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Ising-like antiferromagnetism in $Ca_9La_5Cu_{24}O_{41}$

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Specific heat measurements of a $Ca_9La_5Cu_{24}O_{41}$ single crystal in magnetic fields up to 14 T along the three principal axes were performed. Anomalies of the specific heat indicating long-range antiferromagnetic order are strongly field dependent and exhibit an extreme anisotropy with respect to the magnetic field orientation. In addition, large magnetic contributions to the specific heat above the phase transition were observed revealing the low dimensional character of the chains. Our data strongly suggest that the chains in $Ca_9La_5Cu_{24}O_{41}$ exhibit an Ising-like antiferromagnetism.

In recent years, low dimensional $S=\frac{1}{2}$ antiferromagnetic Heisenberg systems have been intensively studied theoretically as well as experimentally due to their unusual physical properties. Most magnetic materials composed of Cu^{2+} ions are represented by a Heisenberg model, since in general the orbital moment is in reasonable approximation well quenched and thus, the spin is a good quantum number. The exceptional role of Cu^{2+} as a spin magnet is well demonstrated in $CuCl_2 \cdot 2NC_5H_5$ representing an antiferromagnetic linear chain of isotropic Heisenberg spins, whereas Co in $CoCl_2 \cdot 2NC_5H_5$ yields a ferromagnetic Ising chain.[1] The magnetism of Cu^{2+}-based oxides, where CuO squares represent a key structural element, has become of particular interest because of the possible connection to the mechanism of high-T_c superconductivity. The characteristic arrangements of the CuO units, i.e., oxygen squares sharing corners as in high-T_c materials, edges as in the chain compounds[2] $CuGeO_3$ and Li_2CuO_2,[3] or both as in the gapped spin ladder system $SrCu_2O_3$,[4] are closely related to the fundamentally different magnetic properties. The parent compound of a family of high-T_c superconductors, La_2CuO_4, exhibits antiferromagnetic order within the CuO_2 layers[5] and appears to be a nearly ideal realization of a 2 D $S=\frac{1}{2}$ Heisenberg antiferromagnet. The spin-Peierls compound, $CuGeO_3$, is a good example of a quasi-one-dimensional $S=\frac{1}{2}$ Heisenberg antiferromagnet containing CuO_2 chains with a Cu-O-Cu bond angle of $\approx 98°$.[6] A similar chain arrangement is also present in the $(Sr,Ca,La)_{14}Cu_{24}O_{41}$ compound which contains two unique magnetic structures. One consists of Cu_2O_3 two-leg ladders with $S=\frac{1}{2}$ spins coupled by nearly 180° Cu-O-Cu bonds along the *a* and *c* axis, whereas the other is composed of edge sharing CuO_2 $S=\frac{1}{2}$ spin chains with $\approx 90°$ Cu-O-Cu exchange paths along the *c* axis.[7,8] Stoichiometric $(Sr,Ca)_{14}Cu_{24}O_{41}$ is inherently doped with holes which reside predominantly in the chains, as suggested by optical conductivity experiments.[9] The hole distribution in the chains results in an unusual spin arrangement with remarkable magnetic properties,[10–12] whereas the ladders are magnetically inert below room temperature due to their large spin gap of $\Delta = 370$ K,[13] consistent with recent theoretical considerations.[14] In $Ca_{14-x}La_xCu_{24}O_{41}$, the number of holes is substantially reduced upon La substitution, and antiferromagnetic long-range order occurs at ≈ 10 K for $x \geq 5$, with ferromagnetic correlations within the chains.[15,16]

In this study we show that the isotropic Heisenberg model fails to describe the observed thermodynamic properties, suggesting that $Ca_9La_5Cu_{24}O_{41}$ is an Ising-like antiferromagnet. We report on specific heat measurements of a $Ca_9La_5Cu_{24}O_{41}$ single crystal using a quasi-adiabatic heat pulse method in magnetic fields up to 14 T parallel to the principal axes in the 4–35 K temperature range. A sample of $5 \times 4 \times 6$ mm^3 has been used, cut from a single crystal of 110 mm length, grown under several bar oxygen pressure by the travelling solvent floating zone (TSFZ) method.[17] Magnetic measurements were performed using a Foner magnetometer.

