Spin triplet ground-state in the copper hexamer compounds A_{2}Cu_{3}O(SO_{4})_{3}(A=Na,K)

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Spin Triplet Ground-State in the Copper Hexamer Compounds $A_2Cu_3O(SO_4)_3$ (A=Na, K)

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The compounds $A_2Cu_3O(SO_4)_3$ (A=Na, K) are characterized by copper hexamers which are weakly coupled along the b-axis to realize one-dimensional antiferromagnetic chains below $T_N \approx 3$ K, whereas the interchain interactions along the a- and c-axes are negligible. We investigated the energy-level splittings of the copper hexamers by inelastic neutron scattering below and above T_N. The eight lowest-lying hexamer states could be unambiguously assigned and parametrized in terms of a Heisenberg exchange Hamiltonian, providing direct experimental evidence for an S=1 triplet ground-state associated with the copper hexamers. Therefore, the compounds $A_2Cu_3O(SO_4)_3$ serve as novel cluster-based spin-1 antiferromagnets to support Haldane's conjecture that a gap appears in the excitation spectrum below T_N, which was verified by inelastic neutron scattering.

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Progress in quantum magnetism has often been motivated by observations on naturally occurring minerals. There are numerous examples of novel phenomena first discovered in natural samples, before they found the way to the physics laboratories [1,2]. Here we focus on the discovery of the compounds $A_2Cu_3O(SO_4)_3$ (A=Na, K). The minerals fedotovite (A=K) [3] and euchlorine (A_2=KNa) [4] were found in sublimates of the Tolbachik fission eruption (Kamchatka peninsula, Russia) in the years 1975-1976, which was complemented at the same place in the years 2014-2015 by the mineral puninite (A=Na) [5]. All these minerals are built up of edge-shared tetrahedral spin clusters consisting of six Cu^{2+} ions with S=1/2 spins as schematically shown in Fig. 1(a). The hexamer Cu^{2+} clusters are magnetically decoupled along the a and c axes due to the lack of exchange paths, but they are weakly coupled along the b axis giving rise to one-dimensional antiferromagnetic order below $T_N \approx 3$ K. The fascinating properties of the compounds $A_2Cu_3O(SO_4)_3$ have only very recently been recognized by Fujihara *et al.* [6], who carried out experimental studies for A=K by magnetic susceptibility, magnetization, heat capacity, and inelastic neutron scattering (INS) measurements (restricted to energy transfers below 2.5 meV). The presence of a spin triplet ground-state was suggested, which puts fedotovite into a novel Haldane state based on spin-cluster chains. Haldane's conjecture [7] predicts gapless excitations for half-integer spin systems, whereas a gap opens for integer spin systems.

The postulated spin S=1 ground-state in $K_2Cu_3O(SO_4)_3$ essentially relied on an analysis of thermodynamic magnetic properties [6]. However, for large complexes such as the Cu^{2+} hexamers, the latter can be rationalized by a variety of different sets of magnetic exchange parameters, so that the energy-level scheme of the Cu^{2+} hexamers cannot be unambiguously determined. Consequently, the spin triplet ground-ground state postulated in Ref. [6] has to be considered as a hypothesis missing the criteria of being both necessary and sufficient. More specifically, the spin states of Cu^{2+} hexamers comprise five singlets (S=0), nine triplets (S=1), five quintets (S=2), and a septet (S=3) [8], but in principle none of these states can be excluded from being the true ground state. What is needed are spectroscopic methods such as the INS technique to allow a direct determination of the spin states. Therefore, we performed INS experiments for the compounds $A_2Cu_3O(SO_4)_3$ (A=Na, K) in order to arrive at a detailed picture of the spin excitations associated with the Cu^{2+} hexamers, thereby confirming directly the spin triplet ground-state.

The compounds $A_2Cu_3O(SO_4)_3$ (A=Na, K) crystallize in the monoclinic space group C2/c. Polycrystalline samples were synthesized by a solid-state reaction process as described in Ref. [6]. The samples were characterized by X-ray and neutron diffraction, confirming their single-phase character [9]. Table I lists the lattice parameters and the Cu-O-Cu bond angles determined by neutron diffraction at T=2 K. The bond angles exhibit relevant asymmetries with respect to the central Cu3-Cu3 bond.

