1,2,4-Triazole Complexes XIV *

Heat Capacity of the Quasi Two-dimensional Antiferromagnet $Mn(1,2,4\text{-triazole})_2(NCS)_2$

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Heat capacity measurements on $Mn(trz)_2(NCS)_2$ in the range 1–90 K are reported. A λ-anomaly is found at $T_c = 3.292(6)$ K. From a comparison of the high-temperature specific heat to the predictions from series expansions the intralayer exchange constant is found to be $J/k = 0.245(5)$ K. From the total magnetic energy involved in the transition the value $J/k = -0.254(8)$ K is calculated. These results compare favourably with previous data from susceptibility measurements.

From very recent X-ray diffraction experiments on a single crystal the space group is found to be Pbcn instead of Aba2, as was reported previously.

In a recent paper [1] it was shown that the magnetic properties of $Mn(1,2,4\text{-triazole})_2(NCS)_2$ are in good agreement with the predictions for a 2-d (d = dimensional) Heisenberg antiferromagnet. This compound is one of a series $M(II)(trz)_2(NCS)_2$ [2], where M is a 3d-metal, which exhibits 2-d magnetic properties [1, 3, 4] as is to be expected from the layered crystal structure [5, 6].

Very recent X-ray diffraction experiments on a single crystal of $Mn(trz)_2(NCS)_2$ indicated the space group to be Pbcn instead of Aba2, as we reported previously [1]. The axes were found as $a = 8.003(3)$, $b = 10.086(4)$, and $c = 16.256(4)$ Å. Thus the title compound is isomorphous to its Zn analogue, which also has a layered structure, very similar to that of the Co and Fe complexes [5]. This result does not affect the conclusions from the magnetic measurements. Both in Aba2 and Pbcn Mn is positioned on a two-fold axis, which must necessarily be primed. When we assume that below T_c the nuclear frame can still be described in Pbcn, the magnetic space group will be Pbcn′.

From magnetic susceptibility and magnetization measurements on single crystals the intralayer exchange constant was found as $J/k \equiv 0.25(1)$ K, while preliminary results from heat capacity measurements indicated the slightly lower value $-0.23(1)$ K [1].

In this note we present the heat capacity data on a powdered sample of $Mn(trz)_2(NCS)_2$. The measurements were performed in the temperature range 1–90 K, using conventional heat-pulse techniques [7].

Figure 1 shows the measured specific heat. From the peak the ordering temperature is found as $T_c = 3.292(6)$ K. Between 6 and 10 K the data could be well described by the equation

$$C = C_L + C_M = a\,T^3 + b\,T^{-2}, \qquad (1)$$

where C_L and C_M denote the lattice and magnetic contributions, respectively, to the specific heat. A good fit to Eq. (1) was obtained with

$$a = 4.2(1) \times 10^{-3}\ \mathrm{J/K^4\ mole} \ \text{ and}$$
$$b = 115(2)\ \mathrm{JK/mole}.$$

From the value of the coefficient b the exchange constant is calculated as $|J|/k = 0.26(1)$ K, using the Heisenberg model prediction:

$$C_M/R = \frac{2}{3} z (J/k\,T)^2 S^2 (S+1)^2, \qquad (2)$$

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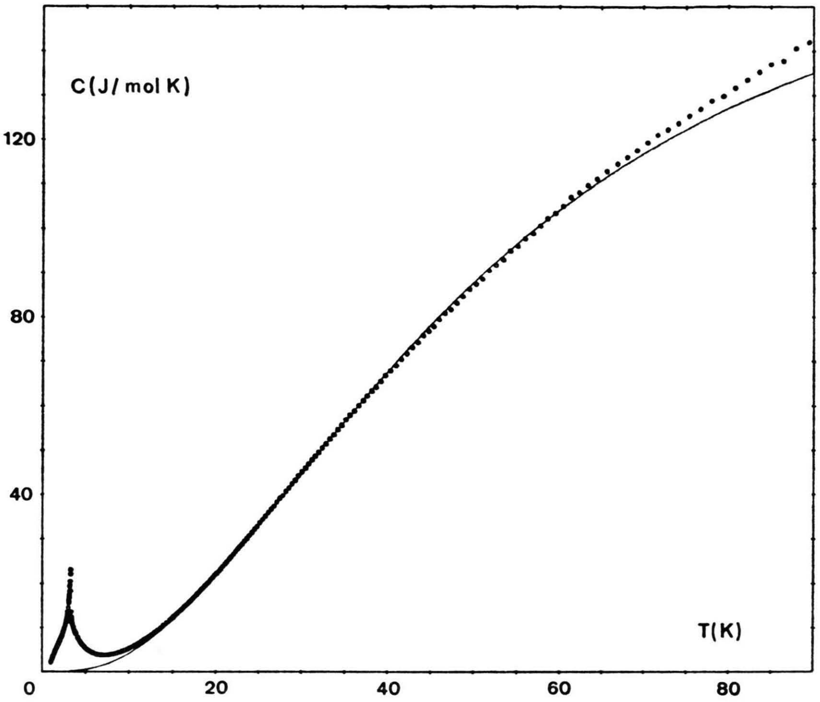

Fig. 1. The heat capacity of $Mn(trz)_2(NCS)_2$ as a function of temperature. The drawn line is the lattice contribution approximated by a combination of Debye functions, as described in the text.

where $z(=4)$ is the number of magnetic nearest neighbours and $R = 8.3143$ J/mole K.

