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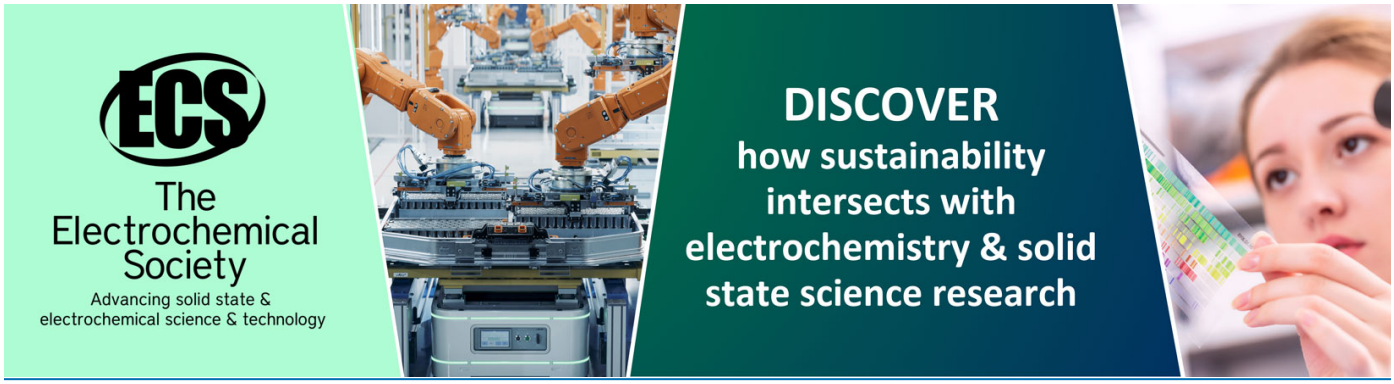

Magnetostriction and Thermal Expansion on 1D Quantum Spin System Azurite

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Abstract. Recently the natural mineral Azurite has been proposed as model substance for the distorted S = ½ diamond chain in the spin fluid state. Azurite has alternating doublet monomers and singlet dimers along the chains yielding plateau-*like* features in the magnetization curves. Although Azurite was also reported to order antiferromagnetically at 1.86 K, the detailed phase diagram and its relationship to the 1/3 plateau is largely unknown. In the present paper, we report preliminary results from a dilatometry study on Azurite carried out in the 0.05 - 2.30 K temperature range at magnetic fields up to 31 T. It is shown that sizable structural distortions accompany the magnetic ordering and that at 100 mK the long range order between monomers is suppressed precisely at the transition field where the 1/3 plateau sets in.

1. Introduction

The effects of magnetic frustration on the ground state of quantum spin systems have been studied extensively, particularly in low dimensional systems. The ground state of the so-called distorted diamond chain, in which diamond units of S = ½ ions form a one-dimensional chain and the exchange coupling constants J_1, J_2 and J_3 between first nearest-neighbour magnetic ions are antiferromagnetic, has been calculated by Tonegawa *et al.* [1]. However, experimental work on the magnetic properties of such a 1D system has made little progress because of the difficulty of finding a model substance. Recently, it was proposed that Azurite, a natural mineral of composition $Cu_3(CO_3)_2(OH)_2$, is a possible candidate [2 - 4].

Azurite has a monoclinic structure of lattice parameters a = 5.011 Å, b = 5.850 Å and c = 10.353 Å [5] in which Cu^{2+} magnetic ions decorate the corners of diamond units forming infinite chains along the *b* axis as shown in Figure 1. The magnetic properties of Azurite are driven by the different exchange pathways between the S=1/2 spins. As the temperature is lowered, dimerization caused by the AF exchange coupling constant J_2 occurs near 20 K, causing two thirds of the Cu ions to become magnetically inactive at low temperatures and low fields. Short-range order between the remaining monomers takes place at 5 K followed by an antiferromagnetic (AF) long-range order at T_N = 1.86 K. Besides this, a magnetization plateau at 1/3 of the saturation magnetization is observed above 10 T [2] as a consequence of the field-induced saturation of the monomers.

