

1,2,4-Triazole Complexes XIII *

Magnetic Properties of the Quasi two-dimensional Weak Ferromagnet β -nickel (II) (1,2,4-triazole)₂ (NCS)₂

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Powdered samples of β -Ni(trz)₂(NCS)₂ have been investigated by measurements of the magnetic susceptibility (in the temperature range $T = 15$ – 300 K), magnetization (at $T = 4.2$ K) and heat capacity ($T = 1$ – 90 K). From the magnetization measurements the material is found to be a weak ferromagnet, with a zero-field magnetic moment of $\sim 0.015 \mu_B$. The ordering temperature is determined as $T_c = 10.14(2)$ K. The susceptibility and heat capacity data are in reasonable agreement with predictions from high-temperature series expansions for the quadratic layer, $S = 1$, Heisenberg antiferromagnet, with an intralayer exchange constant $J/k = -4.5(1)$ K.

Introduction

β -Ni(1,2,4-triazole)₂(NCS)₂(β -Nitrz) and the corresponding compounds with Mn, Fe and Co form an isomorphous group of compounds crystallizing in the space group Aba 2, with $Z = 4$ [1, 2]. The structure of these materials [3, 4] consists of quasi-quadratic layers of metal ions, connected by 2,4-bridging triazole groups. The NCS[−] groups are on either side of the layers. The NiN₆ octahedra are canted in the a-b plane. The Mn, Fe and Co compounds have been shown to possess 2-d (d = dimensional) magnetic properties [5–7] as may be expected from their layered crystal structure.

From the X-ray powder diffraction pattern of β -Nitrz the axes are found to be $a = 7.751(5)$, $b = 16.364(8)$ and $c = 9.597(5)$ Å.

The broad maximum found in the susceptibility vs. temperature curve measured on a powdered sample [2] is an indication that also β -Nitrz has low-dimensional properties. Furthermore, in the magnetization vs. field curve a zero-field moment of about $0.011 \mu_B$ was found, which was ascribed to

the presence of spin canting, associated with the tilted NiN₆ octahedra in the crystal structure [2].

In this paper we will discuss the results from magnetic susceptibility, magnetization and heat capacity measurements on powdered samples of β -Nitrz, using equipment that has been described elsewhere (see references in [6, 7]).

Polycrystalline samples of β -Nitrz were obtained from an acidified aqueous solution containing Ni(II), trz and NH₄NCS in stoichiometric quantities [1]. The pH of the solution should be 2 or less, otherwise the trinuclear α -compound will be formed. The α - and β -forms can be easily distinguished by X-ray powder diffraction. Once formed, the substance appeared to be insoluble. Attempts to grow single crystals were unsuccessful, although a small crystal (~ 1 mg) was obtained by putting a very small crystal of the Zn compound into a solution of β -Nitrz. Unfortunately, this crystal was rather defective and it was used for some qualitative magnetization measurements only.

Susceptibility and Magnetization Measurements

Figure 1 shows the powder magnetization as a function of temperature, measured at $H = 5.61$ kOe. The measured magnetization were corrected for diamagnetism and temperature independent paramagnetism using the values $\chi_{\text{dia}} = -156(5) \times 10^{-6}$

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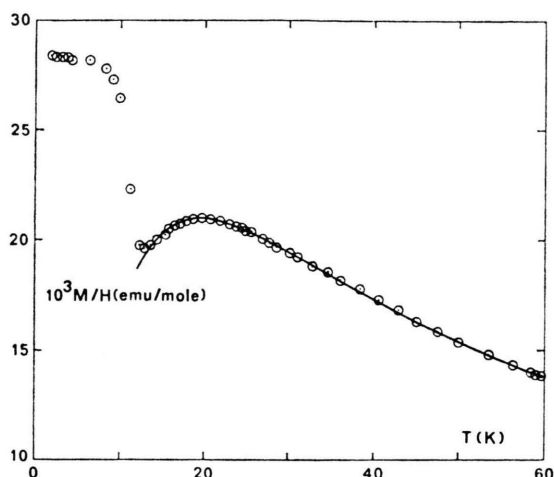


Fig. 1. Temperature dependence of the magnetization of powdered β -Nitrz, at $H = 5.6$ kOe. The curve is the high-temperature series prediction for the Heisenberg $S = 1$, quadratic layer antiferromagnet with $J/K = -4.5$ K and $g = 2.20$.