INS experiments were carried out with use of the high-resolution time-of-flight spectrometer CNCS [10] at the spallation neutron source (SNS) at Oak Ridge National Laboratory. Fig. 2 shows energy spectra observed for $A_2Cu_3O(SO_4)_3$ which exhibit similar features for both A=Na and A=K as expected from the similar structural parameters. Prominent peak features appear in three windows of energy transfers ΔE: $4<\Delta E<12$ meV (I), $12<\Delta E<19$ meV (II), and $24<\Delta E<34$ meV (III). No peak-like features were observed for $\Delta E>35$ meV.

The signals in window I increase upon increasing both the temperature T (see Fig. 2) and the modulus of the scattering vector **Q**, which is characteristic of phonon scattering. In window II phonon scattering is still present, but on top of it there are three narrow peaks (denoted as S_1, S_2, S_3), whose intensities decrease with increasing Q according to the square of the magnetic form factor $F^2(Q)$ [9], so that we associate them with spin excitations of the Cu^{2+} hexamers. This interpretation is furthermore supported by the temperature dependence.

When increasing the temperature from 1.5 K to 6 K, the three peaks are shifted downwards by typically 0.5 meV (see Fig. 2), which results from the opening of a gap below T_N. In window III we observe four partially resolved peaks (denoted as T_2, Q_1, T_3, T_4) whose positions are determined by Gaussian least-squares fits. The Q-dependence of the four peaks follows the square of the magnetic form factor $F^2(Q)$ [9], thereby confirming their origin in terms of spin excitations of the Cu^{2+} hexamers. Upon raising the temperature, all the spin excitations observed in windows II and III gradually lose intensity according to Boltzmann statistics, so that we can associate them with ground-state transitions. In addition, we observe a considerable line broadening of the spin excitations with increasing temperature due to relaxation effects. Raising the temperature from 6 K to 20 K and 60 K results in an increase of the line widths by a factor 2 and 3, respectively, which prevents the observation of excited-state Cu^{2+} hexamer transitions.

The energies of the spin excitations observed for $A_2Cu_3O(SO_4)_3$ (A=Na, K) are summarized in Fig. 1(b). We analyze these results in terms of a Heisenberg spin Hamiltonian which for Cu^{2+} hexamers has the form

$$H = -2\sum_{i,j=1}^{6} J_{ij}\mathbf{S_i}\cdot\mathbf{S_j} \quad , \tag{1}$$

where J_{ij} and $\mathbf{S_i}$ denote the bilinear exchange parameters and the spin operators of the Cu^{2+} ions, respectively. The parameters J_{ij} originate from superexchange interactions provided by the O1 and O12 ions situated in the centers of the two Cu tetrahedra. The nature of the superexchange interaction is strongly dependent on the Cu-O-Cu bond angle [11,12]. Ferromagnetic coupling is obtained for bond angles around 90°. With increasing bond angle the ferromagnetic coupling is gradually weakened and turns into an antiferromagnetic coupling.

Eq. (1) gives rise to twenty Cu^{2+} hexamer states, namely five singlets (S_i), nine triplets (T_i), five quintets (Q_i), and one septet. The energy level splitting is in agreement with an analysis of spin-1/2 hexamers consisting of two isosceles trimers [8], but this coupling scheme is not realized for the compounds $A_2Cu_3O(SO_4)_3$ (A=Na, K). In principle, Eq. (1) involves fifteen independent exchange parameters J_{ij}, whose number can be reduced to seven individual parameters J_{ij} by confining to the leading interactions as well as by using the symmetry properties of the Cu-O-Cu bond angles listed in Table I. In order to avoid spin frustration within the Cu^{2+} hexamers, the coupling scheme involves three ferromagnetic interactions $J_{cd}>J_{ab},J_{cf}$ and four antiferromagnetic interactions $|J_{ad}|,|J_{cf}|>|J_{ac}|,|J_{ce}|$ as defined in Fig. 1(a). The nature as well as the relative sizes of the parameters J_{ij} are dictated by the Cu-O-Cu bond angles. This coupling scheme gives rise to a triplet ground-state (T_1), separated from a group of three excited singlet states (S_1, S_2, S_3) and further separated by a group of excited triplet and quintet states (T_2, Q_1, T_3, T_4), in nice agreement with the observations (see Fig. 2).