Figure 1 displays the magnetization of a $Ca_9La_5Cu_{24}O_{41}$ single crystal as a function of temperature measured for magnetic fields applied along the principal axes. For a field $H=1$ T parallel to the *b* axis, a broad peak emerges in the magnetization at ≈ 15 K followed by a strong decrease below ≈ 10 K, whereas for fields along the *c* axis the magnetization in-

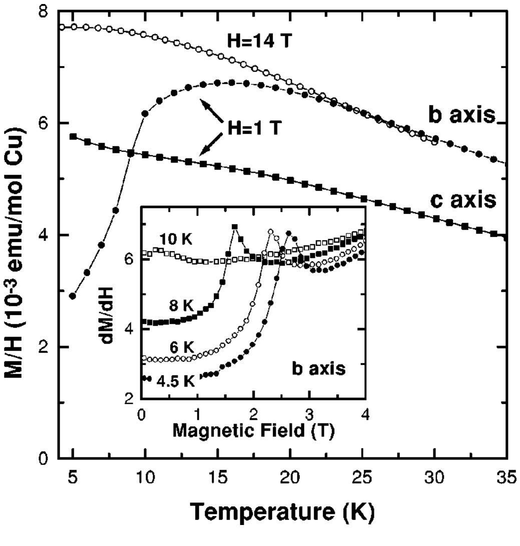

FIG. 1. Magnetization as a function of temperature of a $Ca_9La_5Cu_{24}O_{41}$ single crystal at $H=1$ T applied parallel to the *b* and *c* axis (full symbols) and $H=14$ T along the *b* direction (open circles), respectively. Inset: $\partial M/\partial H$ as a function of magnetic field *H* parallel to the *b* axis for different temperatures (see text).

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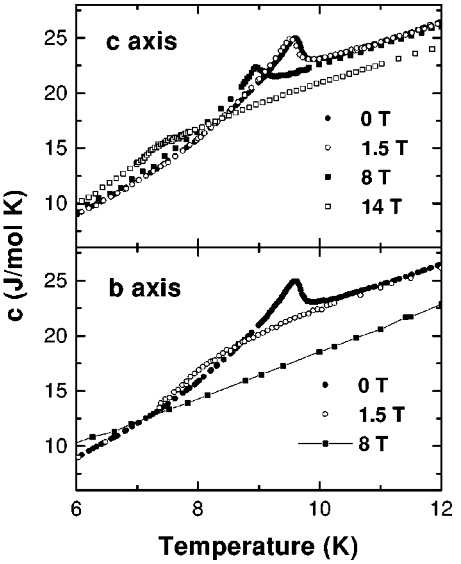

FIG. 2. Specific heat anomalies of a $Ca_9La_5Cu_{24}O_{41}$ single crystal for different magnetic fields applied parallel to the *b* and *c* axis, respectively.

creases continuously with decreasing temperature. The magnetization for fields along the *a* axis is almost identical to that of the *c* direction and therefore not shown. From the magnetization measurements it is evident that long-range antiferromagnetic order occurs at low temperatures with the easy axis parallel to the *b* axis. Elastic neutron scattering experiments on $Ca_9La_5Cu_{24}O_{41}$ showed that the interchain coupling in the *a* and *b* directions is antiferromagnetic, whereas the correlations along the chains are ferromagnetic[16] as suggested by the 90° Cu-O-Cu exchange. However, in the 50–300 K temperature range, the susceptibility can be satisfactorily described by a Curie-Weiss law $\chi=\chi_0+C/[T+\theta]$ with a weak antiferromagnetic interaction, indicating that the ferromagnetic nearest neighbor coupling within the chains and the antiferromagnetic interchain exchange are of similar strength. In fields up to 14 T, parallel to the *b* axis, no spontaneous magnetization could be observed down to 4 K, as shown in Fig. 1. From the magnetization experiments, a strongly anisotropic exchange could not be extracted unambiguously. However, as will be shown in the following, our specific heat experiments reveal that $Ca_9La_5Cu_{24}O_{41}$ exhibits indeed an extreme magnetic anisotropy.

The influence of magnitude and direction of the applied magnetic field on the phase transition is shown in Fig. 2. In zero field a sharp anomaly is observed in the specific heat indicating the antiferromagnetic phase transition at $T_N=9.7$ K. For fields parallel to the *c* direction, i.e., parallel to CuO_2 spin chains, the anomaly shifts to lower temperatures. The transition temperature T_N, determined by an entropy conserving construction, decreases from 9.7 K in zero field to 9.2 K at 8 T and is still present for 14 T at 7.3 K. A drastic magnetic field dependence of the phase transition temperature T_N is observed when applying the field along the *b* direction, i.e., parallel to the easy axis. As can be seen in the lower panel of Fig. 2, already at 1.5 T the anomaly of the specific heat is strongly broadened and considerably shifted to lower temperatures. For $H=8$ T, no evidence for a phase transition could be found down to 4 K. For magnetic fields applied along the *a* axis, i.e., perpendicular to the spin chains and the easy axis, the situation is similar to that of the *c* axis. Figure 3 shows the specific heat measured at 8 T for fields applied along the *a* and *c* axes in comparison with the *b* axis. In the case of the *a* and *c* axes the specific heat is identical with a well-defined anomaly indicating the onset of magnetic order. In contrast, for fields parallel to the easy axis no phase transition could be revealed. The critical fields and temperatures for the antiferromagnetic phase transition are summarized in the form of a magnetic phase diagram, shown in Fig. 4. The field dependence of T_N is identical for the *a* and *c* axes, whereas for fields parallel to the *b* direction, the antiferromagnetic order is already completely suppressed above 3 T. Below 8 K the critical field along the easy axis was determined from magnetization measurements since, at low temperatures, the boundary line becomes very flat. Here, anomalies of the specific heat are considerably broadened and unsuitable for an exact determination of T_N. The phase transition temperature was attributed to the peaks in the $\partial M/\partial H$ curves shown in the inset of Fig. 1. We stress that a spin-flop phase can be excluded unambiguously from specific heat measurements in fields up to 8 T along the *b* axis.

