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Long-range magnetic ordering of quasi-one-dimensional $S = 1/2$ Heisenberg antiferromagnet $Sr_2Cu(PO_4)_2$

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Abstract

Magnetic properties of quasi-one-dimensional $S = 1/2$ Heisenberg antiferromagnet $Sr_2Cu(PO_4)_2$ were investigated by temperature and field dependence of AC susceptibility down to 0.03 K. A sharp peak was observed at $T_N = 0.085$ K on the temperature dependence of AC susceptibility indicating long-range magnetic ordering. Taking into account the exchange constant, $J/k_B = 143$ K (Hamiltonian $= J\sum S_iS_{i+1}$), the ratio k_BT_N/J is 0.06%. $Sr_2Cu(PO_4)_2$ is, therefore, one of the best one-dimensional Heisenberg antiferromagnet known so far.

Keywords: Copper phosphate; Heisenberg antiferromagnet; One-dimensional system; AC magnetic susceptibility; Long-range ordering

1. Introduction

Low-dimensional quantum magnets have been a subject of intense studies in recent years. In particular, one-dimensional (1D) systems have attracted a lot of attention because of interesting ground states and difference between half-integer-spin and integer-spin chains [1,2]. A uniform Heisenberg antiferromagnetic $S = 1/2$ (S is spin) chain has a gapless spin excitation spectrum. The ground state is disordered because of strong quantum fluctuations. Theoretically, 1D gapless systems do not undergo three-dimensional (3D) magnetic ordering. However, real quasi-1D gapless systems exhibit long-range ordering (LRO) due to finite interchain interactions.

To compare theory and experiments and to study 1D magnetism, 1D properties should remain in a wide temperature range suitable for experimental work. There are few excellent realizations of the $S = 1/2$ linear chain Heisenberg antiferromagnet. One example is Sr_2CuO_3 with the exchange coupling constant, J/k_B (Hamiltonian $= J\sum S_iS_{i+1}$ throughout the paper), of about 2200 ± 200 K and $T_N = 5.4$ K having the ratio $k_BT_N/J \approx 0.25\%$ [3,4]. However because of the large J/k_B, the experimental temperature range is limited by $k_BT/J < 0.5$. Another example is copper benzoate $Cu(C_6H_5COO)_2{*}3H_2O$ with $J/k_B = 17.2$ K [2]. The temperature of LRO in this compound is controversial. Recent AC susceptibility experiments showed that $T_N = 0.8$ mK giving $k_BT_N/J = 0.0047\%$ [5]. We have recently found that $Sr_2Cu(PO_4)_2$ [6] ($J/k_B = 143.6$ K) and $Ba_2Cu(PO_4)_2$ [7] ($J/k_B = 132.2$ K) are also excellent $S = 1/2$ linear chain Heisenberg antiferromagnets [8,9]. The J/k_B in these compounds is about one order of magnitude smaller than that of Sr_2CuO_3 and about one order of magnitude larger than that of copper benzoate. No LRO was observed in $Sr_2Cu(PO_4)_2$ and $Ba_2Cu(PO_4)_2$ down to 0.45 K using specific heat measurements [8,9]. $Sr_2Cu(PO_4)_2$ is a good illustration of the importance of super-superexchange interactions, Cu–O···O–Cu, where the O···O is an edge of a PO_4 group, in determining the patterns of strongly interacting exchange paths [10,11].

In this work, we have determined the temperature of LRO in $Sr_2Cu(PO_4)_2$, which is 0.085 K giving the ratio $k_BT_N/J = 0.06\%$.

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2. Experiment section

$Sr_2Cu(PO_4)_2$ was prepared from stoichiometric mixtures of $SrCO_3$ (99.99%), CuO (99.99%), and $NH_4H_2PO_4$ (99.8%) by the solid-state method. The mixture was heated very slowly from room temperature to 770 K in a Pt crucible, reground, then pressed into pellets and allowed to react at 1150 K for 200 h with five intermediate grindings. X-ray powder diffraction (XRD) data showed that $Sr_2Cu(PO_4)_2$ was single-phased.

DC magnetic susceptibilities, $\chi = M/H$, of $Sr_2Cu(PO_4)_2$ were measured on a SQUID magnetometer (Quantum Design, MPMS XL) between 1.8 and 400 K in an applied field of 1 T. Isothermal DC magnetization curves were recorded at 1.8 K from 0 to 7 T.

Zero-field temperature-dependent and field-dependent isothermal AC susceptibility measurements were performed using a 20 T superconducting magnet with a top-loading dilution refrigerator (Oxford Instruments) between 1.8 and 0.03 K at frequency (f) of 17.43 Hz and applied oscillating magnetic fields (H_{AC}) of 2.04×10^{-4} and 1.02×10^{-3} T.

