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SPECIFIC HEAT ANALYSIS OF THE CHAIN-LIKE COMPOUNDS $Ni(C_2H_8N_2)_2Ni(CN)_4$ AND $Zn(C_2H_8N_2)_2Ni(CN)_4$[1]

M. Orendáč[2], A. Orendáčová , E. Čižmár, A. Feher, J. Černák
Faculty of Science, P.J. Šafárik University, Angelinum 9, 041 54 Košice, Slovak Republic

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The specific heat of $Ni(C_2H_8N_2)_2Ni(CN)_4$ (NENC) and its diamagnetic isomorph $Zn(C_2H_8N_2)_2Ni(CN)_4$ (ZENC) was measured between nominally 60 mK and 12 K. The analysis of ZENC specific heat explained the origin of the peculiar linear term observed in NENC magnetic specific heat under 500 mK. The applicability of a pseudoelastic approach for the analysis of ZENC data is discussed.

1. Introduction

In the last years much theoretical and experimental effort was devoted to study dynamic properties of $S = 1$ Heisenberg chains with easy plane anisotropy D. The chains with strong planar anisotropy ($D > |J|$) posses an energy gap between the singlet ground state (SGS) and the first excited level and the concept of (anti)excitons as out of easy-plane fluctuations from the SGS was proposed [1]. This singlet phase is significantly different from the Haldane phase ($D < |J|$) [2]. In this paper we present the results of the specific heat study of NENC and ZENC. The previous analysis [3] identified NENC as an $S = 1$ AF Heisenberg chain with $D/k = 6K$ and $D/|J| = 15 \pm 5$. The corresponding excitonic contribution to the specific heat provided a good description of the low- temperature magnetic specific heat data. A slight discrepancy between the data and theory observed under 500 mK was originally ascribed to the presence of a rhombic term and/or the powder character of the sample (finite length chains). Nevertheless, the recalculation of the excitonic specific heat with the rhombic term included did not remove the discrepancy. The simple comparison of the data with the ZENC specific heat explained the origin of the discrepancy. Here we report the results of a more detailed analysis of the NENC lattice and ZENC specific heat to point out an importance of a regular separation of lattice contribution.

[1] Presented at 9th Czech and Slovak conference on magnetism, Košice, Slovakia, August 28-30 1995
[2] E-mail address: orendac@kosice.upjs.sk

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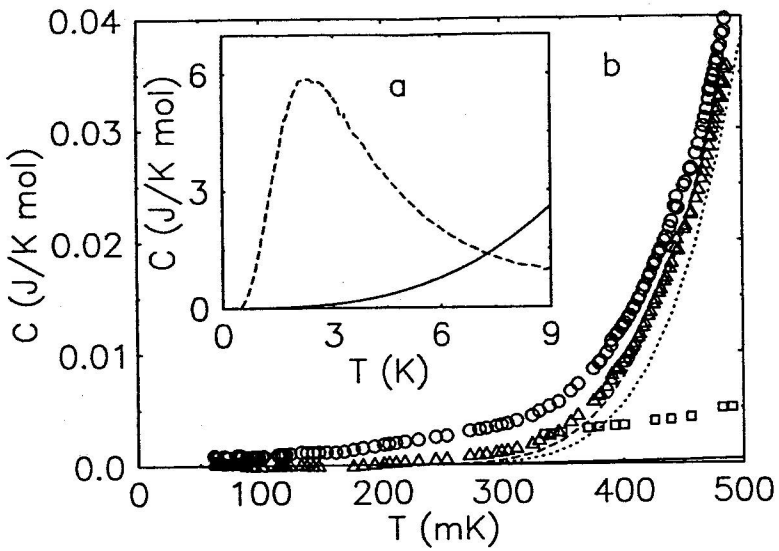

Fig.1. (a) Temperature dependence of NENC specific heat;the solid line represents lattice contribution in the Debye approximation, dashed line is the magnetic contribution. (b) Temperature dependence of the NENC and ZENC specific heat below 500 mK. The circles and triangles represent the magnetic specific heat after subtracting the lattice contribution using the Debye approximation and ZENC data, respectively. ZENC data are represented by squares. The solid line represents the Debye contribution; the dotted line represents the excitonic prediction with D/k=6 K, $D/|J| = 15$, E/k=0; the dashed curve is the result of the theoretical prediction for $D/k = 6.3$, $D/|J| = 15$, $E/k = 0.7K$.

2. Crystal structure

NENC crystallizes in the monoclinic space group $P2_1/n$, a=7.104 Å, b=10.671 Å, c=9.940 Å, $\beta = 114.68°$ [3]. The structure is built up from neutral $-[Ni(en)_2 - NC - Ni(CN)_2 - CN]-$ chains running along the c-axis with no bonding among them. Consequently, NENC posseses all structural features necessary for a quasi - one - dimensional system. ZENC represents a diamagnetic isomorph of NENC with a=7.173 Å, b=10.606 Å, c=10.091 Å, $\beta = 115.91°$ [4].