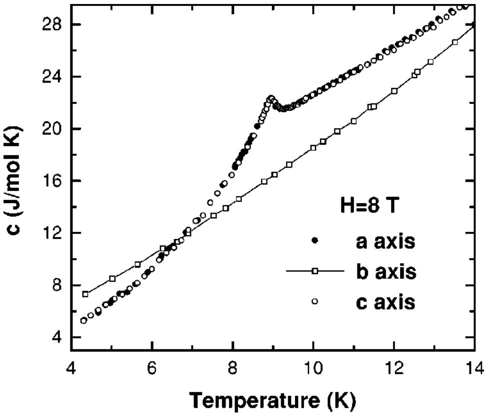

FIG. 3. Specific heat anomalies of a $Ca_9La_5Cu_{24}O_{41}$ single crystal at 8 T for different field orientations.

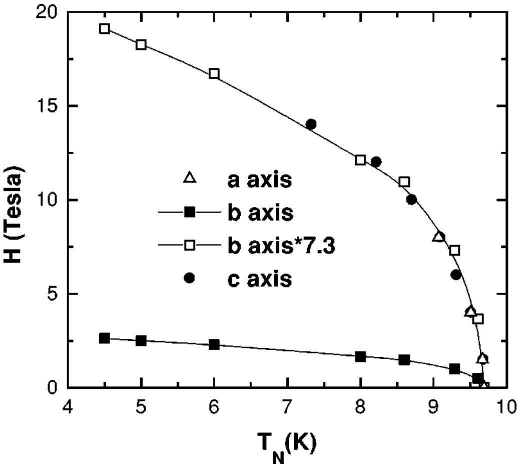

FIG. 4. Magnetic phase diagram for a $Ca_9La_5Cu_{24}O_{41}$ single crystal determined by specific heat and magnetization measurements for fields along the three principal crystallographic axes. The open squares denote the boundary line for fields parallel to the *b* axis where the critical field *H* has been multiplied by a factor of 7.3.

Moreover, the variation of the critical field H_c parallel to the *b* axis as a function of temperature agrees well with that of the *a* and *c* axes after multiplying by a factor of ≈ 7.3. This indicates that the field influence on the antiferromagnetic ordering is similar for all three directions but extremely anisotropic. Note that this enormous anisotropy in association with the absence of a spin-flop phase represents a very unusual and remarkable feature of materials based on copper oxide layers.

A further interesting feature concerns the absolute value of the specific heat as a function of the applied magnetic field for temperatures above the antiferromagnetic phase transition. As can be seen in Fig. 2, for fields below 1.5 T, the absolute value of the specific heat above T_N is almost field independent, whereas the specific heat strongly decreases with increasing field. For example, when applying the magnetic field H along the *b* axis, $\Delta c = c(0\ \mathrm{T}) - c(8\ \mathrm{T})$ amounts to 4 J/mol K at 11 K, which represents already 20% of the absolute value. The strong field dependence above T_N clearly shows that large magnetic contributions c_m are present in the specific heat which are suppressed in high magnetic fields. Further shown in Fig. 3, more above the antiferromagnetic phase transition, a remarkable anisotropy in the specific heat can be observed in magnetic fields applied along the crystal axes. At $H = 8$ T, the specific heat above the phase transition is identical for H parallel to *a* and *c* whereas the absolute value is substantially reduced when the field is applied along *b*. Thermodynamically, the magnetic contributions to the specific heat c_m are related to the magnetic part of the entropy S_m by $S_m(T) = \int_0^T [c_m(T')/T'] dT'$. In a magnetic system with N spins of $S = \frac{1}{2}$ the total magnetic entropy amounts to $N k_B \ln 2$. Due to the large spin gap of the ladders in $\mathrm{Ca_9La_5Cu_{24}O_{41}}$, only the spin chains give a significant contribution to the magnetic entropy at low temperature. Unfortunately, the lattice contributions to the specific heat are unknown, and therefore a precise evaluation of the magnetic part of the entropy is difficult. However, the strong decrease of the specific heat with increasing magnetic field above T_N compared to the absolute value in zero field, clearly shows that a large amount of magnetic entropy S_m is present for temperatures above T_N. Whereas for an ideal 3D antiferromagnet the total magnetic entropy is almost completely recovered at T_N, this is not the case for a low dimensional system due to short range order above the antiferromagnetic order. Thus, we can conclude from our data that the spin chains in $\mathrm{Ca_9La_5Cu_{24}O_{41}}$ exhibit a low dimensional character.[18]