Not all experimental and theoretical observations in Azurite support a scenario in which all three main exchange interactions are antiferromagnetic (J_1, J_2 and $J_3 > 0$) yielding frustration as proposed in [2, 6]. Indeed recent DMRG numerical studies [7] and inelastic neutron scattering studies [8] suggest that J_3 is actually negative (ferromagnetic).

In the present paper, we report thermal expansion and magnetostriction properties in Azurite at low temperatures and high magnetic fields.

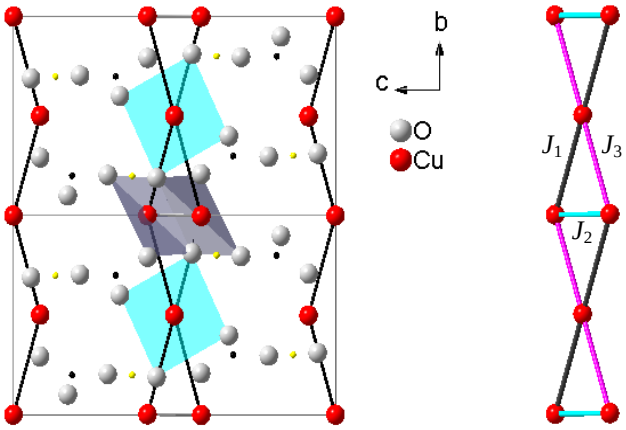

Figure 1. Projection in (*b*, *c*) plane of the atomic structure of two unit cells in Azurite (left picture). The size of the symbols for H (yellow) and C (black) atoms is reduced for clarity. Four O atoms surround each Cu ion allowing us to define an alternating Cu-4O planar arrangements along *b* [5]. S= ½ Cu ions are coupled by the exchange interactions J_1, J_2, and J_3 (right picture).

2. Experimental

We have acquired two large azurite minerals up to 6 cm long mined in Morocco from stone shops. Their purity and single phase quality was confirmed via powder X-ray diffraction, with no observable impurities such as malachite or iron oxide phases. Small specimens were cut out of the original crystals, oriented using X-ray diffraction and then polished into rectangular samples of about 2.5 x 3 x 2 mm size.

Magnetostriction and thermal expansion properties were measured using a titanium parallel-plate capacitive dilatometer 0.75 inches of diameter [9]. The sample, which sits on a screw-platform, is in contact with the bottom moveable capacitance plate while the upper capacitance plate remains fixed. The relative length change $\Delta L/L$ of the sample is determined by measuring the change in capacitance associated with the change in the gap between the two plates as the sample either expands or contracts. The dilatometer can be mounted either vertically or horizontally with respect to the direction of the magnetic field.

In a first experimental setup, the dilatometer was mounted in the vacuum space of a bottom-loading He^3-He^4 dilution refrigerator for thermal expansion and magnetostriction measurements in the 50 mK to 2.3 K temperature range in the 20 T superconducting magnet at the NHMFL facility in Los Alamos. A proper thermal linking to the mixing chamber yields a cooling down to 50 mK. The absence of thermal gradient was checked by recording the temperature on the mixing chamber in the zero magnetic field region and on the sample screw-platform using two ruthenium oxide thermometers calibrated in field. Measurements consisted of sweeping the magnetic field at fixed temperature at rates ranging from 0.05 T/mn at 100 mK to 0.20 T/mn at 1 K and ramping the temperature step-wise at various fixed fields. The cell background was determined to be negligible compared to the signal observed in Azurite by checking a Cu standard in the same experimental conditions.

In a second setup, magnetostriction properties at 1.3 and 2 K were measured up to 31 T (field sweep rate of 2 T/mn) using a resistive magnet at the NHMFL facility in Tallahassee where the cell and sample were immersed directly in He^4 superfluid. In both experimentals, magnetic torque effects were ruled out by comparing up and down sweeps on two different samples.

