Magneto-elastic couplings in the distorted diamond-chain compound azurite

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We present results of ultrasonic measurements on a single crystal of the distorted diamond-chain compound azurite $\text{Cu}_2(\text{CO}_3)_2(\text{OH})_2$. Pronounced elastic anomalies are observed in the temperature dependence of the longitudinal elastic mode $c_{22}$ which can be assigned to the relevant magnetic interactions in the system and their couplings to the lattice degrees of freedom. From a quantitative analysis of the magnetic contribution to $c_{22}$ the magneto-elastic coupling $G = \partial J_2/\partial e_b$ can be determined, where $J_2$ is the intra-dimer coupling constant and $e_b$ the strain along the intra-chain $b$ axis. We find an exceptionally large coupling constant of $|G| \sim (3650 \pm 150) \text{K}$ highlighting an extraordinarily strong sensitivity of $J_2$ against changes of the $b$-axis lattice parameter. These results are complemented by measurements of the hydrostatic pressure dependence of $J_2$ by means of thermal expansion and magnetic susceptibility measurements performed both at ambient and finite hydrostatic pressure. We propose that a structural peculiarity of this compound, in which $\text{Cu}_2\text{O}_6$ dimer units are incorporated in an unusually stretched manner, is responsible for the anomalously large magneto-elastic coupling.

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I. INTRODUCTION

Low-dimensional quantum-spin systems have attracted continuous attention due to the wealth of unusual magnetic properties that result from the interplay of low dimensionality, competing interactions and strong quantum fluctuations. Among these systems, the diamond chain has been of particular interest, where triangular arrangements of spin $S = 1/2$ entities with exchange coupling constants $J_1$, $J_2$ and $J_3$, are connected to form chains. In recent years, great interest has surrounded the discovery of azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, as a model system of a $\text{Cu}^{2+}(S = 1/2)$-based distorted diamond chain with $J_1 \neq J_2 \neq J_3$. The observation of a plateau at 1/3 of the saturation magnetization\textsuperscript{9} is consistent with a description of azurite in terms of an alternating dimer-monomer model\textsuperscript{10}. Two characteristic temperatures (energies) have been derived from peaks in the magnetic susceptibility $\chi(T)$\textsuperscript{9,10} Whereas the peak at $T_1 \approx 25$ K, has been assigned to the dominant intra-dimer coupling $J_2$, the one at $T_2 \approx 5$ K has been linked to a monomer-monomer coupling along the chain $b$ axis\textsuperscript{9}. There have been conflicting results, however, as for the appropriate microscopic description of the relevant magnetic couplings of azurite\textsuperscript{11-15}. Very recently, Jeschke et al.\textsuperscript{16} succeeded in deriving an effective microscopic model capable of providing a consistent picture of most available experimental data for not too low temperatures, i.e., distinctly above the transition into long-range antiferromagnetic order at $T_N = 1.86$ K\textsuperscript{17}. According to this work, the exchange couplings $J_1$, $J_2$ and $J_3$ are all antiferromagnetic, thus placing azurite in the highly frustrated parameter regime of the diamond chain. Within the “refined model” proposed there, $J_2/k_B = 33$ K and an effective monomer-monomer coupling $J_m/k_B = 4.6$ K were found.

Another intriguing property of azurite, not accounted for so far from theory, refers to the strong magneto-elastic couplings in this compound. These couplings manifest themselves, e.g., in a pronounced structural distortion accompanying the magnetic transition at $T_N$, as revealed by thermal expansion\textsuperscript{18,19} and neutron scattering experiments\textsuperscript{19,20}. Here we present a study of these magneto-elastic couplings of azurite by means of temperature-dependent measurements of the elastic constant and uniaxial thermal expansion coefficients. These data are supplemented by thermal expansion and susceptibility measurements under hydrostatic pressure conditions. The salient results of our study is the observation of an extraordinarily large magneto-elastic coupling constant of the intra-dimer coupling $J_2$ with respect to intra-chain deformations. This coupling manifests itself in pronounced anomalies in the elastic constant and uniaxial thermal expansion coefficients, the latter are characterized by a negative Poisson effect. We propose that the anomalous magneto-elastic behavior of azurite is a consequence of the material’s structural peculiarities, in particular, the presence of unusually stretched Cu$_2$O$_6$ dimer units.