emu/mole as determined for the Zn compound and $\chi_{\text{tip}} = +190 \times 10^{-6}$ emu/mole which was calculated from the formula $\chi_{\text{tip}} = 8 N \mu_B^2 / 10 Dq$ [8], with $Dq = 1100 \text{ cm}^{-1}$ [1]. The stepwise increase of the magnetization near $T \cong 10$ K is ascribed to a canting of the spins, which results in a weak ferromagnetic moment (see below). From magnetization measurements at a lower field strength ($H = 1.4$ kOe, not shown in Fig. 1), the point of maximum downward slope is found at $10.1(2)$ K, which can be considered as an estimate of the ordering temperature T_c . The data are representative for the initial susceptibility for $T > 15$ K, where M/H is independent of the applied field. A broad maximum occurs at $19.5(5)$ K, with $\chi_{\text{max}} = 0.210(4)$ emu/mole. In view of the 2-d character observed in the other compounds $M(\text{trz})_2(\text{NCS})_2$, the susceptibility data for $T > 15$ K were compared with the predictions from the high-temperature series expansion for the susceptibility of the 2-d quadratic layer Heisenberg antiferromagnet with $S = 1$. The susceptibility was calculated using the inverted series:

$$\chi = \frac{N g^2 \mu_B^2 S(S+1)}{3 k T} \left[1 + \sum_{n=1}^{\infty} b_n (J/kT)^n \right]^{-1}. \quad (1)$$

The coefficients b_n were calculated from the six coefficients available for the inverted series [9] and the seventh and eight for the non-inverted series [10, 11]. They are given in Table 1.

Table 1. Coefficients for the high-temperature series expansion of the inverse susceptibility (b_n) and the heat capacity (c_n) of the square-planar Heisenberg antiferromagnet with $S = 1$.

$b_1 = -$	5.333333333	$c_1 = -$	1.0
$b_2 =$	9.777777778	$c_2 = -$	1.333333333
$b_3 = -$	9.481481481	$c_3 =$	7.037037037
$b_4 =$	19.06172841	$c_4 = -$	33.33333333
$b_5 = -$	45.08971193	$c_5 =$	41.44691358
$b_6 = -$	25.46392318	$c_6 =$	225.0320974
$b_7 =$	146.5089541	$c_7 = -$	896.7755426
$b_8 = -$	193.7116826		

A good fit to the data is obtained with $J/k = -4.5(1)$ K and $g = 2.20(2)$, which is the solid curve in Figure 1.

Figure 2 presents the powder magnetization vs. field curve measured at $T = 4.2$ K. For $H < 7$ kOe a considerable amount of hysteresis is seen to be present. In zero field a spontaneous moment of $0.013 \mu_B$ is observed, indicating that the system is a weak ferromagnet, due to spin canting.

The canting is attributable to single-ion anisotropy in the tilted NiN_6 octahedra [12].

The insert of Fig. 2 shows magnetization measurements on the small single crystal, along its three orthorhombic directions. The data are very inaccurate due to misalignment and crystal imperfections. Despite these inaccuracies it seems justified to conclude that the weak ferromagnetic moment is probably parallel to the *b* direction. Its magnitude is estimated as $0.015 \mu_B$. The fact that this value is close to $0.013 \mu_B$, which was found for the powdered sample, is explained by a preferred orientation of the plate-like crystallites. It is to be noted that the members of the present series of $M(\text{trz})_2(\text{NCS})_2$ compounds can exhibit either overt or hidden canting.

Heat Capacity Measurements

The measured heat capacity as a function of temperature is shown in Figure 3. From the small peak (see insert of Fig. 3) the ordering temperature is found as $10.14(2)$ K. Like in the Fe and Co compounds [6, 7], the lattice specific heat has been obtained by scaling the lattice specific heat of the Cu compounds according to:

