Proceedings of the European Conference "Physics of Magnetism '99", Poznań 1999

# EXPERIMENTAL STUDIES OF $S = 1$ HEISENBERG PLANAR ANTIFERROMAGNETIC CHAIN $Ni(C_{11}H_{10}N_2O)_2Ni(CN)_4$

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In this paper we discuss the results of experimental studies of specific heat and magnetic susceptibility of chain compound $Ni(C_{11}H_{10}N_2O)_2Ni(CN)_4$. We have observed a Schottky type anomaly at $T = 2.2$ K in a temperature dependence of specific heat and the compound was identified as a $S = 1$ Heisenberg antiferromagnetic chain with the subcritical exchange coupling $D/k_B = 5$ K, $D/|J| = 5.2$ and the strong in-plane anisotropy $E/k_B = 2.8$ K. It has been found that the in-plane anisotropy affects the region of validity of a diluted exciton model [1] and a strong coupling model [2] for $S = 1$ Heisenberg chains with the strong planar anisotropy. The analysis suggests that the in-plane anisotropy should be considered in any attempt to find a compound potentially located in the boundary of Haldane and "large-D" phases.

PACS numbers: 75.40.Cx, 71.20.Be, 75.50.Ee

Antiferromagnetic Heisenberg chains with the spin $S = 1$ have received attention in the connection with the existence of the predicted Haldane gap in their excitation spectrum [1]. This kind of a gap persists in the presence of a weak easy-plane anisotropy and is vanishing at some critical value of the anisotropy constant $D_c \approx J$ [2]. Up to now the existence of Haldane gap has been experimentally confirmed in many compounds [3, 4], the origin of the gap is theoretically explained [5].

For values $D/J > 1$, a gap of a different nature appears and is still present in both antiferromagnetic and ferromagnetic chains. The properties of systems with the strong planar anisotropy the (so-called "large-D" systems) with the elementary excitations from the singlet ground state were studied using both a semiclassical [2] and a strong-coupling method [6]. The extension of the strong-coupling model to the high temperature region includes the effect of external magnetic field and the in-plane anisotropy $E$, which is always present in real systems [7]. The diluted exciton approximation of the (anti)excitonic model [6] was used for a successful identification of $Ni(C_2H_8N_2)_2Ni(CN)_4$ (NENC) as a "large-D" system [8]. Up to date, no $S = 1$ material has been identified as existing close to the $D/J \approx 1$ quantum critical point.

The experimental study of chain-like powdered $Ni(C_{11}H_{10}N_2O)_2Ni(CN)_4$ (hereafter abbreviated as NDPK) has been carried out with the aim to obtain the system close to the phase boundary between Haldane phase and "large-D" phase ($D/J \approx 1$). The detailed crystal structure of NDPK has not been determined yet, but from the infrared spectrum of the compound we can deduce the main structural features. The $Ni^{2+}$ ion surrounded by four CN groups is diamagnetic and the $Ni^{2+}$ ion placed in the center of distorted nitrogen octahedron is paramagnetic. Since the group $C_{11}H_8N_2O$ obtains a different type of delocalization of charge density as $C_2H_8N_2$ in a similar chain material NENC, we have tried to change the surrounding of the magnetic $Ni^{2+}$ ion with the expectation to receive the system with the critical anisotropy.

The specific heat of NDPK was studied in the temperature range from 100 mK to 2.5 K in zero magnetic field using a dual-slope method [9] in a commercial dilution refrigerator TLE 200. $RuO_2$ resistor of Dale type with the nominal value of 4700 Ω was used for monitoring the temperature of the sample. The thermometer was calibrated against the commercial Lake Shore thermometer GR200A-30. For studying magnetic susceptibility in the temperature range of 1.5 K–25 K in the field 5 mT a commercial SQUID magnetometer was used.