II. EXPERIMENTAL DETAILS

The single crystals (samples #1 - #4) used for the measurements described in this paper were cut from a large high-quality single crystal which was also studied by neutron scattering and muon spin resonance ($\mu$SR)\textsuperscript{12,19}. For the ultrasonic experiments two parallel surfaces normal to the [010] direction were prepared and two piezoelec-
tric polymer-foil transducers were glued to these surfaces. Longitudinal sound waves for frequencies around 75 MHz were propagated along the [010] direction to access the acoustic $c_{22}$ mode. By using a phase-sensitive detection technique\(^1\) the relative change of the sound velocity and the sound attenuation were simultaneously measured as the function of temperature for $0.08 \text{ K} \leq T \leq 310 \text{ K}$. A top-loading dilution refrigerator was used for measurements at $T \leq 1.5 \text{ K}$, whereas a $^4 \text{He}$ bath cryostat, equipped with a variable temperature insert, was employed for accessing temperatures $T \geq 1.5 \text{ K}$. The elastic constant $c_{ij}$ is obtained from the sound velocity $v_{ij}$ by $c_{ij} = \rho v^2_{ij}$, where $\rho$ is the mass density. For measurements of the uniaxial thermal expansion coefficients, $\alpha_i(T) = l_i^{-1}(\partial l_i/\partial T)$, where $l_i(T)$ is the sample length along the $i$ axis, two different dilatometers were used. Experiments under ambient pressure along the $a'$, $b$ and $c^*$ axes, where $a'$ and $c^*$ are perpendicular to the (102) and (102) crystallographic planes, respectively, were carried out by means of an ultrahigh-resolution capacitive dilatometer, built after ref.\(^2\), with a resolution of $\Delta l/l \geq 10^{-10}$. In addition, measurements along the $b$ axis were performed by using a different dilatometer\(^3\), with a slightly reduced sensitivity of $\Delta l/l \geq 5 \times 10^{-10}$, enabling measurements to be performed under Helium-gas pressure. The magnetic susceptibility at ambient pressure and at various finite pressure values was measured with a SQUID magnetometer (Quantum Design MPMS). For the measurements under pressure, a CuBe piston cylinder clamped cell was used with Daphne oil 7373 as a pressure-transmitting medium. At low temperature, the pressure inside the pressure cell was determined by measuring the superconducting transition temperature of a small piece of Indium.

### III. RESULTS AND DISCUSSION

#### A. Elastic anomalies and pressure/strain dependence of the relevant magnetic energy scales

Figure 1(a) shows the experimental results (open symbols) of the longitudinal elastic constant $c_{22}(T)$ of azurite (sample #1) over the whole temperature range investigated. Upon cooling, the $c_{22}$ mode initially increases (hardening) as expected for materials with anharmonic phonon interactions dominate. Upon further cooling, however, a pronounced softening becomes visible below about 250 K which is accompanied by various anomalies at lower temperatures $T \leq 30 \text{ K}$. These anomalies can be discerned particularly clearly in the inset of Fig. 1(b), where the low-temperature data are shown on a logarithmic temperature scale. Most prominent is a distinct minimum at a temperature around 27 K. Moreover, the data disclose a small dip slightly below 10 K. The position of this feature is difficult to estimate due to its smallness and the strong variation of $c_{22}$ with temperature caused by the nearby anomalies. We assign these features (labeled $T_{1}^{c_{22}}$ and $T_{2}^{c_{22}}$ in the inset to Fig. 1(b)) to the characteristic temperatures $T_1$ and $T_2$ of azurite, as revealed by susceptibility measurements\(^9,10\). In addition, the elastic data highlight a sharp minimum around 1.9 K, reflecting the transition into long-range antiferromagnetic order ($T_N$), and a transition of unknown, most likely magnetic origin ($T_0$).

