Quantum phase transition in the dioptase magnetic lattice

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(accepted in final form 6 August 2002)

PACS. 71.20.Be – Transition metals and alloys.
PACS. 73.43.Nq – Quantum phase transitions.
PACS. 75.10.Jm – Quantized spin models.

Abstract. – The study of quantum phase transitions (see Sachdev S., Quantum Phase Transitions (Cambridge University Press, Cambridge) 1999), which are zero-temperature phase transitions between distinct states of matter, is of current interest in research since it allows for a description of low-temperature properties based on universal relations. Here we show that the crystal green dioptase Cu\textsubscript{6}Si\textsubscript{6}O\textsubscript{18}·6H\textsubscript{2}O, known to the ancient Romans as the gem of Venus, has a magnetic crystal structure, formed by the Cu(II) ions, which allows for a quantum phase transition between an antiferromagnetically ordered state and a quantum spin liquid.

The gem-stone dioptase Cu\textsubscript{6}Si\textsubscript{6}O\textsubscript{18}·6H\textsubscript{2}O is a transparent green mineral built up from Si\textsubscript{6}O\textsubscript{18} single rings on a lattice, which sandwiches six-membered water rings down the (crystallographic) c-direction [1–3]. The magnetic Cu(II) ions are located between the Si\textsubscript{6}O\textsubscript{18} rings and form chiral chains along c, placed on an ab-honeycomb net and are there edge-sharing connected forming Cu(II) dimers.

We illustrate in fig. 1 the sublattice of the magnetic Cu(II) ions. This three-dimensional magnetic lattice is characterized by only two coupling constants in between the spin-(1/2) Cu(II) moments. The magnetic sublattice is characterized by an antiferromagnetic intra-chain \( J_2 \), which couples the Cu(II) chains and an antiferromagnetic inter-chain coupling \( J_1 \), leading for small \( J_1/J_2 \) to an AB-type Neél-ordered state with doubling of the unit cell along c. Alternatively, one might consider the dioptase magnetic lattice as made up by in-plane dimers of Cu(II) ions, with an intra-dimer coupling strength of \( J_1 \) and an inter-dimer coupling along c of \( J_2 \). For small \( J_2/J_1 \) a singlet-dimer state with a spin-gap and no long-range magnetic order is then realized.

In fig. 3 below, we present the phase diagram of the dioptase magnetic lattice, which we obtained from Quantum Monte Carlo (QMC) simulations, using the stochastic series expansion with worm updates [4, 5]. We used the parameterization \( J_{1,2} = J(1 \pm \delta) \).
Fig. 1 – An illustration of Cu-sublattice of the dioptase crystal structure. The rhombohedral unit cell contains 18 equivalent Cu atoms arranged in six chains with three atoms down the c period. The inter-/intra-chain magnetic coupling with strength $J_1$ and $J_2$ are indicated by white/black sticks. Left: an ab-plane. Not shown are the Si$_6$O$_{18}$ rings, located inside the 12-membered Cu rings. The rhombus denotes the in-plane hexagonal unit cell. Right: two chiral chains along c.

In order to determine the phase diagram, an accurate estimate of the transition temperature to the ordered state is necessary. For this purpose, we evaluated by QMC one of the Binder cumulants [6], namely $\langle m_{AF}^2 \rangle / \langle |m_{AF}| \rangle^2$, where $m_{AF}$ is the antiferromagnetic-order parameter (the staggered magnetization). The temperature at which the cumulants for different finite cluster intersect provide reliable estimates for the Neél temperature [6], see fig. 2. For the numerical simulations we used $(n, n, m)$ clusters with periodic boundary conditions, where $n^2$ and $m$ are the number of unit cells in the ab-plane and along the c-axis, respectively. We performed simulations for $(2, 2, 20)$, $(3, 3, 30)$ and $(4, 4, 40)$ clusters containing 1440, 4860 and 11520 Cu(II) sites, respectively.

The linear raise of $T_N$ in fig. 3 occurring for small inter-chain couplings $J_1$ is a consequence of the quantum-critical nature of the spin-$1/2$ Heisenberg chain realized for $J_1 = 0$. The magnetic correlation length $\xi(T)$ diverges as $\xi(T) \sim T^{-1}$ for a Heisenberg chain at low temperature. For small inter-chain couplings $J_1$ a chain mean-field approach is valid [7] and the

Fig. 2 – QMC results for the dimensionless Binder cumulant $\langle m_{AF}^2 \rangle / \langle |m_{AF}| \rangle^2$ for $(n, n, m)$ clusters with periodic boundary conditions. The lines are guides to the eye, the MC estimates for the statistical errors are given. Shown are the results for $n = 2$, $m = 20$ (1440 sites), $n = 3$, $m = 30$ (4860 sites) and $n = 4$, $m = 40$ (11520 sites) and two values of $\delta$ ($J_{1,2} = J(1 \pm \delta)$).
The critical temperature for the transition, which is in the 3D Heisenberg universality class, is maximal for $\delta \approx -0.1$ and vanishes at a quantum-critical point $\delta_c \approx 0.3$. Long-range magnetism is absent beyond this point and the ground state is a quantum spin liquid. For $J_2 = 0$ the dioptase magnetic lattice decomposes into isolated dimers.

