Ferromagnetism in partially oxidized CuCl

Thomas Saerbeck a,b,*, Juan Pereiro a,b, James Wampler a,b, Jacob Stanley a, James Wingert a, Oleg G. Shpyrko a, Ivan K. Schuller a,b

a Department of Physics, University of California San Diego, La Jolla, CA 92093, USA
b Center for Advanced Nanoscience, University of California San Diego, La Jolla, CA 92093, USA

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1. Introduction

The phase diagram of copper halides shows a rich diversity not only in crystalline structure, but also in magnetic and electronic properties. Cuprous chloride (CuCl) forms the chemically most unstable compound of the series with the Cu ion being easily oxidized from Cu+ to Cu2+. While pure CuCl is reported to be a diamagnetic semiconductor [1], its corrosion products show different types of magnetic order. Direct dissociation of CuCl without the intake of oxygen and hydrogen leads to the formation of cupric chloride CuCl2. The anhydrous form shows antiferromagnetic (AFM) order at TN = 23.9 K [2], while the intercalation of water leads to a structural deformation to CuCl2(H2O) and a reduced Néel temperature of 4.3 K [3]. A second oxidation route leads to the family of the atacamites, which includes three polymorphs of Cu2Cl(OH)3 [4]. These materials are of interest especially because of their frustrated magnetic properties [5,6] which can be related to the S = 1/2 Kagomé antiferromagnet [7]. In fact, all polymorphs show an onset of long range AFM order at temperatures of 9.0 K (atacamite), 7.2 K (botallackite) and 18.1 K (clinoatacamite) [8–10].

Previously CuCl has been proposed in the literature as a candidate for high-temperature superconductivity [1,11,12]. Depending on the experimental conditions of pressure, temperature and cooling rates, anomalies in the diamagnetic susceptibility and large drops in resistivity have been observed [13,14]. However, no reproducible observation of superconductivity has been reported so far [15,16].

Reports of possible excitonic superconductivity above liquid nitrogen temperature, originating at the interface between epitaxially grown CuCl on Si [17,18], add to the controversy of CuCl system. The claim of excitonic superconductivity was based on an unusual diamagnetic and paramagnetic response obtained upon variation of the external field direction and irregularities in the IV characteristics at 77 K [17,19]. These experimental results were not corroborated by other groups. Recent theoretical considerations indicate the possibility of superconductivity in the system, but at temperatures well below those for which the anomalies were reported [16].

In this paper we report on a different approach for preparation of CuCl/Si and CuCl2/Si heterostructures, which do not exhibit any signature of possible superconductivity. Instead, we find an unusual purely magnetic response in several samples at different temperatures. A ferromagnetic (FM) transition just below 20 K was found to be independent of the addition of Si and was investigated in terms of its microscopic origin and underlying crystalline structure. We compare our results to magnetic transitions reported for corrosion products of CuCl and show that the observed transition corresponds to an intermediate state of CuCl oxidation whose magnetic properties do not match with known phases of the copper halides.

2. Experimental

Bulk samples of CuCl+Si and CuCl2+Si have been fabricated by different methods of combining CuCl (99.995% purity) or CuCl2

* Corresponding author at: Department of Physics, University of California San Diego, La Jolla, CA 92093, USA. Tel.: +1 858 246 0101.
E-mail address: tsaebeck@physics.ucsd.edu (T. Saerbeck).

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(99.99% purity) with Si (99.99% purity). All materials were obtained from Sigma Aldrich and used as received. The first method of sample preparation consisted of pressing ground and mixed powders into heterogeneous pellets of 0.5 in. diameter. In the second method, Si was deposited on pure CuCl and CuCl₂ pellets by electron-beam evaporation at room temperature. The CuCl powder from Sigma Aldrich was initially of light greenish color, indicating some oxidation. Phase-pure CuCl powder was obtained by precipitation from aqueous CuCl₂(2H₂O) diluted with sodium sulfite solution and dilute sulfuric acid solution. Due to the reactivity of CuCl in moist air, the precipitate was washed with glacial acetic acid and ether in a dry N₂ filled glove bag. Resultant dry powders were stored under inert atmosphere preserving the initial white color. Different degrees of oxidation, including a color change to light green, were induced by storage in normal air and in humid air next to a beaker filled with water in an enclosed chamber. A second batch of pure CuCl powder was prepared using the same precipitation method, but was washed with water and dried in normal air. The resulting powder from this preparation appears dark green in color due to the high degree of oxidation. In the following, we use the labels “UCSD” for CuCl prepared and stored under inert atmosphere, “UCSD (air)” for CuCl stored in normal air, “UCSD (washed)” for the powder washed with water and “UCSD (humid)” for the CuCl powder stored next to a beaker with water.