For a quantitative analysis of the $c_{22}$ data, we determined the magnetic contribution by subtracting the non-magnetic (normal) elastic background $c_{bg}$. For $c_{bg}$ a phenomenological expression

$$c_{bg}(T) = c_{bg}^0 - \frac{s}{e^{t} - 1}$$

was used\(^{25}\) which is fitted to the experimental data at temperatures high enough so that magnetic interactions can be neglected. Here $c_{bg}^0$ is the value of the elastic constant at $T = 0$, and $s$ and $t$ are constants. The quantity $t$ is usually set to $\Theta_D/2$, where $\Theta_D$ is the Debye temperature (see ref.\(^{25}\) for details). By choosing $t = 175 \text{ K}$, corresponding to $\Theta_D = 350 \text{ K}$ as derived from specific heat\(^{26}\), and by using $c_{bg}$ and $s$ as free parameters, eq. 1 was fitted to the data for temperatures $250 \text{ K} \leq T \leq 90 \text{ K}$.

![Figure 1](image-url)
vestigated here, a two-ion magneto-elastic coupling arises from the modulation of the distance or bond angles between the magnetic ions which changes the interaction. Furthermore the single-ion magneto-elastic coupling for Cu$^{2+}$ is small because of the vanishing quadrupole matrix elements$^{37}$. In order to quantitatively evaluate the corresponding magneto-elastic coupling constant, we introduce in eq. 2 a generalized strain susceptibility $\chi_{\text{str}}$. This model accounts, within a random-phase approximation (RPA)$^{37}$, for the temperature dependence of the elastic constants of coupled dimers characterized by an intradimer coupling constant corresponding to the dimers’ singlet-triplet excitation gap $\Delta$. This results in a temperature dependence for the elastic constant$^{37}$ of:

$$c_{22}(T) = \frac{\partial^2 F}{\partial (\varepsilon_{22})^2} = c_{bg}(T) - NG^2\chi_{\text{str}}(T)$$

where $F$ is the free energy, $\varepsilon_{22}$ is the strain along the [010] direction, and $G = \partial \Delta/\partial \varepsilon_{22}$ is the variation of the singlet-triplet energy gap $\Delta$ of the dimers upon applying a b-axis strain, i.e., $G = \partial J_{2}/\partial \varepsilon_{b}$. The so-derived coupling constant $J_{2}$ is taken from the fitting procedure of the elastic background. From a nonlinear least-squares fit the parameters $\Delta = J_{2}$. From the fit we obtain $J_{2} = 57 \pm 5$ K and a coupling constant $|G| \sim (3650 \pm 150)$ K. The so-derived coupling constant $J_{2}$ is somewhat larger than the one found in the DFT calculations$^{16}$. Most remarkable, however, is the exceptionally large value obtained for the coupling constant $|G|$, reflecting an extraordinarily large strain dependence of the dominant energy scale in azurite. This value, corresponding

![Figure 2](https://example.com/figure2.png)

**FIG. 2:** (Color online). (a) Uniaxial coefficients of thermal expansion of single crystalline azurite (sample #3) along the chain b axis and two orthogonal axes perpendicular to b labeled $a'$, $c'$. Inset: Temperature dependence of the b-axis expansivity measured on crystal #4 for 20 K $\leq T < 100$ K at ambient pressure ($10^{-4}$ GPa) (yellow circles) and at a Helium-gas pressure of 0.104 GPa (blue diamonds) in a double-logarithmic representation, cf. ref. 23. The arrows mark the position of the local maximum in $\alpha_{b}$ at $T_{1}$ derived from the fourth-order polynomial (black solid line) fitted to the experimental data. (b) Volume expansivity, $\beta = \alpha_{a} + \alpha_{b} + \alpha_{c'}$ determined from the data in (a). Arrows labeled $T_{1}^{\beta}$ and $T_{2}^{\beta}$ mark the position of anomalies (minima) in $\beta$. Inset: Details of the phase transition anomaly in $\beta$ at $T_{\gamma}$.
to a softening of approximately 4%, exceeds the coupling constants typically revealed for other low-dimensional quantum spin systems\textsuperscript{28,29} by one to two orders of magnitude. It is even about four times bigger than the very large coupling constant found for the longitudinal mode in the coupled-dimer system SrCu\textsubscript{2}(BO\textsubscript{3})\textsubscript{2}\textsuperscript{30} For the parameter $K$ in eq. 3 the fit yields $-(200 \pm 10)$ K, indicating that the effective magneto-elastic dimer-dimer interaction is antiferrodistortive in azurite.

