Decomposition of the spin-$\frac{1}{2}$ Heisenberg chain compound Sr$_2$CuO$_3$ in air and water: An EPR and magnetic susceptibility study of Sr$_2$Cu(OH)$_6$

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The reaction of Sr$_2$CuO$_3$ with air and liquid water was studied to address the origin of the reported variable Curie-Weiss impurity contribution to the magnetic susceptibility $\chi$ of this compound at low temperatures. Sr$_2$CuO$_3$ was found to decompose upon exposure to either of these environments. The compound Sr$_2$Cu(OH)$_6$ was identified as the primary reaction product. A pure sample of Sr$_2$Cu(OH)$_6$ was then prepared separately. Electron paramagnetic resonance (EPR), isothermal magnetization versus magnetic field $M(H)$ and $\chi$ versus temperature $T$ measurements demonstrate that Sr$_2$Cu(OH)$_6$ contains weakly interacting Cu$^{+2}$ magnetic moments with spin $S = \frac{1}{2}$ and average $g$-factor 2.133. From a fit of $\chi(T)$ by the Curie-Weiss law and of the $M(H)$ isotherms by modified Brillouin functions, the exchange interaction between adjacent Cu$^{+2}$ spins was found to be $J/k_B = -1.06(4)$ K, a weakly antiferromagnetic interaction. Our results indicate that the previously reported, strongly sample-dependent, Curie-Weiss contribution to $\chi(T)$ of a polycrystalline Sr$_2$CuO$_3$ sample most likely arises from exposing the sample to air, resulting in a variable amount of paramagnetic Sr$_2$Cu(OH)$_6$ on the surface of the sample.

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I. INTRODUCTION

The physics of low-dimensional quantum spin systems has been intensively studied over the past decade due to its relevance to the physics of the layered cuprate superconductors and to the variety of unconventional magnetic and electronic properties exhibited by such materials. The field of low-dimensional quantum magnetism has a long history dating back to the early 1930s with the publication of the Bethe ansatz equations from which in principle the eigenvalues of the spin $S = \frac{1}{2}$ Heisenberg chain can be obtained. By the early 1990s, research on spin-chain and spin-ladder materials related to the high-temperature superconductors had become a subfield of condensed matter physics. The current experimental work on spin-ladders has been driven by theory but is limited by the lack of known spin-ladder compounds, particularly metals. Of the cuprates, only (Sr,Ca)$_{14}$Cu$_{24}$O$_{41}$ is known to become metallic and superconducting, and then only under high pressure. However, the interpretation of its properties is complicated by the fact that it is comprised of both Cu$_2$O$_3$ ladder and CuO$_2$ chain layers. To isolate the physics associated with one or the other type of spin configuration, it is desirable to study metallic compounds with either chains or ladders, but not both. For reviews of oxide spin-ladder and spin-chain compounds see Refs. 1,3,4,7.

Sr$_2$CuO$_3$ is a model spin-$\frac{1}{2}$ linear chain compound. It has an orthorhombic structure (space group Immm, Ref. 3) containing Cu$^{+2}$ spins $S = \frac{1}{2}$. The orthorhombic structure is derived from the layered tetragonal K$_2$NiF$_4$ structure by removing lines of oxygen atoms parallel to the b axis from within the CuO$_2$ layers of the hypothetical tetragonal K$_2$NiF$_4$-type compound Sr$_2$CuO$_4$. Magnetic susceptibility studies show this compound to be a nearly ideal one-dimensional (1D) spin-$\frac{1}{2}$ Heisenberg antiferromagnet with a strong intrachain Cu–Cu exchange coupling $J/k_B = 2200$ ± 200 K, while optical measurements yield $J/k_B = 2800–3000$ K. On the other hand, theoretical calculations indicate that $J/k_B$ can be no larger than about $2300$ K in this compound. Muon spin rotation/relaxation ($\mu$SR) and neutron diffraction measurements on single crystals revealed long-range antiferromagnetic ordering in this compound with a Néel temperature $T_N \approx 5$ K and an ordered magnetic moment of $\approx 0.06 \mu_B$/Cu atom. For the 1D Heisenberg model, logarithmic terms in the field theory expression for the magnetic susceptibility at very low temperatures yield an infinite slope as $T$ approaches its finite value at $0$ K. Takigawa et al. (Refs. 21,22,23) have tried to see this behavior in their NMR data: a downturn with decreasing $T$ was observed in the magnetic susceptibility at low $T$, but the downturn was not fitted well by the predicted logarithmic behavior. Theory also predicts separated spin and charge excitations near the Fermi energy called “spinon” and “holon” excitations, respectively, for 1D correlated systems (see for example Ref. 24). Angle-resolved photoemission spectroscopy (ARPES) measurements by Fujisawa et al. (Ref. 24) along the chains (b axis) show good qualitative agreement with these theoretical predictions. They observe two separate dispersions in the Brillouin zone, one which is reflected about $kb/\pi$ (holon) and one which is not (spinon). However, quantitatively their measurements are not fitted well by theory.