A least-squares fitting procedure based on Eq. (1) was applied to the observed excitation energies displayed in Fig. 1(b). The resulting exchange parameters are listed in Table I. The parameter J_{cd} turns out to have little influence on the observed excitation energies, which explains its large experimental uncertainty. We find good agreement between the observed and calculated energies with $\chi^2=1.1$ and $\chi^2=1.8$ for A=Na and A=K, respectively. The differences of the exchange parameters derived for A=Na and K are rather small because of the robust structure of the Cu^{2+} tetrahedra. The assignments of the excited states are also supported by intensity calculations [9]. In particular, almost equal intensities are predicted for the transitions both to the three singlet states S_1, S_2, S_3 and to the three triplet states T_2, T_3, T_4 as experimentally observed. The transition to the quintet state Q_1 is calculated to be about twice as intense as the transitions to the triplet states T_2, T_3, T_4, in agreement with the observed intensities displayed in Fig. 2.

Our parameters predict the overall energy splittings of the Cu^{2+} hexamers to be 67 meV (for A=Na) and 66 meV (for A=K). Our INS experiments revealed spin excitations up to energy transfers of 32 meV. Higher-lying spin excitations could not be detected due to either small transition matrix elements or transitions forbidden by the dipole selection-rules. Nevertheless, we emphasize as the most important conclusion that our analysis of the experimental data clearly results in a triplet S=1 ground state of the Cu^{2+} hexamers.

The opening of a spin gap below T_N was verified by INS experiments as shown in Fig. 3. At T=1.5 K there is clear evidence of gapped energy spectra for both compounds $A_2Cu_3O(SO_4)_3$ (A=Na, K). The energies of the dispersive modes associated with the S=1 ground state extend from 0.6 meV to 1.7 meV. From the corresponding width (1.1 meV) we estimate the antiferromagnetic intercluster exchange interaction provided by the superexchange path Cu1-O-S-O-Cu2 to be $2J_{inter}$=-1.1 meV, which is much smaller than the intracluster parameters J_{ij}, since the superexchange involves three non-magnetic ions. The lower bound of the gap (0.6 meV) is consistent with the downward shift of the spin excitations S_1, S_2, S_3 when going from T=1.5 K to T=6 K, see Fig. 2. At T=3 K the gap is already closed as shown in Fig. 3. The observed intensity above T_N is characteristic of short-range antiferromagnetic correlations associated with the one-dimensional Cu^{2+} hexamer chains. Our results are in agreement with INS data obtained for A=K by Fujihara *et al.* [6].

In conclusion, our analysis of INS spectroscopy data provided direct experimental evidence for the existence of spin triplet ground-states in the Cu^{2+} hexamer compounds $A_2Cu_3O(SO_4)_3$ (A=Na, K). A reliable set of seven parameters describing the Cu^{2+} exchange interactions was derived which considerably differs from the approach adopted in Ref. [6]. The case of edge-shared tetrahedral spin clusters has been generalized in the sense that the ground-state alternates between singlet and triplet depending on the number of tetrahedra, *i.e.*, any cluster compound with an even number of tetrahedra would realize a Haldane state [6,7]. This rule is nicely confirmed when we apply the exchange parameters obtained in the present work to the case of a single Cu^{2+} tetrahedron.

Finally we mention that nature is rich in minerals containing oxocentric Cu^{2+} tetrahedra (OCu_4) as basic constituents in a variety of configurations, ranging from three-dimensional crystal frameworks and two-dimensional layer systems to one-dimensional chains and isle-like complexes discussed in the present work. The topic of one-dimensional chains is of particular significance due to the competition between intra- and inter-cluster exchange interactions, which opens interesting perspectives for spin-frustrated systems such as the emergence of spinon excitations in spin chains [13]. We mention as examples the compounds Cu_2OCl_2 [14], $Cu_3Mo_2O_9$ [15], $AgCuVO_4$ [16], $K_3Cu_3AlO_2(SO_4)_4$ [17], and $KCu_3OCl(SO_4)_2$ [18], which are characterized by chains of corner-sharing tetrahedra, as well as Li_2ZrCuO_4 [19] formed by chains of edge-shared tetrahedra. We are not aware of any experimental work describing the magnetic interactions within a OCu_4 tetrahedron in detail. Since the OCu_4 constituents are structurally rather stable units, the generic exchange coupling scheme determined in the present work for $A_2Cu_3O(SO_4)_3$ (A=Na, K) will be a reliable basis for application to the large number of related compounds.