In order to obtain supplementary information about the magneto-elastic couplings corresponding to the various energy scales, we performed measurements of the coefficient of thermal expansion and the magnetic susceptibility both at ambient- and under hydrostatic-pressure conditions.

Figure 2(a) shows the results of the temperature dependence of thermal expansion coefficients $\alpha_i(T)$ ($i = a', b, c'$) for temperatures $1.6$ K $\leq T \leq 75$ K measured at ambient pressure. Similar to the elastic constant, three distinct anomalies are observed in this temperature range along all three crystallographic axes. Upon cooling, the $b$-axis data show a broad positive maximum around 20 K whereas along the other two axes ($a'$ and $c'$) a negative minimum appears. Upon further cooling to lower temperatures, a minimum shows up in the $b$-axis data, which contrasts with maxima around 3.5 K in the data along the $a'$- and $c'$-axis. Despite having opposite signs, the anomalies in $\alpha_{a'}(T)$ and those in $\alpha_{a'}(T)$ and $\alpha_{c'}(T)$ do not cancel each other out in the volume expansion coefficient $\beta(T) = \alpha_{a'}(T) + \alpha_{b}(T) + \alpha_{c'}(T)$, shown in the main panel of Fig. 2(b). The volume expansivity exhibits a pronounced negative contribution, giving rise to a change of sign around 50 K, and a broad minimum around 25 K followed by a second minimum at $\approx 5$ K. The strong upturn in $\beta(T)$ and $\alpha_i$ at lower temperatures is due to the antiferromagnetic phase transition at $T_N$.

This is shown more clearly in the inset of Fig. 2(b) where $\beta(T)$ is displayed on expanded scales around $T_N$. An extraordinarily large $\lambda$-type anomaly, lacking any hysteresis upon cooling and warming, is observed which demonstrates the second-order character of the phase transition at $T_N$. From the coincidence of the anomalies in $\beta(T)$ (and $\alpha_i(T)$) with those revealed in the magnetic susceptibility\textsuperscript{9} and elastic constant (Fig. 1), we conclude that these anomalies reflect the characteristic temperatures $T_1$ and $T_2$ which are related to the energy scales $J_2$ and $J_m$, respectively. Thus from the evolution of these anomalies under pressure we may determine the pressure dependencies of these energy scales. In the inset of Fig. 2(a) we compare, on a logarithmic temperature scale, the temperature dependence of $\alpha_b$ for a small pressure of at $10^{-4}$ GPa with that of 0.104 GPa. These data, which have been taken on sample #4 by employing a different dilatometer, especially designed for measurements under Helium-gas pressure\textsuperscript{23}, disclose two remarkable features. First, we find a strong change in the temperature dependence of $\alpha_b(T)$, accompanied by a considerable suppression in its absolute value over the whole temperature range investigated, i.e., for $T \leq 100$ K. Note that due to the solidification of the pressure medium, the measurements at 0.104 GPa were limited to $T > 14.5$ K. Since changes of the lattice expansivity under a pressure of 0.104 GPa for a material with a normal bulk modulus are expected to be less than 1%, see ref. 23 and the discussion therein, we attribute these effects to the influence of pressure on the material's magnetic properties and their coupling to the lattice degrees of freedom. The presence of significant magnetic contributions at elevated temperatures $T \gg J_2/k_B$ which strongly couple to the lattice is consistent with the acoustic behavior revealed for the $c_{22}(T)$ elastic mode, yielding an onset temperature for the pronounced softening as high as 250 K, cf., Fig. 1(a).

Second, a thorough inspection of the data around the maximum reveals a shift of the position of the maximum to lower temperatures on increasing the pressure from $p = 0.1$ to 0.104 GPa. This can be quantified more precisely by fitting both data sets in the immediate surrounding of the maximum by fourth-order polynomials\textsuperscript{23}, depicted as solid lines in Fig. 2(a). By identifying the position of the maximum with $T_1$, we find a pressure dependence $\partial T_1/\partial p = -(0.08 \pm 0.03)$ K/GPa.