A superconducting tetragonal phase, Sr$_3$CuO$_{14-\delta}$, has been reported to form under high pressure and to exhibit a superconducting transition temperature $T_c \approx 70$ K. However, the samples contained low superconducting volume fractions and showed semiconducting behavior above $T_c$ rather than metallic behavior. Several groups subsequently reported high...
pressure synthesis of nonsuperconducting samples and Kawashima et al. (Ref. 33) suggested that the superconductivity arose from Sr$_2$CaCu$_2$O$_6$ impurities. Tetragonal Sr$_2$CuO$_2$δ can also be synthesized at ambient pressure and those samples were also nonsuperconducting. The available evidence indicates that the oxygen content in this compound is variable, δ ranges from 0.08 to 0.9. Neutron diffraction measurements carried out on a superconducting and on a nonsuperconducting sample found no major differences between them and could not account for the superconductivity. Both samples showed up to 50% oxygen vacancies in the CuO$_2$ planes as in Sr$_2$CuO$_3$, rather than in the SrO layers. Transmission electron microscopy (TEM) measurements confirmed the presence of the oxygen vacancies in the CuO$_2$ planes. The tetragonal structure of Sr$_2$CuO$_{3+δ}$ thus evidently arises from a random distribution of O vacancies in the CuO$_2$ square lattice planes, rather than the ordered arrangement of oxygen vacancies in the CuO$_2$ planes as in orthorhombic Sr$_2$CuO$_3$.

Due to the very large antiferromagnetic Cu–Cu exchange coupling $J$ in Sr$_2$CuO$_3$, the magnitude of the magnetic susceptibility is so low that even small amounts of paramagnetic impurities contribute significantly to the observed magnetic susceptibility. Polycrystalline samples made by Ami et al. (Ref. 1) which were exposed to air showed significant Curie-Weiss contributions, observable most easily at low temperatures, which obscured the intrinsic spin susceptibility. The paramagnetic impurity concentrations in the samples responsible for this behavior were small, equivalent to the contribution of 0.4% spins $\frac{1}{2}$ (with respect to Cu) with $g$-factor $g = 2$. The impurity concentration decreased dramatically to $\approx 0.1\%$ when the samples were annealed at 600–800°C in nitrogen or at 300–600°C in low-pressure (6 torr) helium. It was proposed that paramagnetic oxygen defects due to the uptake of oxygen from the air may be responsible for the Curie-Weiss impurity contribution, but no test of this proposal was carried out. Mitchell et al. and Kato et al. (Refs. 33, 34) synthesized samples of Sr$_2$CuO$_3$ by dehydration of Sr$_2$Cu(OH)$_6$, Sr$_2$Cu(OH)$_6$ loses two molecules of H$_2$O per formula unit upon heating to 400°C in an argon atmosphere and forms orthorhombic Sr$_2$CuO$_3$. When heated to $\approx 450°C$ in oxygen, however, the insulating tetragonal form of Sr$_2$CuO$_{3+δ}$ discussed above is formed.

In view of the importance of Sr$_2$CuO$_3$ as a model $S = \frac{1}{2}$ antiferromagnetic Heisenberg chain compound, it is important to understand the dependence of sample handling on the magnetic properties of Sr$_2$CuO$_3$. We therefore undertook a study of the chemistry associated with sample handling. We found that Sr$_2$CuO$_3$ decomposes in air to form Sr$_2$Cu(OH)$_6$, Sr$_3$(OH)$_2$, Cu(OH)$_2$ and SrCO$_3$. Sr$_2$Cu(OH)$_6$ is the main product in this reversible reaction. Direct exposure of Sr$_2$CuO$_3$ to liquid water results in immediate irreversible decomposition to Sr$_2$Cu(OH)$_6$ which then further decomposes to SrCO$_3$ and Cu(OH)$_2$. Following Sec. II which gives experimental details of our work, these chemical reactions will be discussed in Sec. III.

In Sec. V we discuss the crystallography of Sr$_2$Cu(OH)$_6$ which we synthesized in pure form. In Sec. V we present and analyze our isothermal magnetization versus magnetic field $M(H)$ and magnetic susceptibility $\chi$ versus temperature $T$ data for Sr$_2$Cu(OH)$_6$. We also report in this section the results of room-temperature electron paramagnetic resonance (EPR) measurements. Our results and conclusions are summarized in Sec. VI. Anticipating that section, we demonstrate that Sr$_2$Cu(OH)$_6$ contains weakly interacting Cu$^{+2}$ magnetic moments with spin $S = \frac{1}{2}$ and average $g$ factor 2.133. From a fit of $\chi(T)$ by the Curie-Weiss law and the $M(H)$ isotherms by modified Brillouin functions, the exchange interaction between adjacent Cu$^{+2}$ spins was found to be $J/k_B = -1.06(4)$ K, a weakly antiferromagnetic interaction.

II. EXPERIMENTAL DETAILS

Several samples of Sr$_2$CuO$_3$ were synthesized by calcining stoichiometric quantities of 99.995% pure (metals basis) SrCO$_3$ (Aithaca Chemical Corp.) and CuO (Alfa Aesar) in air at 950°C for several days, regrounding once per day. A powder x-ray diffraction (XRD) pattern taken on a Rigaku x-ray diffractometer with Cu Ka radiation is shown as the top trace in Fig. 1. A typical sample showed the reported orthorhombic structure, with lattice parameters $a = 12.72(4)$ Å, $b = 3.904(8)$ Å, and $c = 3.496(8)$ Å in good agreement with literature values. XRD also revealed trace amounts of the SrCO$_3$ and CuO starting materials in the samples as shown in the top-most x-ray pattern in Fig. 1.

Samples of Sr$_2$Cu(OH)$_6$ were characterized by XRD analysis using the above diffractometer. Samples were mixed with dry KBr and pelletized for mid-range infrared spectroscopy (IR) measurements on a Hartmann and Braun Bomem FT-IR. Room-temperature EPR measurements were carried out at 9.5 GHz on a Bruker instrument. The derivative spectrum, $dI/dB$, shown in Fig. 1 below was obtained in the usual way as a function of magnetic field, but is plotted as a function of the spectroscopic splitting factor ($g$-factor) $g$ to provide direct comparison with the spectrum reported in the literature.