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TABLE I. Lattice parameters (a,b,c,β), Cu-O-Cu bond angles (Θ), and exchange parameters (J_{ij} as defined in Fig. 1a) of the compounds $A_2Cu_3O(SO_4)_3$ (A=Na, K) determined at T=2 K.

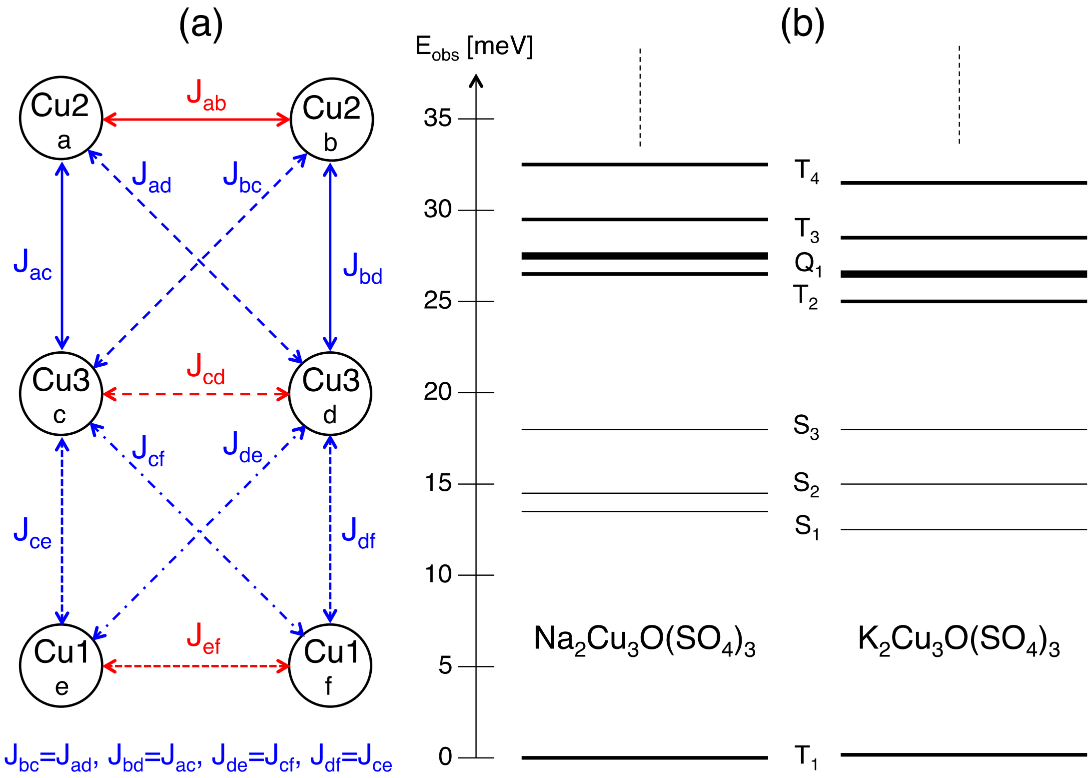
	$Na_2Cu_3O(SO_4)_3$	$K_2Cu_3O(SO_4)_3$
a [Å]	17.21406(67)	18.97550(66)
b [Å]	9.37286(35)	9.50038(35)
c [Å]	14.37014(54)	14.19721(51)
β [°]	111.84364(75)	110.49150(85)
Θ(Cu2$_a$-O12-Cu2$_b$) [°]	105.2(4)	102.2(5)
Θ(Cu2$_a$-O12-Cu3$_{c/d}$) [°]	106.5(4) / 124.4(4)	107.0(5) / 124.2(5)
Θ(Cu2$_b$-O12-Cu3$_{d/c}$) [°]	106.5(4) / 124.4(4)	107.0(5) / 124.2(5)
Θ(Cu3$_c$-O1/O12-Cu3$_d$) [°]	92.7(4) / 91.2(4)	93.0(5) / 94.0(5)
Θ(Cu3$_c$-O1-Cu1$_{e/f}$) [°]	110.6(4) / 121.3(5)	111.7(5) / 123.0(6)
Θ(Cu3$_d$-O1-Cu1$_{f/e}$) [°]	110.6(4) / 121.3(5)	111.7(5) / 123.0(6)
Θ(Cu1$_e$-O1-Cu1$_f$) [°]	101.7(4)	96.8(5)
J_{ab} [meV]	1.6(3)	1.7(4)
J_{ac} [meV]	-3.5(3)	-3.7(4)
J_{ad} [meV]	-9.9(2)	-9.5(3)
J_{cd} [meV]	5(2)	4(2)
J_{ce} [meV]	-4.7(3)	-4.0(3)
J_{cf} [meV]	-8.1(4)	-8.5(3)
J_{ef} [meV]	2.0(3)	1.9(3)