3. Results and Discussion

In Figure 2, Panel A, we show the measured length change along the *b* direction as a function of the temperature in Azurite at several different values of the magnetic field with the field applied along the *b* axis. At each magnetic field H_i, the reference configuration is the one at 50 mK, *i.e.* we compute the relative length change as $[L(T, H_i) - L(T = 50\ mK, H_i)] / L(T = 300\ K)$. In Figure 2, Panel B, we plot the relative length change measured as a function of the applied magnetic field at several different temperatures for the same geometry. At each temperature, the reference configuration is the one at zero field. The relative thermal expansion is about 10^{-5} or less whereas the magnetostriction is one order of magnitude higher, about 10^{-4}. Transitions into the low temperature AF phase appear as kinks and inflection points in the thermal expansion, as shown by arrows in Panel A of Figure 2. With increasing magnetic fields, T_N moves to lower temperature and is suppressed at fields above 17 T for H // *b* and 12 T for H // *c*. Measurements for all three crystallographic directions show that the thermal expansion has a distinct behaviour depending on the direction along which the expansion is measured (not shown here). Outside the ordered phase, deep inside the 1/3 magnetization plateau, regardless of the direction of the field, the expansion is positive along *b*, and negative along *a* and *c*. Inside the low-temperature long range ordered phase, the thermal expansion displays a more complex behaviour. In the magnetostriction data shown in Panel B of Figure 2, the field-induced progressive canting of the monomers yielding paramagnetic-*like* behaviour in magnetization [2] is associated with a H^n power-law field dependence of the relative length change with $n \sim 2.6 - 2.75$. The 1/3 magnetization plateau yields a well defined plateau in the magnetostriction curves for H // *c* as can be seen in Figure 3. Extrema in the coefficients of linear magnetostriction $\beta = \partial(\Delta L/L)/\partial H$ mark the entrance into the 1/3 plateau. As the temperature increases, the transition field for the entrance into the 1/3 plateau moves to lower field. A precise mapping of the field *vs.* temperature phase diagram from the combined thermal expansion and magnetostriction data suggests that the exit from the AF ordered phase merges with the entrance into the 1/3 plateau ordered phase at low temperatures. The 1/3 plateau continues to be observed at temperatures far above 1.85 K where the transition becomes broad.

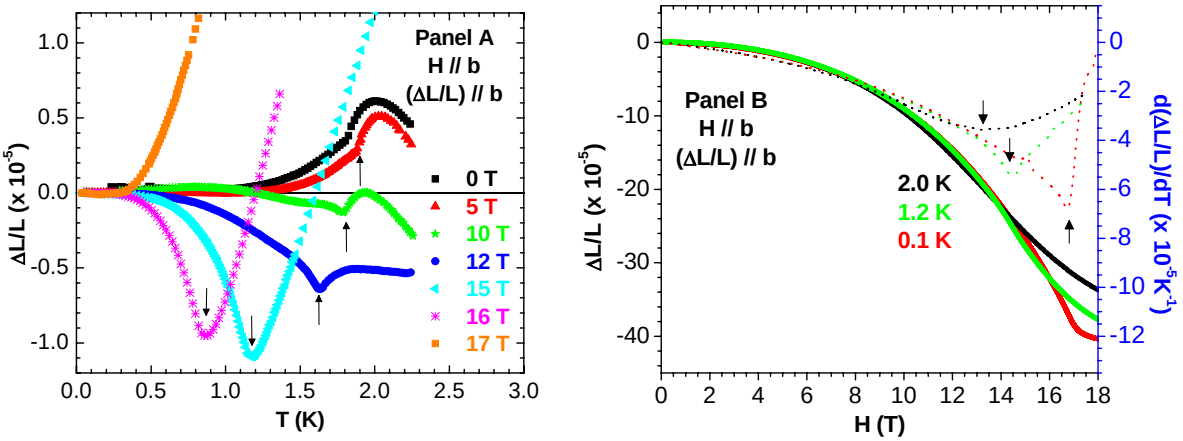

Figure 2 – **Panel A:** Relative length change along the *b* axis as a function of the temperature at several different values of the magnetic field for H // *b*. **Panel B:** Relative length change along *b* as a function of the field at several different fixed values of temperature for H // *b* (full lines) and computed coefficient of linear magnetostriction (dotted lines). Arrows indicate position of the critical temperatures and critical fields at which transitions take place.