Magnetic susceptibility and magnetization measurements below 300 K were carried out using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The contribution of ferromagnetic impurities to the measured magnetization was determined from magnetization versus magnetic field isotherms between 75 and 300 K and was found to be equivalent to that of $\sim 50$ ppm ferromagnetic iron metal impurities; this contribution is corrected for in Figs. 1 and 2 below.
III. DECOMPOSITION OF $\text{Sr}_2\text{CuO}_3$

We initially suspected that $\text{Sr}_2\text{CuO}_3$ reacts with air when we observed that pristine dark brown $\text{Sr}_2\text{CuO}_3$ changes color to blue-gray within about thirty minutes of exposure to air. The subsequent XRD pattern contained the expected $\text{Sr}_2\text{CuO}_3$ peaks, but also contained several impurity peaks which could not be identified with remnants of the $\text{SrCO}_3$ or $\text{CuO}$ starting materials. The above process was repeated with additional samples to confirm the results. We found that the time required for the above color change to occur ranged up to several days, depending on the relative humidity of the laboratory air, which suggested that the samples were reacting with the water vapor in the air. Degraded samples which were heated to 950°C in air exhibited XRD patterns identical to the XRD pattern of a freshly prepared $\text{Sr}_2\text{CuO}_3$ sample (those x-rays were taken with the sample in flowing helium gas to prevent sample degradation while the x-ray data were accumulated). Therefore we conclude that the degradation of $\text{Sr}_2\text{CuO}_3$ in air is reversible. Although not the primary focus of this paper, we describe below some preliminary experiments carried out to investigate the observed sample degradation.

Since the time scale for sample degradation was clearly humidity dependent, for controlled experiments a humidity chamber was constructed in which a flow of hydrated 98% pure nitrogen or oxygen gas was passed over a $\text{Sr}_2\text{CuO}_3$ sample. The gas was hydrated by diffusing it through deionized water. The relative humidity and temperature inside the chamber were measured with a Fisher Scientific Jumbo Thermo-Humidity Meter. For sample exposure times up to forty-five hours, the sample decomposition results in both gases were identical. The gas was hydrated by diffusing it through deionized water. The relative humidity and temperature inside the chamber were measured with a Fisher Scientific Jumbo Thermo-Humidity Meter. For sample exposure times up to forty-five hours, the sample decomposition results in both gases were identical.

A substantial amount of white solid appeared in the solution three to four days later which was identified as $\text{SrCO}_3$ through XRD analysis. We attribute the formation of $\text{SrCO}_3$ to the reaction of unprecipitated $\text{Sr}^{+2}$ ions with $\text{CO}_3^{2-}$ ions and/or dissolved $\text{CO}_2$ gas present in the water.

In order to isolate the primary decomposition product $\text{Sr}_2\text{Cu(OH)}_6$ and minimize formation of $\text{SrCO}_3$, exposure of the sample to $\text{CO}_2$ must be minimized. Therefore reaction of a $\text{Sr}_2\text{CuO}_3$ sample in a vacuum-tight vessel with nanopure deionized, degassed water was carried out. Two methods of removing gases from the water were used: (i) distillation and (ii) repeated sequences of freezing the water from the bottom up in a vacuum-sealed glass vessel followed by pumping on the water while melting the ice. Initially all samples formed blue or purple-blue precipitates. The purple samples may have contained $\text{SrCu(OH)}_4$ which is a violet-colored sister compound to $\text{Sr}_2\text{Cu(OH)}_6$ (see Refs. 10, 11). We were not able to confirm the presence of $\text{SrCu(OH)}_4$ because all of the precipitates changed color before they could be isolated. Samples were dried by decanting off as much water as possible, then pumping off the residual water.
TABLE I: Summary of reactions of Sr₂CuO₃ with nanopure deionized, degassed water in a vacuum-tight vessel. “Initial color” refers to the color of the solid which immediately formed when the Sr₂CuO₃ sample contacted the water. “Final color” refers to the color of the solid after it had been dried.

| METHOD OF DEGASSING WATER | INITIAL COLOR | FINAL COLOR |
|---------------------------|---------------|-------------|
| freeze/thaw               | blue-purple   | pale blue⁴  |
| distilled in N₂ atmosphere| purple        | blue-green  |
| distilled in N₂ atmosphere| dark blue     | green       |
| distilled in N₂ atmosphere| sky blue      | green⁴      |

⁴X-ray had primarily Sr₂Cu(OH)₆ peaks.
⁵Turned to this color before vacuum pumping began.

They were not exposed to the air. All samples except one turned color from purple-blue to a shade of green during the drying process. The XRD patterns of the green samples (not shown or further discussed here) were complex and the phases present in the green samples could not be identified. The purple-blue sample that did not change color during the drying process was identified as primarily Sr₂Cu(OH)₆ by XRD analysis. The method of degassing the water did not seem to affect the overall results of the above experiments which are summarized in Table I.

IV. CHARACTERIZATION AND CRYSTAL STRUCTURE OF SR₂CU(OH)₆

In order to characterize the properties of pure Sr₂Cu(OH)₆, a pure sample of this compound was synthesized in strong hydroxide solution following the method of Scholder et al. (Ref. 40) using 99.2% Cu(NO₃)₂·2H₂O (Fisher Scientific) and 99% Sr(OH)₂·8H₂O (Alfa Aesar). Figure 2 shows an IR scan of the Sr₂Cu(OH)₆ sample. The scan shows no evidence of the sister compound SrCu(OH)₄ and agrees with literature data. Inductively coupled plasma (ICP) analysis revealed a Sr:Cu atomic ratio of 2.195 ± 0.066.