FIGURE CAPTIONS

FIG. 1. (Color online) (a): Schematic picture of the Cu^{2+} hexamers in the compounds $A_2Cu_3O(SO_4)_3$ (A=Na, K). The parameters J_{ij} denote the exchange coupling scheme adopted to describe the observed spin excitations. (b): Energies of the spin excitations observed for $A_2Cu_3O(SO_4)_3$ (A=Na, K) denoted by S_i, T_i, and Q_i for the singlet, triplet, and quintet states, respectively.

FIG. 2. (Color online) Energy spectra of neutrons scattered from $A_2Cu_3O(SO_4)_3$ (A=Na, K). The arrows mark the transitions associated with the excited Cu^{2+} hexamer states. The lines in the right-hand-side panels correspond to Gaussian least-squares fits.

FIG. 3. (color online) Energy spectra of neutrons scattered from $A_2Cu_3O(SO_4)_3$ (A=Na, K). The dashed curves correspond to the tail of the elastic line.



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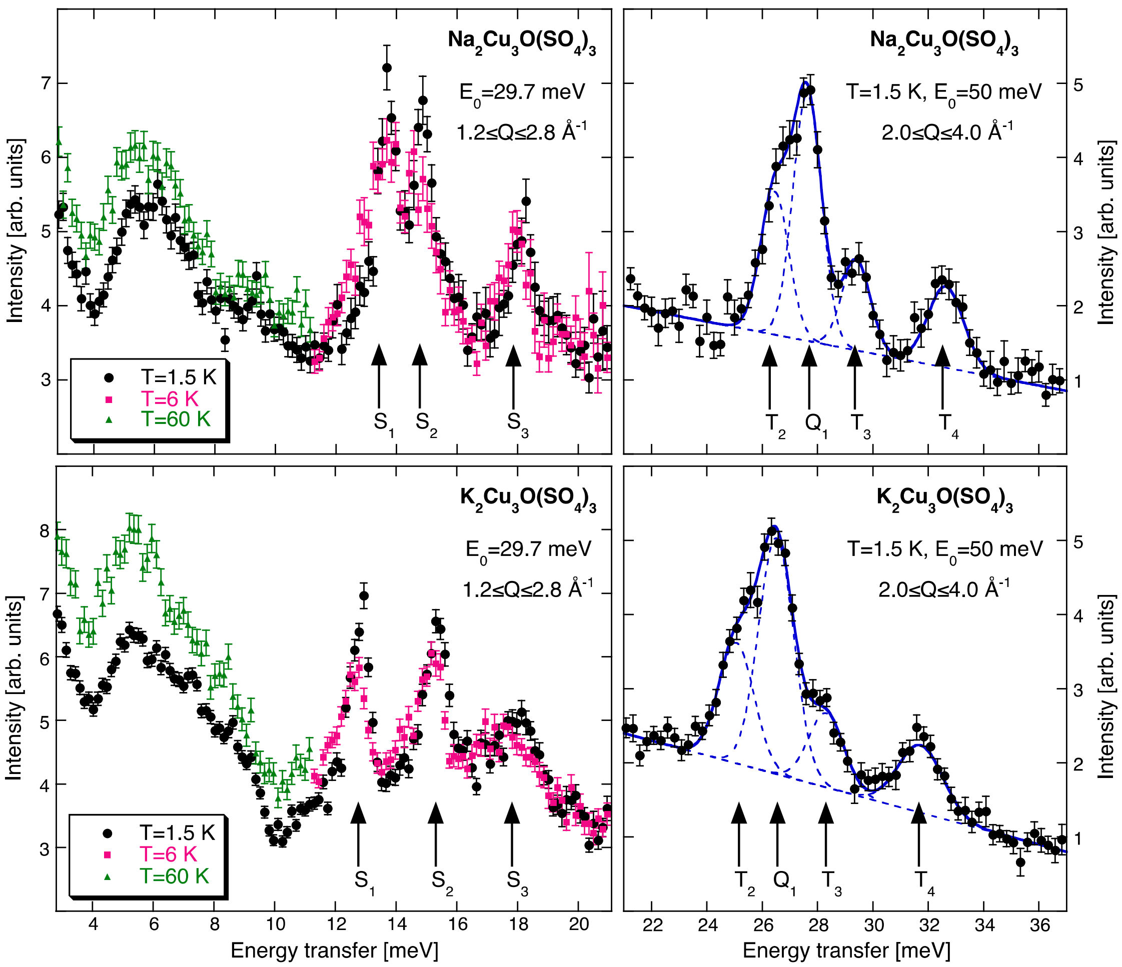