All samples discussed in this paper were primarily investigated with Magnetic Field Modulated Microwave Spectroscopy (MFMMS) in order to quickly and effectively scan for superconductivity and other magnetic phase transitions [20,21]. The technique and experimental procedures are described in detail elsewhere [22]. Due to the magnetic field modulation, MFMMS is sensitive to superconducting volumes as low as 10⁻¹⁳ cm³, but also enables fast detection of purely magnetic phase transitions as a function of temperature [21]. Magnetic characterization was performed using conventional SQUID magnetometry and Vibrating Sample Magnetometer (VSM) techniques (Quantum Design). Structural analysis was performed by x-ray diffraction (XRD) using a Bruker D8 Discover diffractometer with Cu Kα radiation. While magnetic characterizations were performed in vacuum or He atmosphere, XRD measurements were made in air, but on a timescale which showed no difference due to oxidation when comparing two subsequent XRD scans.

For studies on CuCl₂ compounds, anhydrous powder was obtained by dehydration of CuCl₂(2H₂O) at 100 °C for 2 h in Ar atmosphere. For x-ray measurements reported in Section 4, a dehydrated pellet was used, while the magnetization was obtained from different pieces of the same dehydrated pellet exposed to air for varying lengths of time.

3. Results

3.1. Absence of superconductivity

Fig. 1 shows the MFMMS signal as a function of temperature of the CuCl₂ samples containing Si. The measurements were taken in a 15 Oe external bias field with modulation amplitude of 15 Oe in both cooling and warming directions. Both temperature scans exhibit the same MFMMS response and only the scans taken while cooling are shown in Fig. 1. No feature above noise level was observed in CuCl₂/Si between 300 K and 4 K, thus excluding the possibility of superconductivity in these samples with Tc higher than 4 K. This can also be seen in the magnetization as a function of temperature, as discussed in Section 4 of this manuscript. CuCl₂/Si samples on the other hand show a sharp drop of the MFMMS response close to 20 K. This decrease is opposite to the MFMMS response observed for all superconductors studied so far [20]. Instead, the decrease in MFMMS signal is indicative of a FM phase transition [21]. Since CuCl is reported to be diamagnetic over the measured temperature range [1] and the addition of Si is not expected to lead to ferromagnetism, we will discuss the origin of this signal in detail in the following sections. In order to further test for the possibility of superconductivity, all samples have been annealed in a tube furnace under Ar atmosphere at 400 °C. The resultant MFMMS response was featureless over the full temperature range from 300 K to 4 K (data not shown).

3.2. Magnetic transitions in oxidized CuCl

MFMMS of CuCl “UCSD” stored under inert atmosphere without further contact to water does not show any feature (Fig. 2a). The dip in the MFMMS signal similar to the one observed for powders from Sigma Aldrich is only seen in samples that were left to oxidize in air for 3 weeks [UCSD (air)] or samples washed with water [UCSD (washed)]. However, after extensive exposure to humid air for 24 h, the signal is again featureless [UCSD (humid)]. SQUID magnetometry measurements (Fig. 2b), taken in 1000 Oe from low to high temperatures after zero field cooling, show an increase in magnetization close to the temperature where the feature in MFMMS was observed. The data is normalized by the total sample mass in order to provide a direct comparison of the signal obtained. The steep increase in magnetization at finite temperatures is characteristic of FM transitions. CuCl “UCSD” and “UCSD (humid)” show only a paramagnetic increase towards 4 K, in agreement with the featureless MFMMS response.

The FM nature of the transition is further confirmed by the observation of a rectangular hysteretic magnetization as a function of external field and temperature. The data is summarized for all samples at 4 K in Fig. 3. All samples, with the exception of pure unoxidized CuCl “UCSD” show FM hysteresis with varying coercive field strength and saturation magnetization. Due to the unknown origin and mass fraction of the FM part of the sample, the obtained signal is scaled to the total mass of the sample and no correction for diamagnetic or paramagnetic signals is made. For the sample obtained from Sigma Aldrich, a flat loop closure is reached for fields larger than 5 kOe, indicating magnetic saturation. All samples prepared at UCSD show a finite slope reaching out to the highest fields measured (30 kOe), which is a measure of the paramagnetic material present in the sample. Values of the coercive field (Hc) and total FM magnetization (Mf) of the samples