Figure 3 shows the crystal structure of Sr₂Cu(OH)₆ based on structural data from Nadezhina et al. (Ref. 40) using 99.2% Cu(NO₃)₂·2H₂O (Fisher Scientific) and 99% Sr(OH)₂·8H₂O (Alfa Aesar). This figure emphasizes the highly elongated Jahn-Teller distorted Cu(OH)₆ octahedra. The equatorial Cu-O distances are 1.97 and 1.98 Å and the apical distance is 2.63 Å. The latter distance is so large that the Cu coordination by oxygen should probably be considered to be square planar rather than octahedral. The Cu(OH)₆ units are isolated from one another suggesting a weak exchange interaction between the Cu⁺² spins. Figure 3 shows an x-ray diffraction pattern of a typical sample which we indexed on a monoclinic lattice, with space group P2₁/b (# 14) and with lattice parameters a = 8.080(2) Å, b = 9.760(2) Å, c = 6.146(1) Å and γ = 113.6(3)° in agreement with the results of Nadezhina et al. (Refs. 42, 43). A structure study by Dubler et al. (Refs. 42, 43) reported a different unit cell with different atomic positions in the same space group for Ba₂Cu(OH)₆. In order to confirm Dubler et al.’s statement that Ba₂Cu(OH)₆ is isostructural to Sr₂Cu(OH)₆, we undertook a study of the relationships of the two respective unit cells and atomic positions after first correcting for the different space group settings used by the two groups. Figure 3 shows the geometrical relationship between the two unit cells and Table II lists the respective lattice parameters.

The two unit cells coincide in the [1 0 0] direction, but form different parallelograms in the ab plane. The a lattice parameter in Nadezhina et al.’s unit cell (black cell in the foreground of Fig. 3) is the short diagonal of the parallelogram formed by Dubler et al.’s unit cell (gray cell in the background of Fig. 3). The law of cosines was used to obtain the expressions

\[ a = \sqrt{a'^2 + b'^2 + 2a'b' \cos \gamma'} \]
TABLE II: Lattice parameters for Ba$_2$Cu(OH)$_6$ by Dubler et al. (Refs. 14, 15) and Sr$_2$Cu(OH)$_6$ by Nadezhina et al. (Refs. 12, 13). The Ba$_2$Cu(OH)$_6$ primed lattice parameters are listed by Dubler in a different space group setting. The unprimed lattice parameters correspond to the alternate unit cell used by Nadezhina. The relationship between the two unit cells is shown in Fig. 5.

|                | Ba$_2$Cu(OH)$_6$ Primed | Ba$_2$Cu(OH)$_6$ Unprimed | Sr$_2$Cu(OH)$_6$ |
|----------------|-------------------------|---------------------------|-----------------|
| $a'$           | 6.030(2) Å              | 8.391(1) Å               | 8.079(2) Å      |
| $b'$           | 10.115(2) Å             | 10.115(2) Å              | 9.759(2) Å      |
| $c'$           | 6.440(2) Å              | 6.440(2) Å               | 6.165(2) Å      |
| $\gamma'$      | 124.03(1)$^\circ$       | 143.44(2)$^\circ$        | 143.620(1)$^\circ$ |
| vol            | 325.5(3) Å$^3$          | 325.6(4) Å$^3$           | 288.3(2) Å$^3$  |

FIG. 4: CuK$\alpha$ x-ray powder diffraction pattern of Sr$_2$Cu(OH)$_6$. The solid curve is intensity $I$ versus diffraction angle 2$\theta$. The space group is monoclinic $P2_1/b$ (14) with $a = 8.080(2)$ Å, $b = 9.760(2)$ Å, $c = 6.146(1)$ Å and $\gamma = 143.64(1)$$^\circ$. The Miller indices of the six strongest reflections are as indicated.

$$b = b'$$

$$c = c'$$

$$\gamma = 180^\circ - \gamma' + \theta$$

$$\theta = \cos^{-1} \left( \frac{b'^2 - a'^2 - a'^2}{-2aa'} \right)$$

which were used to calculate the unprimed unit cell for Ba$_2$Cu(OH)$_6$, which corresponds to Nadezhina et al.’s unit cell for Sr$_2$Cu(OH)$_6$. The volumes of the unit cells are 325.6(4) Å$^3$ for Ba$_2$Cu(OH)$_6$ and 288.3(2) Å$^3$ for Sr$_2$Cu(OH)$_6$, a difference of 37.3(6) Å$^3$. This difference is similar to four times the difference between the Ba and Sr atomic volumes calculated from structural data for elemental Ba and Sr (Ref. 16): 4(62.99 Å$^3$/atom - 56.325 Å$^3$/atom) = 26.66 Å$^3$/atom (the factor of 4 arises because there are two formula units per unit cell). Also, since in the same (unprimed) unit cell the $\gamma$ angles of the unit cells for the two compounds are essentially the same and the $a$, $b$, and $c$ lattice parameters for the Ba compound are all $\sim$ 4% larger than those for the Sr compound, one sees that substituting Ba for Sr results in a uniform increase in unit cell size.