3. Experimental

The specific heat measurements of powdered coin-shaped (15 mm in diameter and 2 mm thick) samples of 0.1 g were performed in two experimental devices. For $60mK < T < 2.5K$, the dual slope method was used in a dilution refrigerator [3], at higher temperatures, standard adiabatic calorimetry was used in a ^4He cryostat. The overall accuracy of the dual slope data is better than 5% while a 3% accuracy was achieved with the adiabatic technique.

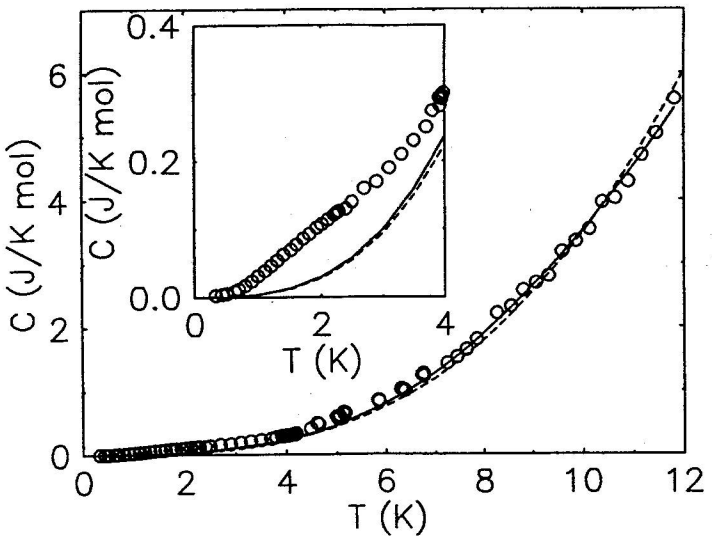

Fig.2: Temperature dependence of ZENC specific heat (circles); the dashed line represents the lattice contribution in the Debye approximation;the solid line is the result of the pseudoelastic approach. The detailed look at the difference between the data and theoretical predictions below 4 K is shown in the inset.

4. Results and discussion

NENC: Only lattice and magnetic systems contribute to the total specific heat. The lattice was separated by a standard procedure based on the finding the temperature region where the data may be described by the equation $C(T) = aT^{-2} + bT^3$. The bT^3 term represents the low temperature lattice contribution in the Debye approximation, while aT^{-2} describes the high temperature magnetic specific heat behaviour. For $5K < T < 9K$, a least squares fit yielded $a = 69 \pm 3.5 JK/mol$ and $b = (3.55 \pm 0.15)\text{x}10^{-3} J/K^4 mol$ (Fig.1a). The value of magnetic entropy S_m calculated from the data after the lattice separation is 8.67 J/K mol which represents 95% from the theoretical R.ln(2S+1) for S=1 system. This way of lattice subtraction led to the appearence of a discrepancy between the data and the excitonic prediction observed under 500 mK (Fig.1b). In order to obtain a better estimation of lattice contribution, a scaling procedure [5] was applied using ZENC; then C(lat,T)= C(ZENC,rT)[1+(dlnr)/(dlnT)], where r is a scaling factor. The analysis yielded $r \approx 1$, thus in the first approximation $C(lat,T) \approx C(ZENC,T)$. The S_m recalculation using C(lat,T) yielded 8.40 J/K mol which is 3% lower than the previous experimental value. Despite of the slight entropy change which is within the measurements accuracy, the agreement between low temperature magnetic specific heat and the excitonic contribution is significantly improved (see Fig. 1b).

ZENC: The specific heat is shown in the Fig.2. The data were also fitted by

bT^3 dependence in the whole temperature region. The obtained value $b = (3.49 \pm 0.15)\text{x}10^{-3} J/K^4 mol$ yielded $\Theta_D = 103K$ and is very near to that obtained for NENC which supports the correctness of the scaling procedure; the discrepancy between the theory and data below 4 K indicates a presence of other terms which might result from the nature of the chain-like system (inset of Fig.2). To verify this assumption, the pseudoelastic approach [6] which takes into account an anisotropy of the system was used; the theoretical prediction is: $C_L = F_1(\Theta_l, \Theta_c, T) + F_1(\Theta_t, \Theta_c, T) + F_2(2\Theta_l, 2\Theta_c, T)$; F_1 is the contribution of longitudinal and transverse modes spreading perpendicularly to the chain, F_2 represents the mode in the chain direction, Θ_l, Θ_t and Θ_c are related to the elastic constants. The fitting procedure in the whole region yielded $\Theta_l = 585K$, $\Theta_t = 245K$, $\Theta_c = 38K$ (Fig.2). Since the curve is nearly identical with the Debye prediction, the anomaly below 4 K cannot be ascribed to the anisotropy which should dominate at higher temperatures. This explaines the fact that the description of the quasi-linear term under 4 K by one-dimensional Debye function (system of independent chains), did not give physical results. Since the anomaly was also observed on the various independent NENC samples (the calorimetry adenda was subtracted), it could be an intrinsic property associated with the powder character of the samples.

5. Conclusion

The analysis showed the importance of a regular separation of lattice, especially when the magnetic contribution is comparable with the lattice one at lowest temperatures. Insight into the origin of the anomaly could be provided by performing the experiments with sufficiently large single crystals.

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