Figure 3 displays the data of the magnetic susceptibility $\chi(T, p = \text{const})$ as a function of temperature for $2$ K $\leq T \leq 300$ K at varying pressure values from ambient pressure.
pressure up to 0.62 GPa. The ambient-pressure data are consistent with those reported by Kikuchi et al.,
yielding an increase in $\chi$ with decreasing temperature and two broadened maxima at $T_1^N$ and $T_2^N$. Upon increasing the pressure we observe a progressive increase of the low-temperature susceptibility, cf. Fig. 3. In addition, a closer look at the low-temperature data in the inset of Fig. 3 discloses a shift of the position of both maxima to lower temperatures albeit at different rates.

For a quantitative analysis of the susceptibility data for not too low temperatures around $T_1$ and up to 300 K, we again use an RPA-molecular field expression for coupled dimers, in analogy to the procedure applied for analyzing the elastic constant $c_{22}(T)$ data:

$$\chi_m(T) = \frac{\chi_0(T)}{1 - K\chi_0(T)}. \tag{4}$$

Here $\chi_0(T) = 2e^{-\Delta/k_B T}/(k_B T Z)$ is the magnetic susceptibility of an isolated dimer, $Z$ the partition function and $K$ an average magnetic inter-dimer coupling. A fit to the experimental data at ambient pressure was performed for 15 K $\leq T \leq 300$ K by using eq. 4 and a Curie contribution, according to the amount of Cu-monomer spins, with $\Delta = J_2$ and $K$ as free parameters. This fit provides a very good description of the data including the height and the position of the maximum at $T_1^N$, cf. the solid red line running through the ambient-pressure data points in Fig. 3. From the fit we obtain $J_2/k_B = (40.5 \pm 0.7)$ K, consistent with the value suggested by DFT calculations for the “full model” discussed there, and $K = (4.1 \pm 0.8)$ K. Note that this value of $K$ indicates that the average magnetic dimer-dimer interaction is small and ferromagnetic. The RPA-molecular field description remains good also for the data taken at finite pressure. For these fits the same Curie susceptibility as used for the ambient-pressure data was used to account for the magnetic contributions of the monomers. The evolution of the parameters $J_2$ and $K$ with pressure, derived from fitting eq. 4 to the finite-pressure data, is shown in Fig. 4. We find a suppression of $J_2$ with increasing pressure which can be approximated by $\partial J_2/\partial p \approx -(0.077 \pm 0.007)$ K/GPa. For the average magnetic inter-dimer interaction we find an approximate linear increase under pressure with a larger rate of $\partial K/\partial p \approx (0.216 \pm 0.002)$ K/GPa. This pronounced increase of $\partial K/\partial p$ is responsible for the growth of the low-temperature susceptibility with pressure.

As will be discussed in more detail below (Sec. C), the dominant ferromagnetic character of the dimer-dimer interaction can be assigned to a particular Cu-O-Cu exchange path connecting dimers of adjacent chains along the $a$-direction.

**B. Magneto-elastic coupling at $T_N$**

As shown in the previous section, the phase transition into the long-range antiferromagnetic order in azurite at $T_N = 1.88$ K is accompanied by a pronounced anomaly in the elastic $c_{22}$ mode, corresponding to a softening of about 0.1% (cf. inset to Fig. 1(b)) which exceeds by far the features usually revealed at a magnetic transition in low-dimensional spin systems where often only a kink-like anomaly is observed, see refs. 29, 31, for typical examples, and ref. 27 for a review. This goes along with an extraordinarily large anomaly in the uniaxial coefficients of thermal expansion $\alpha_i$, see Fig. 2(b). As

![FIG. 4: (Color online). Evolution of the fit parameters, the intra-dimer coupling constant $J_2$ (open squares, left scale) and the average magnetic dimer-dimer interaction energy $K$ (full triangles, right scale), with pressure as derived from fits of eq. 2 to the data in Fig. 3.](image)

![FIG. 5: (Color online). Poisson ratio (black full circles, right scale) together with the relative volume change around $T_N$ (blue open squares, left scale).](image)
a result of the strong magneto-elastic coupling, there is a large \( \lambda \)-type anomaly in the volume expansion coefficient \( \Delta \beta \), (see the inset of Fig. 2(b)), corresponding to a relative reduction of the volume upon cooling from 2 to 1.6 K of \( \Delta V/V = -5.7 \cdot 10^{-5} \) as shown in Fig. 5.