The fractional atomic positions in the primed unit cell for Ba$_2$Cu(OH)$_6$ can be expressed in terms of the unprimed unit cell according to

$$\begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix} = - \begin{bmatrix} a' \sin \gamma' + \gamma' & b' & c' \\ 0 & 0 & 0 \\ a' \sin \gamma' + \gamma' & b' & c' \end{bmatrix} \begin{bmatrix} x'/a' \\ y'/b' \\ z'/c' \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}. \quad (2)$$
The results are shown in Table III. Although the unprimed atomic positions for Ba$_2$Cu(OH)$_6$ do not match those of Sr$_2$Cu(OH)$_6$ within the errors, the close similarities of the respective values demonstrate that Sr$_2$Cu(OH)$_6$ and Ba$_2$Cu(OH)$_6$ are isostructural. Therefore, the primed unit cell used by Dubler et al. is an alternative unit cell for the two compounds.

V. EPR, MAGNETIC SUSCEPTIBILITY, AND MAGNETIZATION OF Sr$_2$Cu(OH)$_6$

Figure 6 shows a typical room-temperature EPR spectrum of a powder Sr$_2$Cu(OH)$_6$ sample and a DPPH internal standard. The hyperfine interaction of the Cu$^{+2}$ electronic spin $I = \frac{3}{2}$ with the Cu nuclear spin $I = \frac{1}{2}$ has a typical width of 20–100 G, but it is not resolved in our data. We believe this is due to several factors. We expect to see “absorption-like” features rather than sharp derivative peaks since the material is a powder. At room temperature, spin-lattice relaxation leads to broadened features which obscure the hyperfine peaks. Since our system is not magnetically dilute, the spin-spin interaction also leads to peak broadening.

The function used to fit the EPR data consisted of a vertical offset term and the sum of the derivatives of four gaussians (including one for the DPPH magnetic field marker) which yielded three principal-axis $g$ values for Sr$_2$Cu(OH)$_6$ consistent with the rhombic symmetry of the Cu site. The DPPH-corrected $g$ values, 2.214(2), 2.114(1), and 2.069(1), are in agreement with the literature values.

In order to incorporate these experimentally determined values into fits to the powder magnetic susceptibility and magnetization data, the spherical (powder) average must be used. The Curie constant which occurs in the magnetic susceptibility fit function [Eqs. (5), (8) below] is a function of $g^2$; therefore, the appropriate average of $g$ is the rms $g$ value, $g_A$, as given in Eq. (3). The Brillouin function [Eq. (10) below] used to fit our low temperature magnetization data is a function of the average of $g$ itself, as given by $g_B$ in Eq. (4).

Not surprisingly, these two values are nearly identical.

\[
g_A = \sqrt{\frac{(g_1^2 + g_2^2 + g_3^2)}{3}} = 2.133
\]

\[
g_B = \frac{(g_1 + g_2 + g_3)}{3} = 2.132
\]

The magnetic susceptibility $\chi$ versus temperature $T$ in an applied magnetic field $H = 10$ kG is shown in Fig. 7. We fitted the data by

\[
\chi = \chi_0 + \frac{C}{T - \theta}
\]

where $\theta$ is the Weiss temperature and $C$ is the Curie constant given by

\[
C = \frac{N g^2 \mu_B^2 S (S + 1)}{3k_B}
\]

in which $N$ is the number of spins in the sample, $g$ is $g_A$ (Eq. 3), $\mu_B$ is the Bohr magneton, $S$ is the spin of the Cu$^{+2}$ ion (assumed to be $\frac{1}{2}$) and $k_B$ is the Boltzmann constant. In the molar units of $\chi$ or $M$ in Figs. 6 and 7 below, $N$ is set to $N_A$ (Avogadro’s number). The $T$-independent $\chi_0$ term

\[
\chi_0 = \chi_{\text{core}} + \chi_{\text{VV}}
\]

is the sum of the contribution from the diamagnetic cores of the atoms $\chi_{\text{core}}$ plus the paramagnetic Van Vleck susceptibility $\chi_{\text{VV}}$ of the Cu$^{+2}$ ions.
A fit to all the $\chi(T)$ data in Fig. 3 by Eq. (3) with $\chi_0$ set to the diamagnetic core contribution for Sr$_2$Cu(OH)$_6$ ($-1.13 \times 10^{-4}$ cm$^3$/mol), yields the fit (solid curve) in Fig. 7 with a Weiss temperature $\theta = -2.74(1)$ K indicating weak coupling between the Cu$^{2+}$ spins, as expected. The negative sign of $\theta$ corresponds to an antiferromagnetic coupling between the Cu spins. When $\chi_0$ was allowed to vary, $\chi_0$ became more negative than the diamagnetic core contribution, which is physically unreasonable. We were able to obtain a better fit when $C$ was allowed to vary. However, the fitted $C$ value yielded a $g$ value from Eq. (2) which was significantly lower than the measured average $g$ value obtained from EPR.

Figure 8 shows the inverse of the magnetic susceptibility corrected for the contribution of $\chi_0$, $(\chi - \chi_0)^{-1}$, versus temperature $T$ in an applied magnetic field $H = 10$ kG. The dashed line is a linear fit

$$\frac{1}{\chi - \chi_0} = \frac{T - \theta}{C}$$

[see Eq. (5)] with fixed $C$ given by Eq. (3) which yields $\theta = -8.0(5)$ K. This $\theta$ is significantly larger in magnitude than obtained from the $\chi(T)$ fit in Fig. 3. The solid line in Fig. 8(a) is a linear fit with fitted $C$ and is clearly a better fit to the data. Although the latter $\theta = -2.75(9)$ K agrees with that from the fit in Fig. 3, the average $g = 2.074(1)$ obtained from $C$ is lower than the average value obtained from EPR. We could not obtain an optimum fit to our data with physically reasonable parameters using the $g$ value from the EPR measurements. At low temperatures, shown in Fig. 8(b), both the “Fitted $g$” and the “Fixed $g$” fits deviate from the data.