We next discuss the remarkable magnetic phase diagram in terms of a simple uniaxial two-sublattice meanfield model. If an external field is applied along the preferred axis of spin alignment, the moments tend to turn perpendicular to the field in order to gain a magnetic energy of $\frac{1}{2}(\chi_\perp - \chi_\parallel)H^2$. The spin-flop transition takes place at a field H_{SF} where the gain of magnetic energy overcompensates the loss due to the anisotropy energy responsible for the preferred spin orientation. Upon further increase of H, the moments rotate gradually until the critical field H_c is reached where the main direction of the spins is parallel to the easy axis and the paramagnetic phase is entered. The critical fields are related by

$$H_{SF} = (2 H_{AF} H_A - H_A^2)^{1/2} \tag{1}$$

and

$$H_c = 2 H_{AF} - H_A, \tag{2}$$

where H_{AF} denotes the antiferromagnetic exchange field and H_A the corresponding anisotropy field.[19] From Eqs. (1) and (2) it can be seen that an increase of the anisotropy raises the spin-flop field H_{SF}, whereas H_c is reduced. For $H_A = H_{AF}$, it follows that the critical fields H_{SF} and H_c are identical. From our data we can exclude unambiguously the presence of a spin-flop phase above 4 K, indicating that the anisotropy energy must be very large. Therefore, the experimental situation is reminiscent of that expected for an Ising antiferromagnet. To our knowledge, this is the first observation of an Ising-like behavior attributed to $S = \frac{1}{2}$ $\mathrm{Cu^{2+}}$ magnetism.

Taking into account the low dimensional magnetic behavior of the chains, the anisotropic field influence may be interpreted in terms of a microscopic picture of rectangular Cu-O-Cu bonds recently proposed by Yushankhai *et al.*[20] and Tornow *et al.*[21] In a 180° Cu-O-Cu arrangement the isotropic antiferromagnetic superexchange is the dominating interaction, whereas smaller anisotropy terms due to spin-orbit coupling account for the in-plane alignment of the spins in cuprates exhibiting corner sharing $\mathrm{CuO_2}$ planes. However, the situation drastically changes in the case of 90° Cu-O-Cu coupling. The leading order interaction in a rectangular Cu-O-Cu bond is weakly ferromagnetic, and higher order perturbation processes or side groups can have significant influence.[22] It has been shown that for a ferromagnetic 90° exchange, interaction between copper spins results in an easy axis perpendicular to the copper oxide plane.[20] These findings are in good agreement with the calculations by Tornow *et al.* where the out-of-plane anisotropy $J^{op} = J^z - (J^x + J^y)/2$ amounts to $J^{op} \approx -1.2$ meV (≈ -14 K). This means, for the chains in $\mathrm{Ca_9La_5Cu_{24}O_{41}}$, that H_c is drastically reduced for fields parallel to *b* and magnetic order is only possible for a spin alignment parallel to the *b* axis. The theoretical estimate of the anisotropy energy, which is of the same order as T_N, is consistent with the observed anisotropic field influence and the absence of a spin-flop transition. The same arguments are valid in order to explain the extreme anisotropic field influence above T_N shown in Fig. 3. Due to the large anisotropy energy leading to a preferred spin orientation perpendicular to the $\mathrm{CuO_2}$ squares, short range order above T_N is strongly suppressed in fields applied along the *b* axis in analogy to the reduction of H_c for the long-range ordered phase below T_N, according to Eq. (2). However, further theoretical and experimental studies are highly desirable in order to gain a better insight into the nature of the highly anisotropic behavior.

In summary, measurements of the specific heat of a $\mathrm{Ca_9La_5Cu_{24}O_{41}}$ single crystal, in magnetic fields along the three principal crystallographic axes up to 14 T, were performed in the 4–35 K temperature range. Antiferromagnetic long-range order occurs below 9.7 K with the easy axis perpendicular to the $\mathrm{CuO_2}$ squares. It has been shown that the field influence on the phase transition temperature is extremely anisotropic with respect to the applied field direction, suggesting an Ising-like character of the magnetism related to the chains. In addition, large anisotropic magnetic contributions to the specific heat above T_N were found, indicating the low dimensionality of the chains.

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