![Fig. 1](https://example.com/fig1.png)

**Fig. 1.** MFMMS response of CuCl₂+Si system from 4 K to 300 K, showing absence of a superconducting transition. Individual scans are offset along the Y-axis for clarity. While CuCl₂/Si samples show no features between 300 K and 4 K, CuCl/Si samples show a sharp transition at around 15 K, opposite in sign to MFMMS response expected for a superconducting transition.
are extracted after subtracting a linear fitted slope of the paramagnetic increase from the data (Table 1). The values are symmetric for positive and negative external fields within a few Oe and therefore only positive values are listed.

While the coercive field values do not show a clear trend between samples, the magnetization increases if the powder is brought into contact with water. However, an extended exposure to humidity lowers the magnetization again, which indicates that the FM signal originates from an intermediate phase in the oxidation process of CuCl.

The FM hysteresis is observed in samples from Sigma Aldrich and “UCSD (air)” up to a temperature of 20 K with decreasing magnetization and coercivity. For CuCl washed with water, the ferromagnetism has already fully collapsed at 20 K and only the paramagnetic slope is observed. An FM hysteresis is observed with VSM at 4 K in “CuCl (humid)”, which was not detected by SQUID. This is likely due to the stronger paramagnetic (PM) contribution and the low onset of the transition in temperature. The coercivity of the loop is drastically reduced and the curve sheared due to the presence of PM magnetization. The FM opening of the hysteresis loop is only observed up to 7 K.

Once the ferromagnetism has evolved, the sample cannot be reversed to the original CuCl by thermal annealing in temperatures below 200 °C. This indicates that the ferromagnetism indeed emerges from a new chemical structure and is not simply related to intercalation of H2O or (OH) groups. Conversely, annealing temperatures above 200 °C change the sample color to gray and the FM signal is lost.

3.3. Phase analysis

Since the oxidation of CuCl in humid environments involves a change in the crystallographic structure [2,3], x-ray diffraction was performed to determine the phase composition of each sample. Fig. 4 summarizes the powder diffraction scans and difference profiles between individual measurements. The top profile of CuCl “UCSD” has been analyzed via Rietveld refinement using a single phase of CuCl. A subsequent measurement of the same sample reproduced the data within the uncertainty of the x-ray system, indicating that the timescale of the measurement is short enough for the powder not to change due to oxidation. The difference profile indicates good agreement between data and refinement (A-Ref.) and limits other phases to a fraction below 0.5% of the total volume. Refinement parameters for the CuCl phase are in agreement with literature values for CuCl in cubic symmetry [space group F – 4 3 m (21)] with a lattice constant a = 5.415 Å [23].

A measurement of the powder obtained from Sigma Aldrich, taken under the same conditions, does not show a drastic difference in the diffraction profile. This is surprising because this sample shows the strongest coercivity and smallest PM contribution. Only at low angles (2θ = 16°) is a small increase in intensity observed. This could be related to either CuCl2(2H2O) or Cu2Cl (OH)3, both of which show the highest diffraction intensity at this angle. The phase concentration can be limited to 2% with respect to the main CuCl phase, which does not give sufficient scattering information for refinement.

A similar result was obtained for the sample stored in normal air. After 3 weeks of oxidation in normal air, the magnetic results and structural pattern agree with the Sigma Aldrich measurement.
within experimental uncertainties. When more water was added to the sample, for example by washing, new phases were observed in the diffraction pattern. Again, the new phases can be related to CuCl₂(2H₂O) or polymorphs of Cu₂Cl(OH)₃. However, diffraction lines of the two compounds lie too close together to be identified individually, which prevents a quantification of the phase concentration.

A prolonged exposure to humid air does not lead to the observation of new phases. Instead, all previous observed diffraction peaks grow in intensity in a homogeneous fashion with respect to the CuCl main phase peak. Still, it is not possible to separate contributions of Cu₂Cl(OH)₃ and CuCl₂(2H₂O) to enable a refinement and obtain the phase concentration, but the intensity indicates that the CuCl is no longer the main phase.

