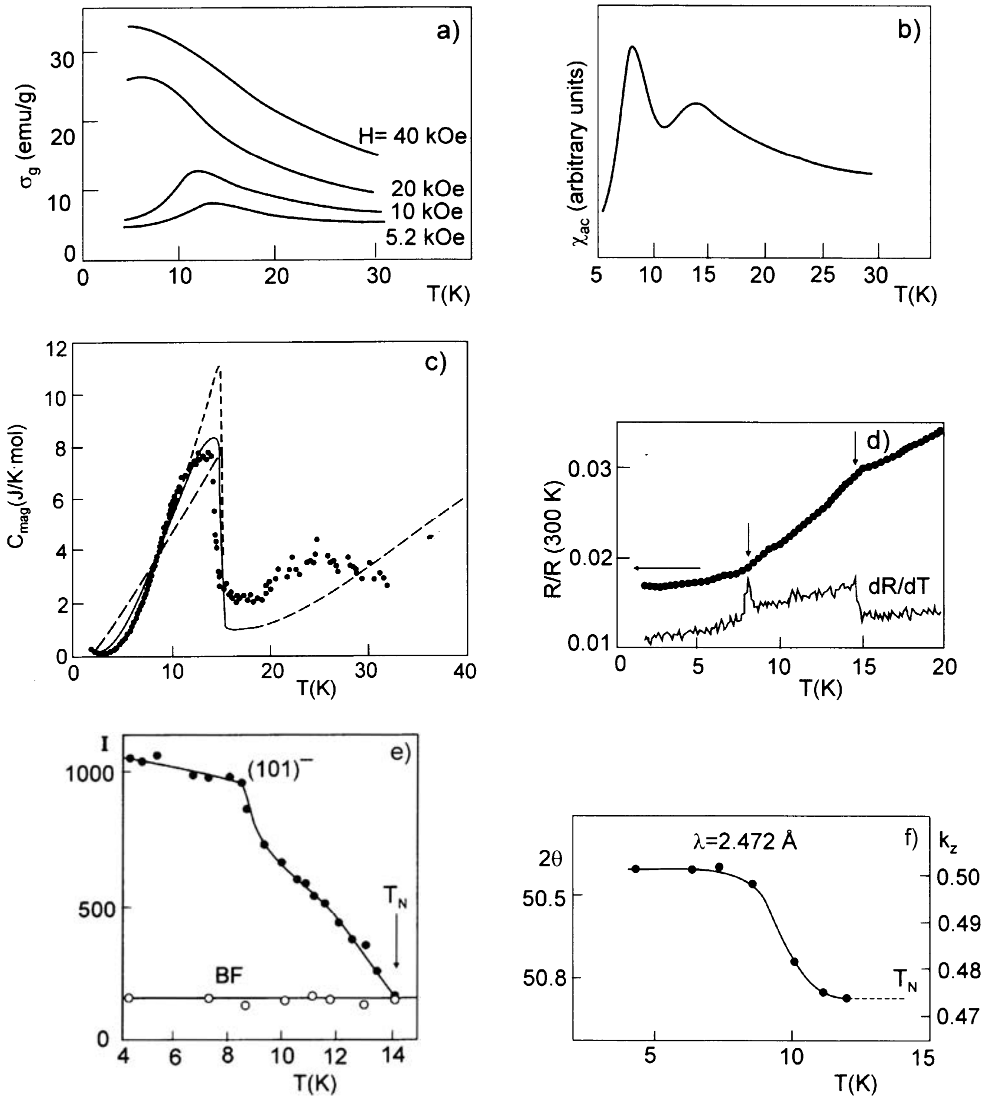


Fig. 2. Thermal dependences of: dc magnetization at various magnetic fields (a), ac magnetic susceptibility (b), specific heat [8] (c), resistivity *R* and its temperature derivative d*R*/d*T* [9] (d) as well as integrated intensity of the magnetic 101, reflection (e) and 2θ position of the $110^{\pm}$ reflection and propagation vector $\mathbf{k}_z$ for $PrFe_2Ge_2$ [10] (f). The dashed and the dotted lines represent the specific heat curves calculated for a simple antiferromagnet and for a modulated magnetic structure below T_N, respectively

2.3. $NdRu_2X_2$ (X = Si, Ge)

The magnetic data indicate that both $NdRu_2X_2$ compounds are ferromagnets at low temperatures [12, 13]. With increasing temperature the change in the magnetic structure from the ferromagnetic ordering to the sinusoidally modulated one for both compounds is observed at T_t = 10 K. Above T_t, sine-wave modulated structure develops with the propagation vector **k**= (k_x, k_x, 0), where k_x = 0.13 for $NdRu_2Si_2$ [12] and 0.12 for $NdRu_2Ge_2$ [14].