$$C_{\text{L,Ni}}(T) = C_{\text{L,Cu}}(T/1.14). \quad (2)$$

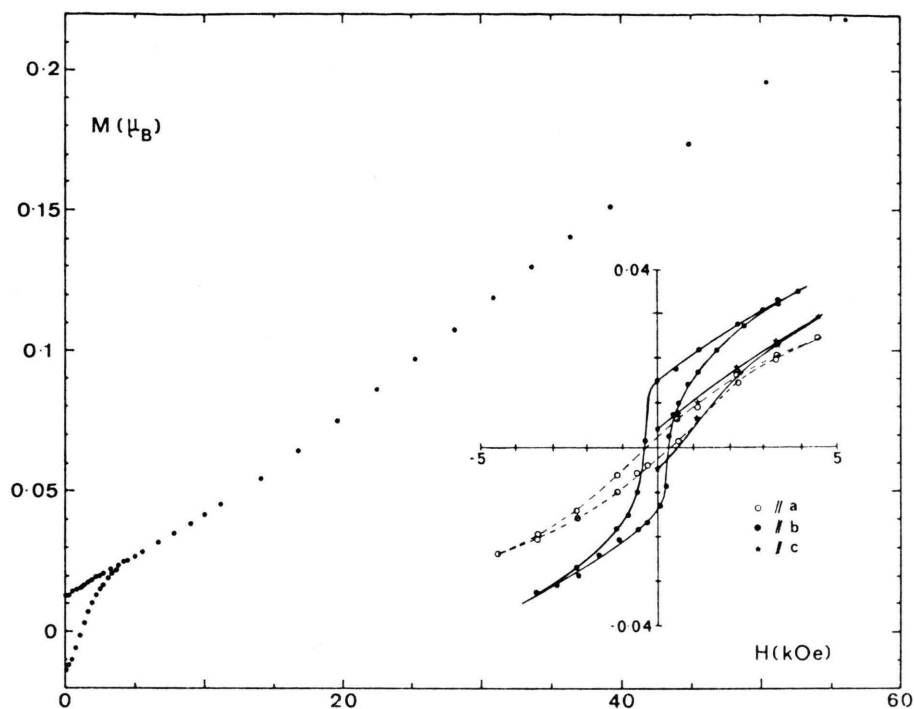


Fig. 2. Magnetization curve of powdered β -Nitrz. The insert shows magnetization measurements on an imperfect single crystal.

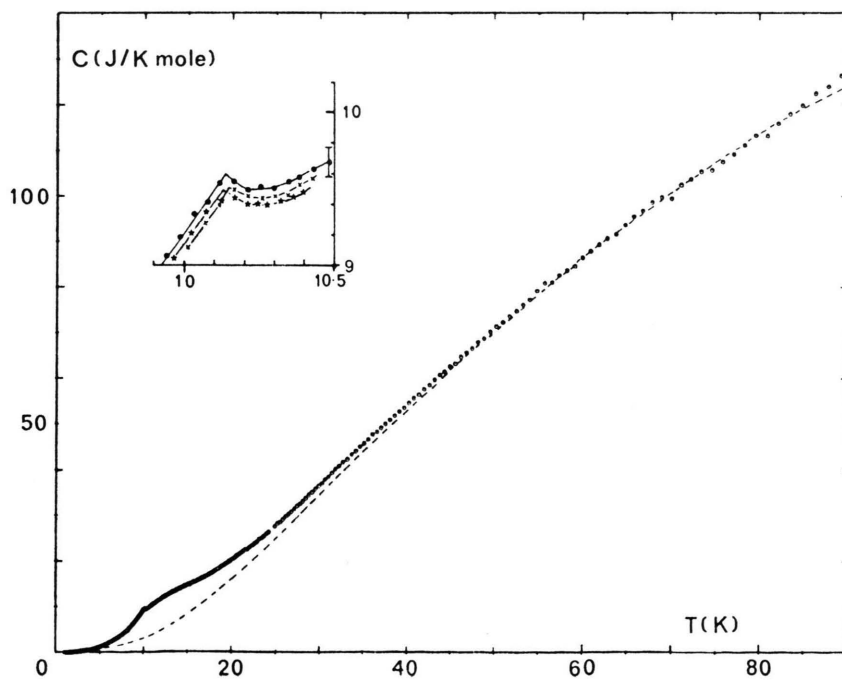


Fig. 3. The total heat capacity of β -Nitrz as a function of temperature. The drawn line is the lattice contribution. Measurements near T_c (three different runs) are shown in the insert.

The magnetic specific heat resulting after the subtraction of the above lattice contribution is shown in Figures 4 a and 4 b.

Theoretical predictions for the 2-d Heisenberg model are available only for the low-temperature region (spin-wave theory) and the high-temperature region (series expansion).

Analogous to the susceptibility, the high-temperature series for the magnetic specific heat can be written as:

$$C/R = \frac{2}{3} z S^2 (S+1)^2 (J/kT)^2 \cdot \left[1 + \sum_{n=1}^{\infty} c_n (J/kT)^n \right], \quad (3)$$

where $R = 8.3143$ J/mole K and $z (=4)$ is the number of nearest magnetic neighbours. The seven known coefficients for the $S=1$, quadratic layer Heisenberg model [9–11] are listed in Table 1.

With $J/k = -4.5$ K, as found from the susceptibility measurements, a fair fit is obtained (full line

in Figure 4 a). Below 20 K the convergence of the series is not very good, as can be seen from the curves calculated with six and seven terms of the series. The total magnetic energy E_0 and entropy S_{∞} have been determined by numerical integration of the data below 25 K and by integration of the series above 25 K. This procedure yielded $S_{\infty} = 8.9(3)$ J/mole K, which is close to the theoretical value of 9.13 J/mole K for a $S=1$ system. About 25% of the entropy is gained below T_c . For the total magnetic energy the value $E_0 = 173(7)$ J/mole is found, of which 9.8% is gained below T_c . The value of the exchange constant can be calculated from E_0 by means of the expression from spin-wave theory [13]:

$$E_0/R = z |J| S^2 (1 + e_0/z S) / k \quad (4)$$

where e_0 is a correction for zero point spin motions. With $e_0 = 0.632$, which is the value for the quadratic Heisenberg lattice [13], Eq. (4) yields $J/k = -4.5(2)$ K.