It turned out that the lattice specific heat could not be described satisfactorily by a single multidimensional Debye function. Therefore, it was assumed that the lattice contribution can be approximated by a combination of Debye functions, each representing a different vibrational mode [8]. From Fig. 1 the total specific heat at room temperature is estimated to be ~ 175 J/mole K or ~ 20 R. Thus the total number of vibrational modes will be about 20. The trz groups were represented by a 6-d Debye function and Mn + NC by a 9-d one. The S atoms were treated separately by a 2-d and a 4-d Debye function. This was done since in all X-ray single crystal experiments on members of the present series the S atoms appeared to have large, anisotropic thermal parameters [5, 6]. Thus the data above 10 K were fitted to four Debye functions, plus a magnetic contribution 115 T^{-2}. The drawn line in Fig. 1 represents the fit obtained with ${}^2\Theta_D = 81$ K and ${}^4\Theta_D = 127$ K (for S), ${}^6\Theta_D = 217$ K (for trz) and ${}^9\Theta_D = 260$ (for Mn and NC). Below 40 K the fit is seen to be quite good. The deviations above 40 K need not concern us here, since we were mainly interested in separating the lattice and magnetic contributions at low temperatures.

The magnetic specific heat obtained after subtraction of the above lattice contribution is given in Figure 2. The high temperature specific heat has been compared with the predictions from the series expansion for the 2-d Heisenberg model with $S = 5/2$, using the available seven terms [9, 10, 11]. For $T > 5$ K (full line in Figure 2) there is good agreement with an intralayer exchange constant $J/k = -0.245(5)$ K.

In order to find the total magnetic energy E_0 and entropy S_∞ involved in the transition, the data in Fig. 2 were extrapolated to $T = \infty$ and $T = 0$ K. For the extrapolation to $T = 0$ K the spin-wave approximation [12]:

$$C_M/R = \frac{14.424}{\pi}\left(\frac{kT}{2zJS}\right)^2 \qquad (3)$$

was adopted. This prediction is given by the dashed line in Fig. 2, calculated with $J/k = -0.245$ K. The dotted line is the interpolation between the experimental data and the spin-wave prediction. The total magnetic entropy is found as $S_\infty = 15.0(5)$ J/mole K, which is in accordance with the theoretical value for an $S = 5/2$ system (14.9 J/mole K). The entropy gain below T_c amounts to 62% of the total. The magnetic energy is $E_0 = 56(2)$ J/mole, of which 35% is gained below T_c. From the magnetic

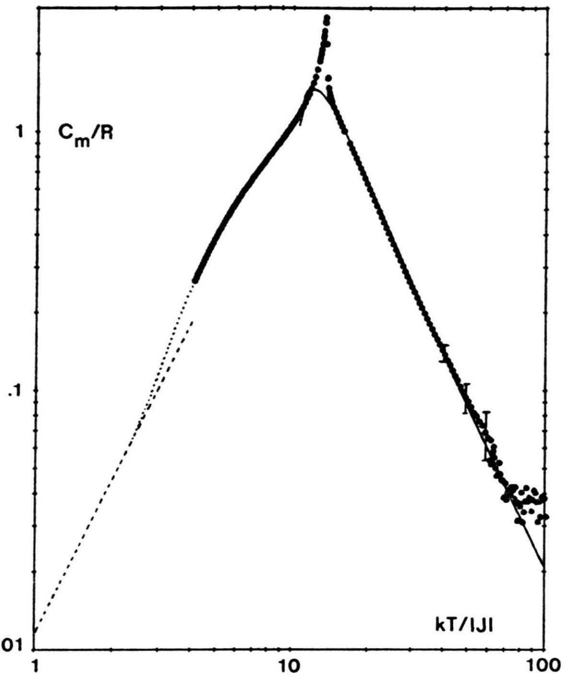

Fig. 2. The magnetic specific heat of $Mn(trz)_2(NCS)_2$. The full line is the prediction from the high-temperature series expansion with $J/k = -0.245$ K, the dashed line is the spin-wave prediction and the dotted line is the interpolation between the experimental data and the spin-wave prediction.

energy the value $|J|/k = -0.254(8)$ K is calculated using the formula given by spin-wave theory [13]:

$$E_0 = -N\,|J|\,zS^2(1 + e(\alpha)/zS)\,. \qquad (4)$$

$e(\alpha)$ is a correction arising from zero point spin motions. The anisotropy parameter α was previously found to be 0.04 [1]. For a quadratic Heisenberg antiferromagnet $e(\alpha) = 0.63$ when $\alpha = 0.04$ [13]. We conclude that the values for J/k resulting from the above analyses are in good agreement with $J/k = -0.25(1)$ K, found previously from the susceptibility and magnetization measurements.

Table 1. Comparison between some quadratic layer Mn antiferromagnets.

	T_c(K)	J/k(K)	$kT_c/\|J\|$
$Mn(trz)_2(NCS)_2$	3.29	− 0.25	13.1
$Mn(C_2H_5OH)_2(NCS)_2$ [14]	10.30	−10.88	11.7
$Mn(HCOO)_2 \cdot 2\,H_2O$ [15]	3.68	− 0.34	10.8

Table 1 presents a comparison with two other 2-d Mn antiferromagnetic with relatively low ordering temperatures. Since deviations form the ideal 2-d behaviour usually show up as an increase of $kT_c/|J|$, the title compound is apparently a less good example of a 2-d Heisenberg $S = 5/2$ antiferromagnet than the other two. The deviations from the ideal 2-d magnetic behaviour are mainly caused by the anisotropy, which is fairly high for a Mn compound. It should be pointed out that, strictly speaking, Eq. (3) is only valid for $\alpha = 0$. However, Eq. (3) was used only to determine the magnetic energy and entropy below 1 K. These were found to be about 2% and 10%, respectively, of E_0 and S_∞. Therefore we expect that the neglect of anisotropy in Eq. (3) will not influence the values for E_0 and S_∞ by more than a few percent.

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