As noted above, the $\theta$ values obtained from the fixed-$g$ fits to $\chi(T)$ and $(\chi - \chi_0)^{-1}$ versus $T$ do not agree. Fitting $\chi(T)$ emphasizes the low-temperature regime where $\chi$ is varying most strongly with $T$ due to the Curie-Weiss behavior. The $(\chi - \chi_0)^{-1}$ data, however, emphasize the high-temperature behavior, where weak temperature dependence of $\chi_0$ and/or the contribution to $\chi(T)$ from small amounts of impurities could most strongly influence the parameters obtained from the fit. Therefore, the parameters obtained from the one-parameter $\chi(T)$

\begin{table}[h]
\centering
\begin{tabular}{c|ccc|ccc|ccc}
& $x'/a'$ & $y'/b'$ & $z'/c'$ & $x/a$ & $y/b$ & $z/c$ & $x/a$ & $y/b$ & $z/c$ \\
Ba, Sr & & & & & & & & & \\
Cu & 0 & 0 & 0 & & & & & & \\
O1 & 0.4327 & 0.2576 & 0.0566 & 0.4326 & 0.3740 & 0.2425 & 0.429(2) & 0.366(2) & 0.233(2) \\
O2 & 0.1956 & 0.7629 & 0.0393 & 0.1956 & 0.1563 & 0.7371 & 0.202(2) & 0.156(2) & 0.724(2) \\
O3 & 0.1387 & 0.4756 & 0.2267 & 0.1387 & 0.9120 & 0.0250 & 0.122(2) & 0.889(2) & 0.033(2) \\
\end{tabular}
\end{table}

FIG. 8: (a) Inverse magnetic susceptibility corrected for the contribution of $\chi_0$, $(\chi - \chi_0)^{-1}$, versus temperature $T$ (⊙) of Sr$_2$Cu(OH)$_6$. The dashed line is the “Fixed $g$” fit yielding the $\theta$ parameter shown in the figure where the fixed $g$ is $g_A$ in Eq. (4). The solid line is the “Fitted $g$” fit which yields the indicated $g$ and $\theta$ values. $\chi_0$ is fixed at $\chi_{\text{core}}$ for both fits. (b) Expanded plot of the low temperature data and fits below 50 K.
fit,
\[
\chi_0 = -1.13 \times 10^{-4} \text{ cm}^3/\text{mol}
\]
\[g = 2.133\]  
\[
\theta = -2.74(1) \text{ K},
\]
are considered to be more reliable and best represent the intrinsic behavior of Sr$_2$Cu(OH)$_6$.

To investigate the low temperature behavior further, several magnetization versus applied magnetic field \(M(H)\) isotherms at low temperatures and both zero-field-cooled (ZFC) and field-cooled (FC) \(M(T)\) data at \(H = 100 \text{ G}\) were taken. The ZFC and FC data show no evidence of long-range ordering above 1.8 K as shown in Fig. 11. The \(M(H)\) isotherms at low temperatures are shown in Fig. 11. The data up to \(H = 1\ T\) are in the low-field proportional part of the \(M(H)\) curves, which explains why all the magnetization data in Fig. 11 lie on a common curve.

We obtained a robust fit to the \(M(H)\) isotherm data in Fig. 11 using a modified Brillouin function \(g\) for \(S = \frac{1}{2}\)
\[
M = NgS \tanh \left( \frac{gS\mu_B H}{k_B(T - \theta)} \right),
\]
where \(g\) is \(g_B\) as given in Eq. (3), and \(T\) in the usual Brillouin function \(g\) is replaced by \(T - \theta\). This change was necessary so that the high-temperature and/or low-field expansion of Eq. (3) yielded the observed Curie-Weiss behavior \(M = CH/(T - \theta)\). The fit yielded \(\theta = -2.575(4) \text{ K}\). This value for \(\theta\) agrees with the value in Eq. (4) obtained from the fit to the magnetic susceptibility data, as it should. A comparison of the two values gives the estimate \(\theta = -2.66(9) \text{ K}\). When we allowed the spin \(S\) to vary during a fit, the fitted \(S\) value ranged from 0.471 to 0.516 indicating that the spin is indeed \(\frac{1}{2}\) as expected for Cu$^{+2}$. Allowing \(g\) to vary at fixed \(S = \frac{1}{2}\) produced a slightly better fit, but with an incorrect \(g\) value \((g = 2.179\) compared to the actual value 2.132). In Fig. 11, a scaling plot of the magnetization \(M\) versus the ratio of magnetic field energy to the modified thermal energy \(\mu_B H/k_B(T - \theta)\) for Sr$_2$Cu(OH)$_6$ at 1.8 K (\(\circ\)), 2.5 K (\(\blacklozenge\)), 3.0 K (\(\square\)), 3.5 K (\(\triangledown\)), 4.0 K (\(\blacktriangle\)) and 4.5 K (\(\triangleleft\)). The solid curve is a fit to all the data by Eq. (10), with fitting parameter \(\theta\), fixed \(g = g_B\) as given in Eq. (3) and \(S = 1/2\).

