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Lattice Dynamics in $Cu(en)(H_2O)_2SO_4$ — A Low-Dimensional Quantum Magnet with Spin 1/2

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The present work is devoted to the refinement of lattice contribution to the specific heat of magnetic insulator $Cu(en)(H_2O)_2SO_4$. The analysis of thermodynamic and elastic measurements revealed that the uncertainty in the determination of this contribution did not affect the selection of the magnetic model.

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PACS/topics: lattice specific heat, Debye temperature, Heisenberg antiferromagnet

1. Introduction

The quantum magnets with a reduced lattice dimension are intensively investigated because such systems can display the interplay between geometrical frustration and quantum fluctuations and show various crossover phenomena [1]. One of these attractive magnetic systems is an organo-metallic compound $Cu(en)(H_2O)_2SO_4$, ($en = C_2H_8N_2$), (CUEN) whose nature of magnetic interactions has gradually evolved over time. CUEN was originally identified as a representative of a partially frustrated $S = 1/2$ Heisenberg antiferromagnet (HAF) on the spatially anisotropic triangular lattice with the Néel ground state [2]. A subtracting of a lattice contribution described by a simple Debye approximation bT^3 yielded the magnetic specific heat, which was analyzed within the models available at that time (i.e., HAF chain, HAF on the isotropic square and isotropic triangular lattice). The analysis did not provide a suitable description of the specific heat data due to the absence of more sophisticated two-dimensional (2D) HAF models. The magnetic specific heat data of CUEN served as a hint for the subsequent *ab initio* investigation of the exchange interactions in CUEN [3]. The studies [3] identified the magnetic subsystem of CUEN as a 2D array of weakly coupled zigzag chains forming a spatially anisotropic zigzag square lattice. The lack of corresponding theoretical predictions triggered further complex study of CUEN involving the spin and spatial anisotropy analysis completed with the extended quantum Monte Carlo (QMC) calculations of finite-temperature properties of the $S = 1/2$ HAF on the spatially anisotropic zigzag square lattice [4]. The application of the QMC predictions provided the best agreement with experimental specific heat, susceptibility and magnetization data for the intra-chain coupling $J_1/k_B = 3.5$ K and the inter-chain coupling $J_2 = R\,J_1$, with $R = 0.3$–0.4. It should be noted that the theoretical predictions for the specific heat of the spatially anisotropic zigzag square lattice are very similar for such close R values. Thus, to exclude any impact of the subtracting of the phonon contribution on the choice of the magnetic model, theoretical study of elastic properties in CUEN was performed only recently [5].

The results of the work [5] have motivated the present analysis of the experimental total specific heat data to verify whether the subtraction of the lattice contribution can potentially affect the selection of an adequate magnetic model describing magnetism in CUEN.

2. Experimental details

The crystal structure of $Cu(en)(H_2O)_2SO_4$, established at 300 K, is monoclinic (space group $C2/c$) with unit-cell parameters $a = 7.232$ Å, $b = 11.725$ Å, and $c = 9.768$ Å, $\beta = 105.5°$, $Z = 4$ (number of molecules in the unit cell), and $\rho = 1.96$ g/cm^3 [6]. The covalent chains formed by Cu(II) ions running along the a-axis are coupled via a system of hydrogen bonds to the 3D structure. The local surrounding of the Cu(II) ion is built of four Cl and two N atoms forming a distorted octahedron elongated along the a-axis.

The specific heat of CUEN single crystal was measured in the temperature range from 1.8 to 15 K in zero magnetic field using a commercial Quantum Design PPMS device at P.J. Šafárik University in Košice. The measurement of elastic properties of CUEN including Young modulus was performed by a nanoindentation technique applying pressure along the b-axis direction using a commercial CSM Nanohardness Tester device at The Vienna University of Technology.

3. Results and discussion

Since the studied material is an insulator, the total specific heat consists of two contributions which have a dominant influence in a proper temperature region (Fig. 1).

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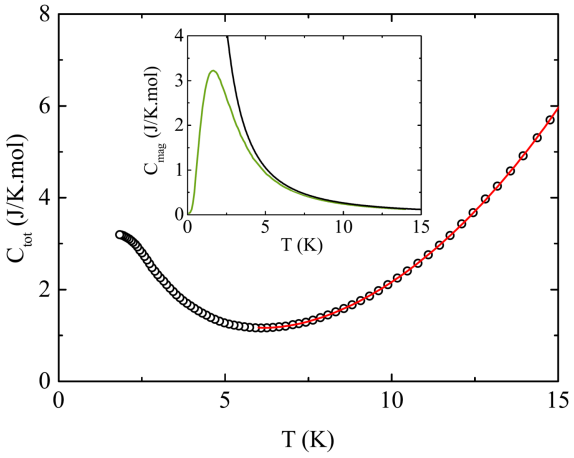

Fig. 1. The temperature dependence of total specific heat of $Cu(en)(H_2O)_2SO_4$ single crystal in zero magnetic field (symbols). The red solid line represents the fit by (1). Inset: the temperature dependence of the magnetic specific heat — the green line represents the $S = 1/2$ HAF on the spatially anisotropic zigzag square lattice with $J_2/J_1 = 0.35$, $J_1/k_B = 3.5$ K [4]. The black line represents the fitting formula $26.32/T^2$.