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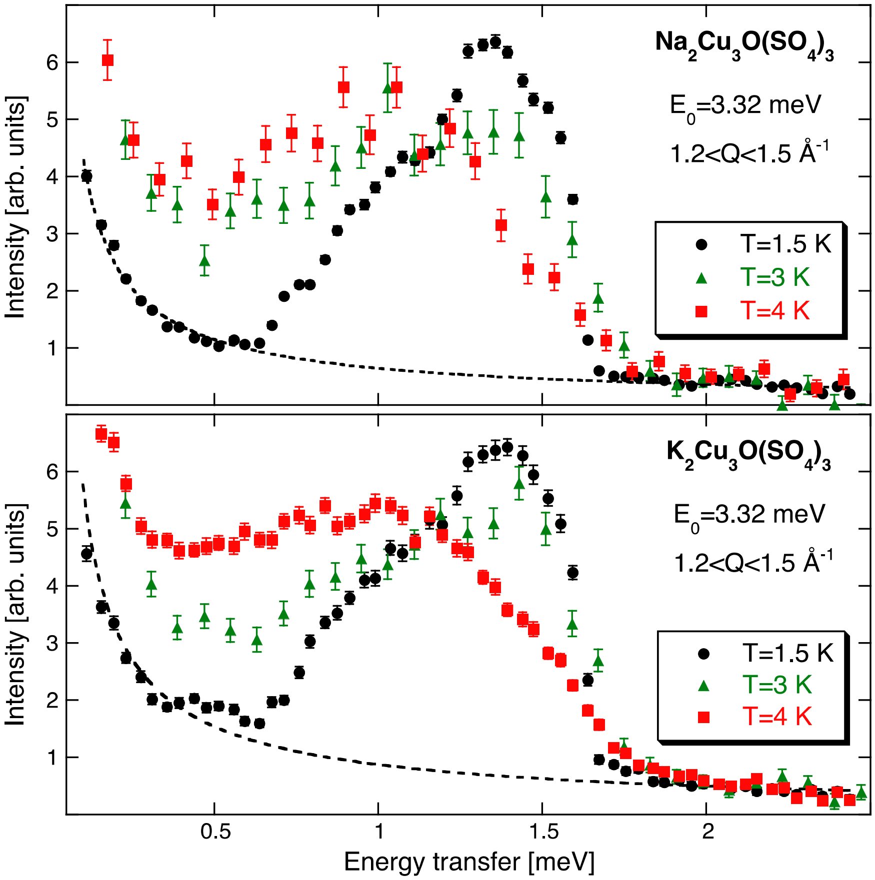

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