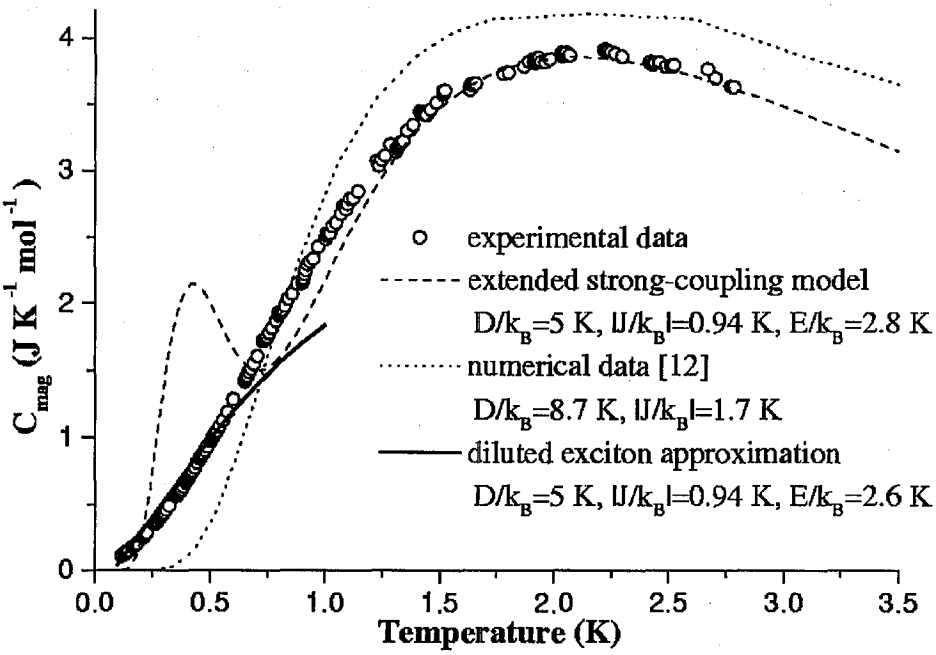


Fig. 1. Specific heat of NDPK. The dashed line represents the extended strong-coupling model [7] for $D/k_B = 5$ K, $|J/k_B| = 0.96$ K and $E/k_B = 2.8$ K, the dotted line denotes Blöte's numerical data [11] for $D/k_B = 8.7$ K and $|J/k_B| = 1.7$ K. The full line represents the diluted exciton approximation [7].

In a temperature dependence of the specific heat of NDPK we can observe the broad maximum at $T_{max} \cong 2.2$ K (Fig. 1). The previously studied properties of the $Ni(X)_2Ni(CN)_4$ group of compounds suggest that we can neglect the lattice contribution to the specific heat below 2.5 K [10]. The obtained data were compared with numerical prediction of Blöte [11]. The best agreement between the numerical prediction and the experimental data was obtained for $D/k_B = 8.7$ K and $D/|J| = 5$. This result suggests that the system is located in the "large-D" phase rather than near the phase boundary. The unsatisfactorily quantitative agreement prompted us to reanalyse the data using the extended strong-coupling model [7] to study the influence of the in-plane anisotropy $E$ as a potential source of the discrepancy. The validity of the used model for $E = 0$ is limited to $(D/J)_c = 2.5$, the deteriorating of the theory at low temperatures manifests itself as a kink-like anomaly of artificial origin on the ascending side of the specific heat curve [7]. We found good quantitative agreement with the experimental data for $D/k_B = 5$ K, $|J/k_B| = 0.96$ K and $E/k_B = 2.8$ K. The formation of the aforementioned anomaly in the theoretical prediction suggests a significant increase in $(D/J)_c$ for non-zero $E$. Also, the diluted exciton approximation [7] fails in the description of the low temperature data of NDPK as can be seen in Fig. 1. This confirms that the validity of dilute approximation is also restricted to low $E$ values.

The experimental data of magnetic susceptibility were also evaluated using the extended strong-coupling model. The bestagreement between experimental