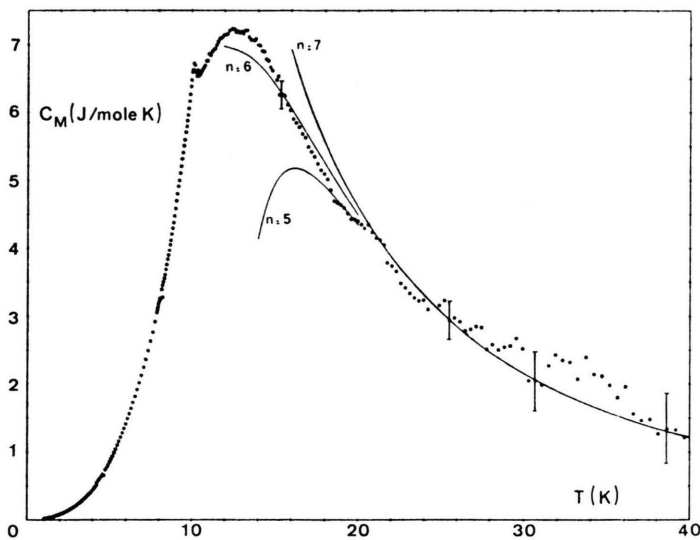


Fig. 4a.

Fig. 4a. The magnetic specific heat of β -Nitrz. The solid curves are the high-temperature series predictions for the quadratic 2-d Heisenberg antiferromagnet ($S=1$) with five, six and seven terms of the series, for $J/k = -4.5$ K.

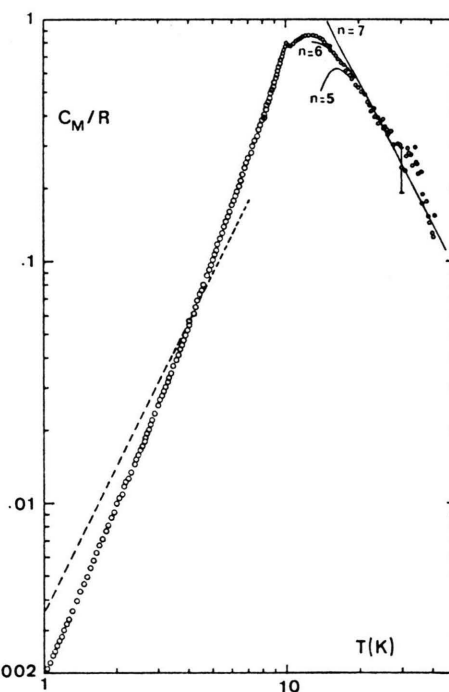


Fig. 4b. ▶

Fig. 4b. The magnetic specific heat of β -Nitrz in a double logarithmic plot. The dashed line is the spin wave prediction with $J/k = -4.5$ K. The solid curves are the high-temperature series predictions for the quadratic layer Heisenberg antiferromagnet ($S=1$) with five, six and seven terms, for $J/k = -4.5$ K.

Figure 4b gives the magnetic specific heat in a double logarithmic plot. The dashed line represents the spin-wave approximation [14] with $J/k = -4.5$ K, given by:

$$C_M/R = \frac{14.424}{\pi} (kT/2zJS)^2. \quad (5)$$

This prediction will at most be valid at low temperatures ($kT < |J|$). This explains the deviations above $T = 4$ K. The discrepancy between theory and experiment for $T < 4$ K might be due to the neglect of anisotropy in Equation (5) [15]. On the other hand, the validity of simple spin-wave theory for low-d antiferromagnets is still in doubt [16], in particular for small spin values. The only example in the literature with which our results can be compared are specific heat measurements on K_2NiF_4 by Salamon and Ikeda [17].

However, by scaling their data to ours we found a complete disagreement, not only with our specific heat curve, but also with the predictions obtained from the high-temperature series. Apparently, an accurate determination of the magnetic specific heat of K_2NiF_4 is hampered by its high ordering temperature ($T_c = 97$ K [18]). Thus, despite the scatter at higher temperatures, the data in Figs. 4a and 4b provide the only good example of the magnetic specific heat of the quadratic layer $S = 1$ Heisenberg antiferromagnet measured so far.

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