Ultrasonic Investigation on the Distorted Diamond Chain Compound Azurite

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Abstract. The natural mineral Azurite [Cu₃(CO₃)₂(OH)₂] has been considered as a model substance for the 1D distorted antiferromagnetic diamond chain, the microscopic couplings of which, however, are still under discussion. Here we present results of the longitudinal elastic constant \(c_{22}\) down to 80 mK and magnetic fields up to 12 T. \(c_{22}\) reveals clear signatures of the magnetic energy scales involved and discloses distinct anomalies at the Néel ordering \(T_N = 1.88\) K. Based on measurement as a function of temperature and magnetic field, a detailed \(B-T\) phase diagram is mapped out which includes an additional phase boundary of unknown origin at low temperature \((T < 0.5\) K). Entering the new phase is accompanied by a pronounced softening of the \(c_{22}\) elastic constant. These observations, together with results obtained by spectroscopic investigations reported in the literature, reflect an unusual long-range magnetically ordered state at very low temperatures.

1. Introduction

Low-dimensional (low-D) quantum spin systems are of great interest in solid state physics due to the wealth of exciting phenomena originating from the interplay of reduced dimensionality, competing interactions and strong quantum fluctuations. Recently, great interest and controversy has surrounded the proposal that the spin \(S = \frac{1}{2}\) moments of the Cu\(^{2+}\) ions in azurite \([\text{Cu}_{3}(\text{CO}_{3})_{2}(\text{OH})_{2}]\) form a frustrated 1D distorted diamond chain [1-3]. The magnetic structure of azurite and the relevant microscopic couplings, however, have been disputed both in experimental and theoretical studies [4-6]. In addition, the detailed phase diagram at low temperature and high magnetic fields is still unknown and some recent experiments suggest that there exists a more complicated micromagnetic structure than has previously been thought [7, 8].

2. Results and Discussion

Using a phase-sensitive detection technique, we have measured the relative change of the velocity of a longitudinal ultrasonic wave propagating along the spin-chain direction (\(b\) axis) of a high-quality single crystal of azurite. This geometry corresponds to the \(c_{22}\) acoustic mode. The elastic constant can be calculated from the sound velocity \(v\) and the crystal’s mass density \(\rho\) by \(c_{22} = \rho v^2\).
Measurements have been performed both as a function of temperature and magnetic field. The external field was applied either perpendicular or parallel to the \( b \) axis.

Figure 1 shows the temperature dependence of \( c_{22} \) together with the molar magnetic susceptibility \( \chi_{mol} \). The latter has been determined by utilizing a homemade SQUID magnetometer. At \( T_N = 1.88 \) K we observed in both curves a pronounced anomaly - a minimum in \( c_{22}(T) \) coinciding with a sharp kink in \( \chi(T) \) - reflecting long-range antiferromagnetic ordering. The size of the elastic anomaly (of the order of 0.1\%) is typical for an antiferromagnetic (AFM) transition. A surprising result obtained from the ultrasonic measurements is the observation of another pronounced softening of \( c_{22} \). The onset of this softening coincides with an abrupt increase of \( \chi_{mol}(T) \) for \( T < 0.45 \) K. Note that this softening of the elastic constant is of comparable size to the one observed at \( T_N \).

Figure 2. (Colour online) a) Field dependence of \( \Delta c_{22}/c_{22} = (c_{22}(B)-c_{22}(0))/c_{22}(0) \) for \( B // b \) at fixed temperature. b) Temperature dependence of \( \Delta c_{22}/c_{22} = (c_{22}(T)-c_{22}(0.7 \) K))/\( c_{22}(0.7 \) K) at fixed fields (for \( B // b \)) of 0 T. The inset shows the position of the kinks observed in \( B \) (stars) - , \( T \) (squares) - sweeps. The broken line, delimiting the new phase, is a guide for the eyes.
These two findings suggest the presence of another, most likely magnetic phase transition at temperatures below 0.45 K. The different behavior of $c_{22}(T)$ at the two phase transitions indicates that different coupling schemes between the strain and the order parameter are realized here.