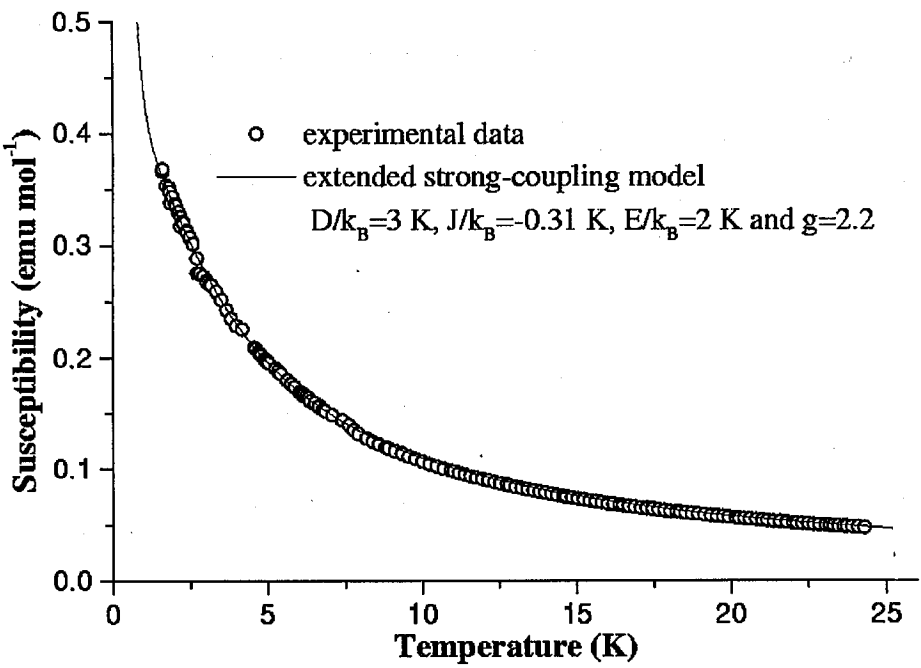


Fig. 2. Magnetic susceptibility of NDPK. The full line represents the extended strong-coupling model [7] for $D/k_B = 3$ K, $J/k_B = -0.31$ K, $E/k_B = 2$ K, and $g = 2.2$.

data and theoretical model was obtained for $D/k_B = 3$ K, $J/k_B = -0.31$ K, $E/k_B = 2$ K and $g = 2.2$ (Fig. 2). Taking into the account that powder material was used for susceptibility studies the agreement between the $D, J, E$ values as obtained from the analysis of specific heat and susceptibility data can be considered reasonable. These results confirm the presence of the strong in-plane anisotropy in the studied system.

It may be concluded that the replacing of $C_{11}H_8N_2O$ for $C_2H_8N_2$ group induces the strong in-plane anisotropy thus NDPK is not a system near the boundary of Haldane and "large-D" phases. The obtained results suggest that NDPK is a $S = 1$ Heisenberg chain with a subcritical exchange coupling and strong in-plane anisotropy. The analysis of experimental data yields the result that the region of the validity of the strong-coupling model is significantly delimited by the value of the in-plane anisotropy. The renormalization of $D, J$ values after involving $E$ term revealed that the influence of the in-plane anisotropy should be taken into account in search for a system potentially located near the phase boundary of Haldane phase and "large-D" phase.

This investigation has been supported by a grant of Slovak Ministry of Education and Science (No. 1/4385/97) and by Slovak–Greek bilateral program. Support of the Large Scale Facility Program of the European Community under contract No. ERB-CHGE-CT920002, ERB-CIPD-CT940091 is gratefully acknowledged.

## References

[1] F.D.M. Haldane, *Phys. Lett. A* **93**, 464 (1983).

[2] O. Golinelli, T. Jolicoeur, R. Lacaze, *Phys. Rev. B* **46**, 10854 (1992).

[3] J. Darriel, L.P. Regnault, *Solid State Commun.* **86**, 409 (1993).

[4] T.M. Brill, J.P. Boucher, L.C. Brunel, J.P. Renard, M. Verdaguer, *Physica B* **204**, 303 (1995).

[5] I. Affleck, *Phys. Rev. B* **43**, 3215 (1991).

[6] N. Papanicolaou, P. Spathis, *J. Phys., Condens. Matter* **2**, 6575 (1990).

[7] N. Papanicolaou, P. Spathis, *Phys. Rev. B* **52**, 16001 (1995).

[8] M. Orendáč, A. Orendáčová, J. Černák, A. Feher, P.J.C. Signore, M.W. Meisel, S. Merah, M. Verdaguer, *Phys. Rev. B* **52**, 3435 (1995).

[9] S. Riegel, G. Weber, *J. Phys. E, Sci. Instrum.* **19**, 790 (1986).

[10] M. Orendáč, A. Orendáčová, J. Černák, A. Feher, *Solid State Commun.* **94**, 833 (1995).

[11] H.W.J. Blöte, *Physica B* **79**, 427 (1975).