3. Results and discussion

Fig. 1 presents plots of experimental and calculated χ against temperature, T, for $Sr_2Cu(PO_4)_2$. The experimental data were fitted using the equation

$$\chi_{fit}(T) = \chi_0 + C_{imp}/(T - \theta_{imp}) + \chi_{chain}(T), \quad (1)$$

where $\chi_{chain}(T)$ is the spin susceptibility curve of the uniform $S = 1/2$ chain [12] parameterised by Johnston et al. (Eqs. (50) in Ref. 1). The fitted parameters are $\chi_0 = -3.68(2) \times 10^{-4}$ cm^{3}K/Cu-mol (temperature independent term), $C_{imp} = 1.495(10) \times 10^{-3}$ cm^{3}K/Cu-mol (impurity Curie constant), $\theta_{imp} = -0.061(16)$ K (impurity Weiss constant), $g = 2.140(2)$, and $J/k_B = 143.21(14)$ K. The obtained J/k_B is similar to the previously reported value [8,9]. In Ref. [13], the J/k_B of 152(12) K was deduced from magnetic susceptibility data. Such difference can be attributed in part to the much larger contribution of the impurity term in Ref. [13] because of the presence [14] of a noticeable amount (5–8%) of an impurity, $Sr_3Cu_3(PO_4)_4$. However magnetic susceptibility of $Sr_3Cu_3(PO_4)_4$ cannot be fit by the second term in Eq. (1) ($C_{imp}/(T - \theta_{imp})$) because of the formation of trimers in $Sr_3Cu_3(PO_4)_4$ [15].

Inset of Fig. 1 gives the DC isothermal magnetization curve at 1.8 K up to 7 T. The magnetic moment was $0.015\mu_B$ at 7 T. Because of a small intrinsic magnetic moment compared with the excepted saturated value of about $1\mu_B$, the $M(H)$ curve is influenced by the presence of paramagnetic impurities or defects which is the origin of the upturn on the $\chi(T)$ curve at low temperatures. This is a possible reason of the deviation from the linear behavior of the $M(H)$ curve (inset of Fig. 1).

Fig. 2 depicts the temperature dependence of the AC susceptibility curve. A sharp peak was observed at 0.085 K. This is the indication of the onset of LRO. The peak was observed using $H_{AC} = 2.04 \times 10^{-4}$ and 1.02×10^{-3} T. However in the case of $H_{AC} = 2.04 \times 10^{-4}$ T, the signal-to-noise ratio was worse. The presence of the sharp peak on the AC susceptibility curve may exclude the possibility of a spin-glass phase transition however no dependence on frequency was studied in our work.

The field dependence of AC susceptibility is given in Fig. 3. At high magnetic fields, there is no difference between the curves measure below and above 0.085 K (Fig. 3a). At low magnetic fields, we observed difference between the curves measure below and above 0.085 K (Fig. 3b). At 30 mK, the isothermal AC susceptibility steeply decreased with increasing or decreasing field, having minima at ± 0.004 T, and then had a tendency to saturate at higher fields above 0.03 T (Fig. 3b). It is likely that the LRO is suppressed by a small amount of magnetic field (about 0.004 T) because of a very weak inter-chain interaction. The origin of this field-induced phase transition may be a spin-flop or metamagnetic transition. After the field-induced phase transition, the AC susceptibility below 0.085 K behaves in the similar way as that above

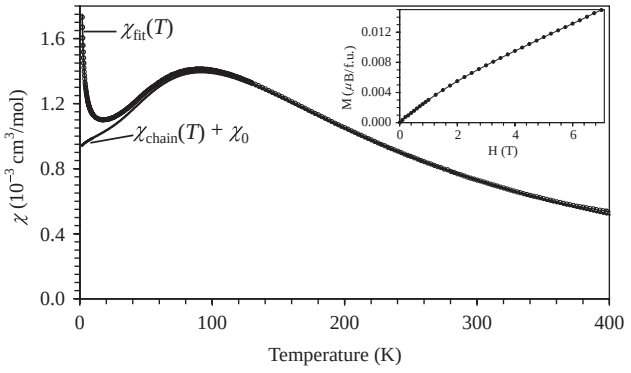

Fig. 1. Experimental magnetic susceptibilities (circles) against temperature, $\chi(T)$, for $Sr_2Cu(PO_4)_2$. Solid line represents the fit by Eq. (1), $\chi_{fit}(T)$. Solid line with small dots is contribution of $\chi_0 + \chi_{chain}(T)$. Inset gives the DC isothermal magnetization curve at $T = 1.8$ K up to 7 T; f.u. is a formular unit.