Figure 3 displays representative field-induced changes of the sample's length at 1.3 K along the high symmetry axes *a*, *b* and *c* for the field applied along *c*. The magnetostriction measured in all three directions is of the same order of magnitude. The canting of the monomers yields a contraction along the chains but an expansion perpendicular to the chains. These observations still remain valid when the magnetic field is applied along *b* and *a* (not shown here). This latter result supports a scenario in which the interactions between the chains are negligible at low temperatures below 32 T and a one-dimensional picture applies for Azurite. In such a situation, at low field, the prevailing interactions are between the monomers along each chain. Thus, more likely, those are the magnetostrictive forces along *b* that drive the behaviour shown in Figure 3. Subsequently the magnetostriction along *a* and *c* results from the Poisson effect, which exerts a volume-conserving force on the

chain. At intermediate fields, a plateau in the magnetostriction curves follows the 1/3 magnetic plateau observed in the magnetization properties of Azurite [2]. The antiferromagnetic long-range order transition sets in at 14 T for H // *b* and 10 T for H // *a* and H // *c* at 1.3 K. The 1/3 plateau corresponds to a situation in which all monomers are aligned with the field. Interestingly, such a ferromagnetic arrangement of the monomers yields a contraction along *b* and is better achieved when the field is applied along either *a* or *c* rather than along *b* as indicated by the lower strength of the field required to reach the plateau for those two directions. The exit from the 1/3 plateau ordered phase occurs at 32 T [2] when the field is strong enough to break the dimer bonds and saturation is achieved. A sudden reversal of the low field magnetostriction trends is then observed with an expansion along *b* and a shrinking along *a* and *c* axis as shown in Figure 3.

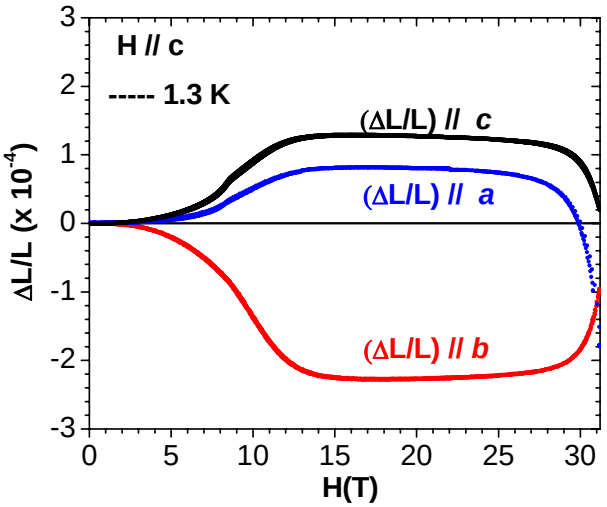

Figure 3 – Relative length change measured along the *a*, *b* and *c* axes as a function of the field at T = 1.3 K for the magnetic field applied along *c* up to 31 T.

4. Conclusion

We have measured thermal expansion and magnetostriction in Azurite at temperatures down to 50 mK and at magnetic fields up to 31 T along the three main crystallographic axes with the magnetic field applied either parallel or perpendicular to the direction of expansion. We observe marked changes in thermal expansion and magnetostriction at the transition temperatures and transition fields into the long-range AF ordering and 1/3 magnetization plateau. Structural distortions are evidenced that supports a 1D scenario for Azurite at low temperatures and low fields. The comprehensive phase diagrams and the detailed anisotropy of the magneto-elastic effects will be published and discussed further elsewhere.

References

[1] Tonegawa, T. *et al.*, Journal of Physical Society of Japan 69, 332 (2000)
[2] Kikuchi, H. *et al.*, Physical Review Letters 94, 227201 (2005)
[3] Ohta, H. *et al.*, Journal of Physical Society of Japan 72, 2464 (2003)
[4] Lang, M. *et al.*, Journal of Physics : Conference Series 51, 1 (2006)
[5] Belokoneva *et al.*, Phys. Chem. Minerals 28, 498 (2001)
[6] Mikelska, H.-J., Luckmann, C., Cond-mat arXiv: 0709.2863v1 (2007)
[7] Gu, B., Su, G., Physical Review B 75, 174437 (2007)
[8] Rule, K. C. et al., Physical Review Letters 100, 117202 (2008)
[9] Schmiedeshoff, G. M. *et al.*, Review of Scientific Instruments 77, 123907 (2006)