In summary, we find that the best description of the
Cu next-nearest neighbors are at distances of from Table V in Ref. 5.

\[
\text{powder } \text{Sr nearest neighbors (}z\text{)} \text{cally oxidized in aqueous base without any noticeable } \theta \text{ing compound } \text{La} = 3 J. \text{est neighbors.}
\]

\[
\chi \text{and } M \text{from } EPR \text{ and is similar to those of other cuprates. For } g = 2.133; \text{the Weiss temperature in the Curie-Weiss law is } \theta = -2.66(9) K. \text{ Assuming a Heisenberg interaction between nearest-neighbor spins with Hamiltonian } \mathcal{H} = -J \sum_{<i,j>} \vec{S}_i \cdot \vec{S}_j, \text{ where the sum is over all distinct nearest-neighbor pairs of spins and } J > 0 (J < 0) \text{ corresponds to a ferromagnetic (antiferromagnetic) interaction, the exchange constant } J \text{ is given in terms of } \theta \text{ by } J = 3k_B\theta/[x(S + 1)] \text{ where } z \text{ is the number of nearest neighbors.} \]

\[
\text{In } \text{Sr}_2\text{Cu(OH)}_6, \text{ each Cu atom has } 10 \text{ Cu nearest neighbors (}z = 10\) at a distance of } 5.8-6.2 \text{ Å; the Cu next-nearest neighbors are at distances of } \geq 8.1 \text{ Å. Using } \theta = -2.66(9) \text{ K, one thus obtains } J/k_B = -1.06(4) \text{ K.}
\]

VI. SUMMARY AND CONCLUSIONS

We have demonstrated that Sr$_2$CuO$_3$ decomposes in both air and liquid water and that the primary decomposition product is Sr$_2$Cu(OH)$_6$. In contrast, the compound La$_2$CuO$_4$ can be successfully electrochemically oxidized in aqueous base without any noticeable decomposition.

The magnetic susceptibility of Sr$_2$Cu(OH)$_6$ exhibits Curie-Weiss behavior down to low temperatures and indicates only very weak interactions between the Cu$^{+2}$ spins. The crystallography, EPR, and magnetization measurements are consistent with a nearly isolated, spin $S = \frac{1}{2}$ local moment model for Sr$_2$Cu(OH)$_6$. We obtained unusually good consistency between the $M(H)$ and $\chi(T)$ fits which yielded a small $\theta = -2.66(9) \text{ K}$. The spherically averaged $g$ of the Cu$^{+2}$ spins is 2.133 obtained from EPR and is similar to those of other cuprates. For example, $g$ in CuO is 2.125(5); in La$_2$BaCuO$_5$ and in powder Sr$_{14}$Cu$_{24}$O$_{44}$ it is 2.103 and 2.14, respectively (from Table V in Ref. 5).

Since the magnitude of the magnetic susceptibility of the linear chain compound Sr$_2$CuO$_3$ is small due to the strong antiferromagnetic coupling between the Cu spins, one would expect even a small impurity concentration of Sr$_2$Cu(OH)$_6$ to produce a significant paramagnetic contribution at low temperatures. Although we cannot rule out the possibility that paramagnetic oxygen species are generated upon exposure of Sr$_2$CuO$_3$ to air as proposed by Ami et al. (Ref. 9), our experiments indicate that the reported variable Curie-Weiss contributions to the magnetic susceptibility of polycrystalline Sr$_2$CuO$_3$ were most likely mainly due to varying amounts of Sr$_2$Cu(OH)$_6$ on the sample surfaces due to exposure of the sample to the humidity in the air.

The Cu–Cu exchange coupling $J/k_B = -1.06(4) \text{ K}$ in Sr$_2$Cu(OH)$_6$ is very weak compared to $J/k_B \sim -1600 \text{ K}$ in the high-$T_c$ cuprate superconductors, due to the isolated square-planar coordination of the Cu$^{+2}$ ions in Sr$_2$Cu(OH)$_6$. The nearest-neighbor Cu–Cu exchange path is Cu–O–O–Cu with a zig-zag geometry and a Cu–Cu distance of 5.8 Å, whereas in the planar high-$T_c$ cuprates the nearest-neighbor distance is 2.80 Å with a strong 180° Cu–O–Cu antiferromagnetic superexchange coupling. Thus Sr$_2$Cu(OH)$_6$ serves as nice reference material for comparison to the magnetic properties of more strongly interacting systems such as the high-$T_c$ cuprates.

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1. H. A. Bethe, Z. Phys. 71, 205 (1931).
2. M. Uehara, T. Nagata, J. Akimitsu, H. Takahashi, N. Mőri, and K. Kinoshita, J. Phys. Soc. Jpn. 65, 2764 (1996).
3. H. Takahashi, N. Mőri, T. Nakanishi, T. Nagata, M. Uehara, J. Akimitsu, and K. Kinoshita, Physica B 237–238, 112 (1997).
4. D. C. Johnston, R. K. Kremer, M. Troyer, X. Wang, A. Klümpfer, S. L. Bud’ko, A. F. Panchula, and P. C. Canfield, Phys. Rev. B 61, 9558 (2000).
5. D. C. Johnston, M. Troyer, S. Miyahara, D. lidsky, K. Ueda, M. Azuma, Z. Hiroi, M. Takano, M. Isobe, Y. Ueda, M. A. Korotin, V. I. Anisimov, A. V. Mahajan, L. L. Miller, cond-mat/0001147, and cited references.
6. D. C. Johnston, T. Saito, M. Azuma, M. Takano, T. Yamauchi, and Y. Ueda, Phys. Rev. B 64, 134403 (2001), and cited references.
7. E. Dagotto and T. M. Rice, Science 271, 618 (1996).
8. C. L. Teske and H. Muller-Büsschbaum, Z. Anorg. Allg. Chem. 371, 325 (1969).
9. T. Ami, M. K. Crawford, R. L. Harlow, Z. R. Wang, D. C. Johnston, M. Huang, and R. W. Erwin, Phys. Rev. B 51, 5994 (1995).
10. D. C. Johnston, Acta Phys. Pol. A 91, 181 (1997).
11. N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. Lett. 76, 3212 (1996).
12. S. Eggert, Phys. Rev. B 53, 5116 (1996).
13. H. Suzuura, H. Yasuhara, A. Furusaki, N. Nagaosa, and Y. Tokura, Phys. Rev. Lett. 76, 2579 (1996).
14. J. Lorenzana and R. Eder, Phys. Rev. B 55, R3358 (1997).
15. S.-L. Drechsler, J. Mäle, S. Zaliś, and K. Rościszewski, Phys. Rev. B 53, 11328 (1996).
16. K. M. Kojima, Y. Fudamoto, M. Larkin, G. M. Luke, J. Merrin, B. Bachumi, Y. J. Uemura, N. Motoyama, H. Eisaki, S. Uchida et al., Phys. Rev. Lett. 78, 1877 (1997).
17. A. Keren, L. P. Le, G. M. Luke, B. J. Sternlieb, W. D.
Wu, Y. J. Uemura, S. Tajima, and S. Uchida, Phys. Rev. B 48, 12926 (1993).