The magnitude of the singlet-triplet gap $\Delta$ in the spin liquid state can be estimated by a fit of the low-temperature QMC susceptibility to

$$\chi(T) \approx (k_B T / \Delta)^{d/2 - 1} e^{-\Delta / (k_B T)},$$

where $d$ is the dimensionality of the triplet dispersion above the gap. For an isolated dimer $d = 0$, for a spin ladder $d = 1$ [8]. This analysis would predict $d = 3$ for the dioptase magnetic sublattice, but fits of the QMC results for $\chi(T)$, presented in fig. 3, favor $d = 0$.

In fig. 4 we present the susceptibility of green dioptase (using a crystal from Altyn Tyube, Kazakhstan) down the He temperatures measured with a commercial SQUID magnetometer (Quantum Design). The data for magnetic field aligned parallel and perpendicular to the $c$-axis presented in the inset of fig. 4 show clearly a transition to Neél-ordered states at $T_N^{(\text{exp})} = 15.5$ K. The moments are aligned along $c$ for $T < T_N^{(\text{exp})}$.

The QMC results for the susceptibility are to be compared, due to spin-rotational invariance, with the directional-averaged experimental susceptibility, presented in the main panel of fig. 4. We have determined the Hamiltonian parameters $J_1 = J(1 + \delta)$ and $J_2 = J(1 - \delta)$ appropriate for dioptase in the following way. For every $\delta < \delta_c$ the overall coupling constant $J$ was determined by fixing the transition temperature to the experimental $T_N^{(\text{exp})} = 15.5$ K. The spin susceptibility in experimental units is then

$$\chi^{(\text{exp})} = 0.375 \times Z (g^2 / J ) \Lambda_{mm},$$

where $Z = 3$ is the number of Cu$^{2+}$ ions in the primitive unit cell. The dimensionless magnetization fluctuation is $\Lambda_{mm} = (J \beta) \left( \langle m^2 \rangle - \langle m \rangle^2 \right)$, where $m$ is the magnetization. The $g$-factor was then determined, for every $\delta < \delta_c$, by adapting the right-hand side of eq. (1) to the experimental susceptibility at high temperatures. The results are shown in fig. 4 together
Fig. 4 – QMC results for the susceptibility (in emu/mol) for various $\delta$ in comparison with the directional-averaged experimental susceptibility (solid line). Inset: the susceptibility $\chi$ for magnetic fields parallel/orthogonal to the $c$-axis (lower/upper) curve. The vertical dashed lines in the main panel and in the inset indicates the location of the Neél temperature.

with the optimal values for $J$ and $g$. We see that the optimal value $g \approx 2.1$ for the $g$-factor is relatively independent of $\delta$.

We find two possible values for the ratio of the two-coupling (antiferromagnetic) constants $J_1$ and $J_2$, namely $\delta = 0.1$ and $\delta = -0.1$, which fit the experimental data equally well. Note that $\delta = -0.2$ does not agree well for $T < T_N^{(exp)}$. We attribute the residual discrepancies in

Fig. 5 – Low-energy Raman spectrum of dioptase in xx-polarization. The modes at 48 and 85 cm$^{-1}$ ($\equiv 69$ and 122 K) show a strong increase of intensity for $T < T_N = 15.5$ K and correspond to one- and two-magnon processes. The temperature-independent modes at 70 and 100 cm$^{-1}$ are phonons.
between the theory and the experimental data to residual interactions, in addition to $J_1$ and $J_2$. It has been suggested previously [9] that the in-chain coupling $J_2$ might actually be ferromagnetic. We have studied therefore also the case for negative $J_2$ and found a quantum phase transition to a state with alternating ferromagnetic chains for $J_2 \approx -0.7 J_1$. We have performed the corresponding analysis to the one shown in fig. 4 for the the case of ferromagnetic $J_2$. We found very large deviations in between experiment and theory in this case, due to the fact that the susceptibility of ferromagnetic chains diverges for $T \to 0$.

To settle the ambiguity concerning the $\delta$ parameter, we investigated the magnetic Raman spectrum of dioptase as a function of temperature, as shown in fig. 5. The Raman scattering experiments were performed in quasi-backscattering geometry with a triple grating optical spectrometer (DILOR XY) with the $\lambda = 514$ nm laser line. Two modes at 48 and 85 cm$^{-1}$ ($\equiv 69$ and 122 K) are magnetic as they exhibit a temperature dependence related to the transition. They show no anisotropy concerning the scattering selection rules. The excitation energies 69 K and 122 K correspond, for $\delta = +0.1$, to one and two inter-chain dimer excitation energy $J_1 = J(1+\delta)$, as expected for one- and two-magnon scattering processes. The lineshape of the magnetic two-magnon 122 K mode is very unusual, it is symmetric and not substantially broadened by either magnon-magnon scattering or density-of-states effects, in contrast to usual two-magnon scattering in normal 3D antiferromagnets [10]. This behavior indicates a very small dispersion of the underlying magnon branch. We consequently conclude that dioptase is relatively close to a quantum-critical point.

In conclusion, we have presented a novel magnetic lattice structure, the dioptase magnetic lattice, which allows for a quantum phase transition. This lattice is realized in green dioptase $\text{Cu}_6\text{Si}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ and in the recently synthesized isostructural germanate $\text{Cu}_6\text{Ge}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ [11,12], a promising candidate to study further aspects of the phase diagram presented in detail in fig. 3.

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We acknowledge fruitful discussions with M. TROYER on the stochastic series expansion and F. CAPRARO for data analysis.

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