For $NdRu_2Si_2$ both phase transitions (at T_t and T_N = 23 K) are clearly visible in the thermal dependence of specific heat and electrical resistivity [15].

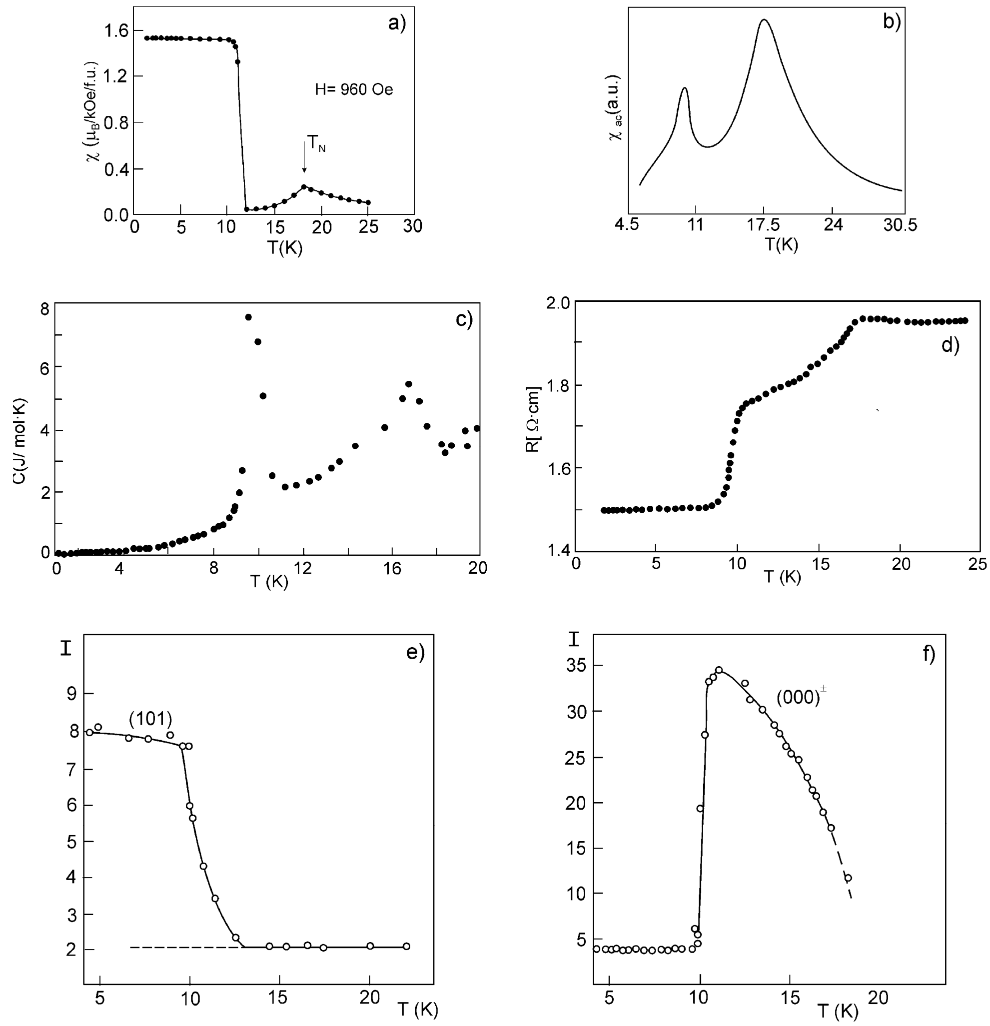


Fig. 3. Temperature dependence of the dc magnetization (a), ac magnetic susceptibility (b), specific heat (c), resistivity (d) and integrated intensities of the 101 (e) and $000^{\pm}$ (f) peaks for $NdRu_2Ge_2$ [14]

In Figure 3, the data concerning the phase transitions in $NdRu_2Ge_2$ are shown. The low temperature thermal variation of the dc susceptibility confirms the first order transition between the ferro- and antiferromagnetic phases at 10 K and the Néel temperature at 18 K. These transitions are confirmed by the ac data which exhibit the maxima at 9.6 and 17.5 K [16]. At these temperatures, anomalies in the thermal dependences of specific heat and electric resistivity are observed. At T_t = 10 K, the neutron diffraction data show a decrease in the intensity of the 101 magnetic peak corresponding to the ferromagnetic phase and an increase in the intensity of the $000^{\pm}$ reflection corresponding to the modulated phase.