A. Keren, K. Kojima, L. P. Le, G. M. Luke, W. D. Wu, Y. J. Uemura, S. Tajima, and S. Uchida, J. Magn. Magn. Mater. 140-144, 1641 (1995).

S. Eggert, I. Affleck, and M. Takahashi, Phys. Rev. Lett. 73, 332 (1994).

A. Klümpfer and D. C. Johnston, Phys. Rev. Lett. 84, 4701 (2000).

M. Takigawa, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. Lett. 76, 4612 (1996).

M. Takigawa, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. B 55, 14129 (1997).

M. Takigawa, O. A. Starykh, A. W. Sandvik, and R. R. P. Singh, Phys. Rev. B 56, 13681 (1997).

H. Fujisawa, T. Yokoya, T. Takahashi, S. Miyasaka, M. Kimbune, and H. Takagi, Phys. Rev. B 59, 7358 (1999), and cited references.

Z. Hiroi, M. Takano, M. Azuma, and Y. Takeda, Nature 364, 315 (1993).

P. D. Han, L. Chang, and D. A. Payne, Physica C 228, 129 (1994).

Y. Y. Wang, H. Zhang, V. P. Dravid, L. D. Marks, P. D. Han, and D. A. Payne, Physica C 255, 247 (1995).

P. Laffez, X. J. Wu, S. Adachi, H. Yamauchi, and N. Morii, Physica C 222, 303 (1994).

T. Ami, M. K. Crawford, R. L. Harlow, Z. G. Li, T. Vogt, Q. Zhu, and D. E. Cox, Physica C 235-240, 1003 (1994).

T. Kawashima, Y. Matsui, and E. Takayama-Muromachi, Physica C 282-287, 513 (1997).

T. Kawashima and E. Takayama-Muromachi, Physica C 267, 106 (1996).

R. C. Lobo, F. J. Berry, and C. Greaves, J. Solid State Chem. 88, 513 (1990).

J. F. Mitchell, D. G. Hinks, and J. L. Wagner, Physica C 227, 279 (1994).

M. Kato, T. Miyajima, I. Nagai, and Y. Koike, J. Low Temp. Phys. 105, 1499 (1996).

M. Bonvalot, E. Beaupron, D. Bourgault, M. Núñez-Regueiro, and R. Tournier, Physica C 282-287, 539 (1997).

Y. Shimakawa, J. D. Jorgensen, J. F. Mitchell, B. A. Hunter, H. Shaked, D. G. Hinks, R. L. Hitterman, Z. Hiroi, and M. Takano, Physica C 228, 73 (1994).

H. Zhang, Y. Y. Wang, L. D. Marks, V. P. Dravid, P. D. Han, and D. A. Payne, Physica C 255, 257 (1995).

C. Friebel, Z. Naturforsch. 29b, 295 (1974).

V. G. Krishnan, Indian J. Pure Appl. Phys. 16, 794 (1978).

V. R. Scholder, R. Felsenstein, and A. Apel, Z. Anorg. Allg. Chem. 216, 138 (1933).

B. N. Ivanov-Emin, L. P. Petrishcheva, B. E. Zaitsev, and A. S. Izmailovich, Zh. Neorg. Khim. 29, 1497 (1984).

T. N. Nadezhina, E. A. Pobedimskaya, and N. V. Belov, Sov. Phys. Dok. 25, 73 (1980).

T. N. Nadezhina, E. A. Pobedimskaya, and N. V. Belov, Dokl. Akad. Nauk SSSR 250, 1126 (1980).

E. Dubler, P. Korber, and H. R. Oswald, Acta Crystallogr. Sect. B 29, 1929 (1973).

E. Dubler, P. Korber, and H. R. Oswald, Naturwissenschaften 59, 467 (1972).

W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, vol. 2 (Pergamon Press, New York, 1967).

J. W. Orton, Electron Paramagnetic Resonance: An Introduction to Transition Group Ions in Crystals (Iliffe Books Ltd, London, 1968).

J. R. Pilbrow, Transition Ion Electron Paramagnetic Resonance (Clarendon Press, Oxford, 1990).

K. D. Bowers and J. Owen, Rep. Prog. Phys. 18, 304 (1955).

A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions (Clarendon Press, Oxford, 1970).

C. Kittel, Introduction to Solid State Physics (John Wiley & Sons, Inc., New York, 1996), 7th ed.

F. C. Chou and D. C. Johnston, Phys. Rev. B 54, 572 (1996), and cited references.