In order to obtain more information on the low-temperature region, the field (temperature) dependence of $c_{22}$ at various fixed temperatures (fields) has been determined. In figure 2(a), we show a selection of field sweeps for $B$ // $b$ axis. A pronounced increase of $c_{22}$ is observed at very low temperature of 0.13 K upon increasing the field. At a field of 1.15 T this increase is abruptly terminated and $c_{22}$ starts decreasing with further growing field. The position of this kink in $\Delta c_{22}/c_{22}$ is shifted to lower fields with increasing temperature. Above a temperature $T = 0.41$ K, however, this anomaly can no longer be discerned. The temperature dependence of $c_{22}$ at different fields is shown in figure 2(b). The onset temperature of the softening gradually shifts to lower temperature with increasing the field. No softening can be observed within the accessible temperature range $T \geq 0.08$ K for $B \geq 1.25$ T. The positions of the kinks derived from these experiments are summarized in the $B$-$T$ phase diagram for $B$ // $b$ axis in the inset of figure 2(b). The strong field dependence observed suggests that the $c_{22}$ anomaly signals a low-temperature phase transition of magnetic origin. To the best of our knowledge this is the first report of such an additional low-temperature phase in azurite.

![Figure 3.](image)

**Figure 3.** (Colour online) Relative change of the elastic $c_{22}$ mode as a function of magnetic field (applied perpendicular to the $b$ axis) at different fixed temperatures.

Figure 3(a) shows a selection of isothermal $c_{22}$ data as a function of magnetic field applied perpendicular to the $b$ axis. The field orientation was close to the setting employed in ref. [11], where the transition at 2 T was assigned to a spin-flop (SF) transition. For this field orientation, the 1/3 magnetization plateau is reached above 11 T [1]. To map out the $B$-$T$ phase diagram, numerous measurements have been carried out in the field ranging from 0 to 12 T at temperatures varying from 0.072 to 3.6 K. A great deal of information can be obtained from such ultrasonic experiments, especially about the magnetoelastic coupling at the edges of the magnetization plateaus, see, e.g. [9]. Upon entering the plateau state of azurite above 10 T, the elastic constant increases considerably as shown in fig 3(a). Details of the elastic anomalies associated with the plateau phase will be published elsewhere [10]. Here we concentrate on the anomalies within the magnetically ordered state.

Generally, at a phase transition the ultrasonic attenuation (not shown) abruptly changes, whereas the elastic constant exhibits a softening. As displayed in figure 3(a), we find several distinct anomalies which become more pronounced and develop a fine structure with decreasing temperature. The feature around $B = 2$ T was assigned in ref. [11] to the transition from the antiferromagnetic to the SF state (for $T < 1.6$ K) or the paramagnetic (PM) state (for $T > 1.6$), see fig. 4. Figure 3(b) shows details of the data at 0.65 K and 0.31 K. At temperatures above 0.45 K, a single minimum is observed
around 2 T which we tentatively assigned to the SF transition. For $T < 0.45$ K, however, the data reveal a splitting into two closely spaced minima. Note that these features for $B \perp b$ occur in the same temperature region where the large softening was observed in $c_{22}(T)$, cf. fig.1, and have the same size as the elastic anomaly at the AF transition. The features between 8 and 10 T are attributed to the transition from the SF state, either to the plateau state (PL) via the PM state ($T > 1$ K) or directly into PM state ($T < 1$ K), cf. fig. 4. We stress that the phase boundaries obtained here are consistent with the ones derived from magneto-thermal measurement in ref. [11] at $T \geq 1$ K and $B \leq 2.5$ T.

![Figure 4. B-T phase diagram for B \perp b axis as determined from the c_{22} anomalies in B- (spheres) and T- (stars) sweep measurements. The broken line is a guide for the eyes.](image)

3. Conclusion

From measurements of the longitudinal elastic constant $c_{22}(T,B)$, the low-temperature $B$-$T$ phase diagram of azurite has been mapped out in detail. The measurements reveal an as yet unknown phase boundary at very low temperatures which is likely to be of magnetic origin.

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