3. Discussion

The results presented in this work clearly show that it is possible to obtain complete information on magnetic phase transitions in rare earth intermetallic compounds only from investigations carried out by means of complementary macro- and microscopic methods. The data presented here show that information obtained from various methods depicts these transitions in different ways. Especially interesting are the results concerning phase transitions in the ordered phase. Also, the results obtained for $NdCo_2Ge_2$ and $PrFe_2Ge_2$ are worth to notice. For these compounds, no anomaly connected with the change in the magnetic structure from a commensurate to an incommensurate one was observed in the temperature dependence of specific heat, while other macroscopic methods, as well as the neutron diffraction method, show an anomaly at T_t. A similar situation is observed in $TbNi_2Si_2$ where at T_t = 8.5 K the neutron diffraction experiment shows a change in the magnetic structure from a commensurate one with **k** = (1/2, 1/2, 0) to an incommensurate one with **k** = (0.604, 0.396, 0), while the thermal dependence of specific heat shows only a λ-type anomaly at T_N = 13.7 K [17]. The data on the magnetic phase transitions in some RT_2X_2 compounds with R = Pr and Nd [18–24] are summarized in Table 1.

Table 1. Magnetic phase transitions in RT_2X_2 (R = Pr, Nd; T – d-electron element; X = Si, Ge) determined from the specific heat measurements

Compound	T_N [K]	T_t [K]	$\Delta C(T_N)$ [J/(mol·K)]	$\Delta C(T_t)$ [J/(mol·K)]	$S(T_N)$ [J/(mol·K)]	$S(T_t)$ [J/mol·K]	ΔS(50 K) /Rln2	Ref.
$PrFe_2Si_2$	7.7	–	0.1		0.6		0.885	[9]
$PrFe_2Ge_2$	14.2		5.7		4.7		1.128	[9]
$PrCo_2Si_2$	29.7	16.4, 9.6	4.7	12.2, 4.7				[18]
$PrNi_2Si_2$	20.0		0.3					[19]
$PrNi_2Ge_2$	20.4	–	8.0		10.3		1.79	[20]
$PrCu_2Ge_2$	15	5.5	9.6	3.25				[21]
$PrRu_2Si_2$	16	14	~0.1	14.0	4.5		1.3	[22]
$NdFe_2Ge_2$	16.4	13.5	7.6	4.9	6.7		1.17	[8]
$NdCo_2Ge_2$	28	–	9.4		9.78		2.47	(this work)
$NdNi_2Ge_2$	16.6	2.6	4.4	0.5	11.5		2.386	[7]
$NdRu_2Si_2$	23.5	10	2.46		4.6	1.5	1.16	(this work)
$NdRu_2Ge_2$	17	10	2.62	6.3	1.84	0.8	0.55	[6]
	18	10	12.0	0.5	2.8	0.47	0.694	[24]

In the mean field description of magnetic phase transitions at T_N, the dependence of the $\Delta C_{\mathrm{mag}}(T_N)$ value on the momentum J is described by the equation:

$$\Delta C_{\mathrm{mag}}(T_N) = 2.5R\frac{(2J+1)^2-1}{(2J+1)^2+1}$$

with the related entropy given by $\Delta S_m = R\ln(2J+1)$. For the reported Pr and Nd compounds J is equal 4 and 9/2, respectively, and the respective values of $\Delta C_{\mathrm{mag}}(T_N)$ are 20.28 J/(mol·K) for Pr and 20.37 J/(mol·K) for Nd, and $\Delta S(T_N)$ should be equal to 18.27 J/(mol·K) for Pr and 19.14 J/(mol·K) for Nd compounds. In all the discussed compounds, the discontinuity of the specific heat at T_N is reduced. This is in good agreement with the experimental [25] and theoretical [26] results for the compounds with the phase transition from an amplitude modulated magnetic structure to the paramagnetic phase. For some compounds, the magnetic entropy near the Néel temperature is close to the value $R\ln 2$ = 5.76 J/(mol·K), the theoretical entropy of a two level system.

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