4. Discussion

Experimental observations made with MFMMS, SQUID and VSM show a FM response of CuCl exposed to normal air or direct contact to water for a short time. Fresh CuCl only shows weak diamagnetic behavior. Structural analysis only shows minor differences in the diffraction pattern, which can be related to the existence of CuCl₂(2H₂O) or polymorphs of Cu₂Cl(OH)₃. The concentration of these new phases is limited to below 2% for samples oxidized in air and as obtained from Sigma Aldrich. As the degree of oxidation increases and new phases are observed with stronger intensity, the FM signal doubles, until it decreases again when the material is exposed to higher degrees of humidity.

Pure CuCl₂(2H₂O) is reported to show a paramagnetic to AFM transition with a Néel temperature of 4 K [24]. The transition temperature is increased to 22 K for the anhydrous phase of CuCl₂ [2]. No ferromagnetism has been reported for either stoichiometry. In order to confirm that no intermediate state of water intercalation exists that exhibits a FM transition, we performed studies of CuCl₂ with different exposures to humidity. Since the intercalation of water involves a structural expansion in the interlayer distance of CuCl₂ chains, the two structures can be distinguished with x-ray diffraction. Fig. 5 shows a plot of the relative intensity obtained for (001) CuCl₂ and (101) CuCl₂(2H₂O) diffraction peaks which are observed at 2θ of 15.34° and 16.18°, respectively. The measurement was repeated in sequences of 180 s in order to trace the evolution of water intake during the measurement in air. Over time, the intensity of (101) CuCl₂(2H₂O) increases at the cost of the intensities observed from anhydrous (001) CuCl₂. The time dependence appears to be linear, but a substantial presence of the hydrated phase is visible even at the start of the experiment.

A similarly prepared pellet was cut into pieces and exposed to air, while the magnetic properties were measured at consecutive time intervals. Results shown in Fig. 5b show the evolution of the magnetic response over temperature in a 1000 Oe field. A first AFM transition should become visible in dehydrated samples at a temperature of 22 K [2,3]. This temperature is marked with a vertical line labeled “AFM1” in Fig. 5. In our measurements, the signal is already strongly affected by the presence of the hydrated phase even after short exposure to air during sample mounting. However, close to the expected transition temperature AFM1, a change in slope is observed for samples with shorter exposure times, which is indicative for the presence of the anhydrous AFM phase. At a lower temperature of 4 K, a peak is observed in all measurements, indicating the AFM transition of the hydrated phase (AFM2). Upon longer exposure to air, the paramagnetic signal increases and the second AFM transition becomes more pronounced. This shows that both AFM transitions coexist during
the intake of water and are purely related to the fraction of the material in either phase. Therefore, CuCl₂ can be excluded in the considerations for the FM phase.

The case of Cu₄Cl(OH)₃ is more complicated due to the polymorphic character and complex frustrated magnetism [4,25,26]. Due to the ambiguity of single phase preparation we refrained from the synthesis of these compounds. However, the magnetic properties have been studied in detail in recent years with the conclusion that all polymorphs show an AFM transition below 20 K. Only the case of clinoatacamite appears to be a point of controversy due to its frustrated magnetic properties. While Zheng et al. report an AFM transition at \( T_{N1} = 18\) K, a second transition into a spin-fluctuation state is reported around \( T_{N2} = 6.5\) K [9]. Controversies arise on the exact nature of both transitions, because only below \( T_{N2} \) can a long range ordered Néel state be identified with neutron scattering [27,28]. Magnetization measurements below the second transition on the other hand reveal FM character as a hysteresis opens in the field dependence [9,27]. However, the observed ferromagnetism decays already at a temperature below 6 K and only a paramagnetic-like slope remains. Similar FM signatures were observed for Cu₄(OH)₆Cl₂ [7,29]. To our knowledge, no occurrence of FM properties with \( T_c \) above 15 K has been reported to date in the discussion of the frustrated CuCl based antiferromagnets.

In conclusion, no simple corrosion product of cuprous chloride can account for the observed magnetic properties. AFM transition temperatures of the candidates are however very close to the \( T_c \) of oxidized CuCl and could therefore give a hint on the origin of the effect. Speculations in this direction can include additional geometric spin frustration due to stoichiometric imbalances in neighboring grains hindering the formation of long range AFM order. Our results highlight the instability of copper halides regarding structure and magnetism and show that different magnetic phases can emerge although structural properties remain unchanged. A more detailed study of the origin of the FM signal is outside the scope of this report. Suggestions include in-situ investigations of the x-ray absorption to measure the disproportionation from Cu⁺ to Cu²⁺ and the corresponding volume fractions. Furthermore, detailed high resolution x-ray studies will shed light on the evolution of the grain structure and formation of the intermediate AFM phase.

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