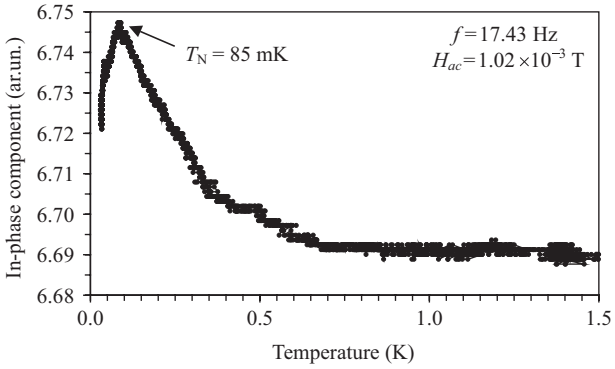

Fig. 2. Temperature dependence of the in-phase component of the AC susceptibility between 0.03 and 1.5 K.

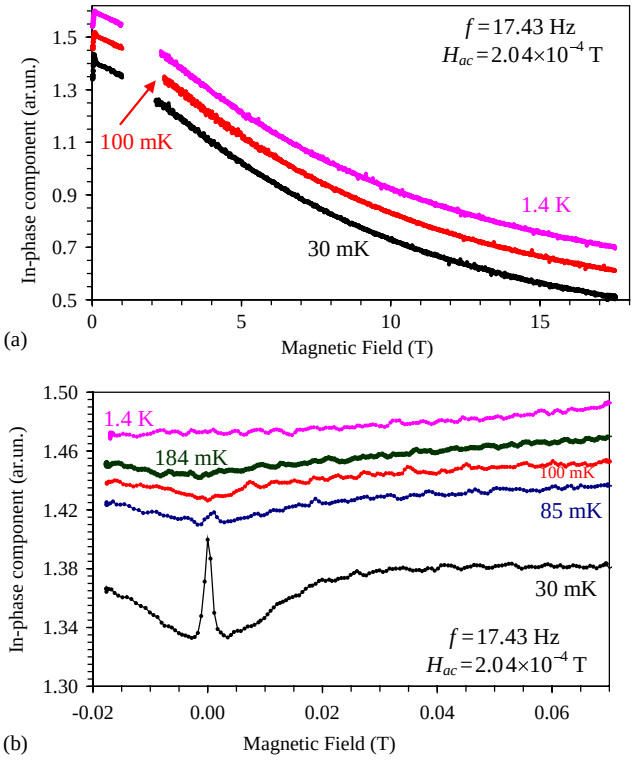

Fig. 3. (a) Isothermal AC magnetization curves at 30 and 100 mK and 1.4 K. The curves at 100 mK and 1.4 K were shifted for the clarity. These curves were measured from 0 to 17.5 T at a rate of 0.5 T/min. The measurements between 1 and 2 T were not possible due to instrument's features. The step-like anomalies at about 0.1 T are instrument's features. (b) Isothermal AC magnetization curves at 30, 85, 100, 184 mK and 1.4 K. The curves at 85, 100, 184 mK and 1.4 K were shifted for the clarity. Magnetic field was increased at a rate of 0.05 T/min.

0.085 K (Fig. 3a). Therefore, the isothermal AC susceptibility data gave additional support that $Sr_2Cu(PO_4)_2$ undergoes LRO below 0.085 K.

^{31}P NMR spectra of $Sr_2Cu(PO_4)_2$ were recorded between 0.02 and 300 K [13]. A clear anomaly was seen in the NMR shift, $K(T)$, at low temperatures. However only a weak anomaly was observed in the temperature dependence of spin–lattice relaxation rate, $1/T_1(T)$, and no significant changes were found in the temperature dependence of spin–spin relaxation rate, $1/T_2(T)$. Therefore, the presence or absence of LRO al low temperatures in $Sr_2Cu(PO_4)_2$ could not be unambiguously established [13]. The ^{31}P NMR measurements were carried out at magnetic fields of 0.4 and 5.5 T. According to our results, LRO in $Sr_2Cu(PO_4)_2$ is suppressed at these magnetic fields. This may be the reason why no clear evidence of LRO was found from the ^{31}P NMR data. Therefore, in the present case of $Sr_2Cu(PO_4)_2$, the zero-field AC susceptibility measurements are superior over a local-probe NMR technique in determination of the LRO temperature.

Spin-flop field-induced phase transitions are observed in antiferromagnetically ordered substances [16]. Sometimes a very small magnetic field can cause such a phase transition [16]. For example, in $Sr_3Cu_3(PO_4)_4$ with $T_N = 0.91$ K, a spin-flop transition occurs at $H = 0.03$ T and $T = 0.08$ K [15]. In $SrCuV_2O_7$ with $T_N = 1.36$ K, a spin-flop transition was observed at $H = 0.05$ T and $T = 0.08$ K [17]. Therefore, it is not surprising that the field of 0.004 T causes a phase transition in $Sr_2Cu(PO_4)_2$ with $T_N = 0.085$ K.

In conclusion, we have shown using the AC susceptibility data that $Sr_2Cu(PO_4)_2$ undergoes long-range magnetic ordering at 0.085 K giving the ratio $k_BT_N/J = 0.06\%$. $Sr_2Cu(PO_4)_2$ is, therefore, one of the best 1D Heisenberg antiferromagnet known so far.

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