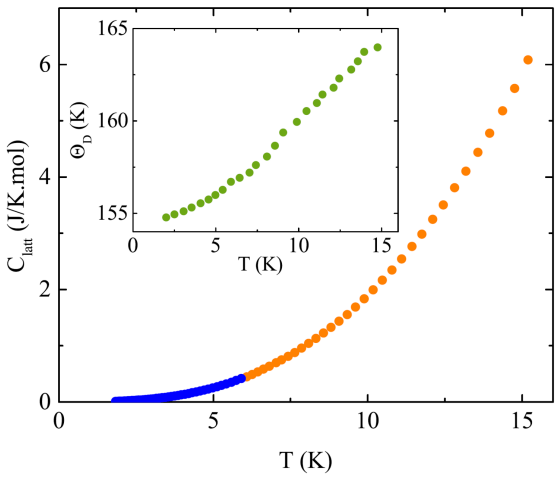

Fig. 2. The temperature dependence of lattice specific heat in $Cu(en)(H_2O)_2SO_4$. The different colours of symbols relate to different methods for the determination of the lattice specific heat. Inset: the temperature dependence of Debye temperature in $Cu(en)(H_2O)_2SO_4$.

At sufficiently high temperatures, the magnetic specific heat $C_{\rm mag}$, behaves as $C_{\rm mag} \cong 1/T^2$ [7], while at low temperatures the lattice contribution $C_{\rm latt}$, can be approximated by $C_{\rm latt} = bT^3 + cT^5 + dT^7$ [8]. Thus, at sufficiently hight temperatures the total specific heat is equal to

$$C_{\rm tot} = \frac{a}{T^2} + bT^3 + cT^5 + dT^7. \qquad (1)$$

The temperature dependence of total specific heat was fitted with Eq. (1) in the temperature range from 6 to 15 K. The best agreement was obtained for the parameters values $a = 26.32$ J K/mol, $b = 2.11 \times 10^{-3}$ J/(K^4 mol), $c = -2.43 \times 10^{-6}$ J/(K^6 mol), $d = 3.29 \times 10^{-9}$ J/(K^8 mol). The fitting parameter b relates to the Debye temperature $\Theta_{\rm D}$ as follows [9]:

$$b = \frac{12\pi^4}{5}\frac{ZR}{\Theta_{\rm D}^3}, \qquad (2)$$

where $\Theta_{\rm D} = 154$ K was obtained (R is gas constant).

The suitability of the selected temperature fitting region was verified by comparing $C_{\rm mag} = 26.32/T^2$ with the theoretical prediction for the $S = 1/2$ HAF on the spatially anisotropic zigzag square lattice with $J_2/J_1 = 0.35$ and $J_1/k_{\rm B} = 3.5$ K (inset in Fig. 1). As mentioned earlier, the model was used in the previous complex study [4]. As Fig. 1 demonstrates, a comparison of both dependences indicates that they have very similar behaviour above 6 K. Therefore, to extract the lattice specific heat, the entire temperature region was divided into two intervals: (i) above 6 K the lattice specific heat is determined as $C_{\rm latt} = C_{\rm tot} - 26.32/T^2$, and (ii) below 6 K we use $C_{\rm latt} = bT^3 + cT^5 + dT^7$ considering obtained fitting parameters.

In the further steps, the obtained C_{latt} of CUEN was analyzed using 3D Debye function [9]:

$$C_{\rm latt} = 3ZNk_{\rm B}^3\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_{\rm D}/T} \frac{z^4\exp(z)}{(\exp(z)-1)^2}\,{\rm d}z, \qquad (3)$$

where N is number of unit cells in a unit volume and $z = \Theta_{\rm D}/T$. The application of (3) for each data point of lattice specific heat [9] provided a temperature dependence of $\Theta_{\rm D}$ which decreases with lowering the temperature (inset in Fig. 2). The values of $\Theta_{\rm D}$ range from 154 to 165 K. Apparently, the value $\Theta_{\rm D} = 154$ K obtained from the fitting parameter b using (2) falls into the interval serving as a low-temperature limit for $\Theta_{\rm D}$.

The C_{latt} could also be determined from the elastic constants of the material which are related directly to

$$\Theta_{\rm D} = \frac{\hbar v}{k_{\rm B}}\sqrt[3]{6\pi^2 NZ}. \qquad (4)$$

The formula considers an average velocity v of the acoustic waves propagating through the material.

The experimental value of the Young modulus E along the b-axis was estimated from nanoindentation measurement $E_b = 48 \pm 9$ GPa which is in a good agreement with the value 41 GPa obtained from first principles calculations [5]. It should be emphasized that the (4) considers the averaging of velocities across all directions and polarizations in the studied material. Since the shape of the single crystal did not allow to obtain reliable results in other directions, we used for comparison with thermodynamic data the results from *ab initio* studies of the elastic properties of CUEN [5]. The calculations provided the average velocity $v = 3031$ m/s and corresponding $\Theta_{\rm D} = 156$ K which is in the excellent agreement with $\Theta_{\rm D} = 154$ K.

In further step, we verified, whether experimental magnetic specific heat maximum $C_{\max}^{\mathrm{mag}}$ (the $C_{\max}^{\mathrm{mag}}$ values are crucial for the choice of the magnetic model) is not affected by the separation of C_{latt}. The difference between theoretical $C_{\max}^{\mathrm{mag}}$ values for $R = 0.3$ and 0.4 is $\Delta C_{\max}^{\mathrm{mag}} = 0.161$ J/(K mol). The value of C_{latt} at 1.8 K (the position of the experimental $C_{\max}^{\mathrm{mag}}$) is 0.013 J/(K mol), which is one order of magnitude lower than theoretical $\Delta C_{\max}^{\mathrm{mag}}$. This indicates that in CUEN the separation of C_{latt} should not affect the choice of the magnetic model.

4. Conclusion

The analysis of the total specific heat in zero magnetic field based on the latest theoretical and experimental studies of CUEN enabled reliable separation of lattice contribution which is characterized by $\Theta_{\mathrm{D}} = 154$ K. It was revealed that the uncertainty in the determination of the lattice specific heat in CUEN should not significantly affect the selection of the proper magnetic model made in [4].

Acknowledgments

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