According to the Ehrenfest relation, the discontinuities at this second-order phase transition in \( \beta, \Delta \beta \), and that in the specific heat, \( \Delta C_p \), can be used to determine the pressure dependence of the Néel temperature in the limit of vanishing pressure

\[
\left( \frac{\partial T_N}{\partial p} \right)_{p\to0} = V_{mol} T_N \frac{\Delta \beta}{\Delta C_p}. \quad (5)
\]

By using \( \Delta \beta = (550 \pm 30) \times 10^{-6} \text{ K}^{-1} \) and \( \Delta C_p = (6.18 \pm 0.4) \times \text{J mol}^{-1}\text{K}^{-1} \) taken from ref. 12, we find \( \left( \frac{\partial T_N}{\partial p} \right)_{p\to0} = (0.15 \pm 0.02) \text{ K/GPa} \). This extraordinarily large pressure dependence, exceeded only by some exceptional cases, such as the coupled antiferromagnetic/structural transition in Co-substituted CaFe\(_2\)As\(_2\), highlights the strong magneto-elastic coupling and the unusual elastic properties of azurite.

The large \( \Delta \beta \) at \( T_N \), tantamount to a large pressure dependence of \( T_N \) in eq. 5, is partly due to the fact that in azurite at \( T_N \) the discontinuities in the uniaxial expansion coefficients, \( \Delta \alpha \), all have the same (positive) sign. Hence, this phase transition is characterized by an anomalous Poisson effect.

In general for an isotropic material, the Poisson ratio, which measures the material’s cross section under tension, is defined as:

\[
\nu = -\frac{\epsilon_y}{\epsilon_x}, \quad (6)
\]

where \( \epsilon_x \) is the strain in stretching direction and \( \epsilon_y \) perpendicular to it. In most materials \( \nu \) is positive, which reflects the fact that an expansion along one axis is usually accompanied by a compression in the perpendicular direction, to keep the overall volume change small. In many materials \( \nu \) values are found in the range 0.2 \( \leq \) 0.5\(^{34} \). The latter value corresponds to the situation that the material keeps its volume under tension. A positive \( \nu < 0.5 \) means that the material becomes thinner when it is stretched, the behavior encountered for most materials. In contrast, materials with a negative Poisson ratio become thicker when they are stretched. Those compounds, called auxetic materials, are of interest due to potential technical applications\(^{34} \).

In Fig. 5 we show the Poisson ratio \( \nu \) of azurite for temperatures around \( T_N \). For the present anisotropic case, \( \nu \) has been determined by using the relative length changes (\( \Delta l/l \)) (corresponding to the integral of \( \alpha_b(T) \) with respect to temperature) for the strain \( \epsilon_x \) along the stretching \( b \) direction and \( \overline{\epsilon_y} = (\epsilon_{y'} + \epsilon_{y''})/2 = ((\Delta l/l)_{y'} + (\Delta l/l)_{y''})/2 \) perpendicular to it. We stress that \( \nu \) of azurite reaches a normal value of 0.23 around room temperature (not shown). However, as indicated in Fig. 5, \( \nu \) exhibits a large negative value of \(-0.8 \) for temperatures slightly above \( T_N \). This value increases to \(-0.65 \) upon cooling to \( T_N \) below which it further decreases, reaching almost \(-1 \) at 1.6 K. Note that this value is close to the stability limit of any elastic linear, isotropic material where the requirement of positive Young’s shear and bulk moduli dictates \( \nu > -1 \).
C. Relationship between structural and magnetic properties

We start the discussion by considering the dimer-dimer interaction $K$ revealed from the analysis of the susceptibility measurements under variable pressure. The dominant ferromagnetic character of this interaction is assigned to the Cu$_2$-O$_3$-Cu$_2$ exchange path (cf. Fig. 6). The corresponding Cu$_2$-O$_3$-Cu$_2$ bond angle amounts to 91.57° at 5 K, consistent with a weak ferromagnetic interaction as revealed for hydroxo-bridged Cu(II) complexes. Note that also the DFT calculations for the "full model" of azurite exhibit a small ferromagnetic exchange. It is likely that under hydrostatic pressure the structure will deform in a way such that this angle decreases with increasing pressure. This is consistent with an increase of the ferromagnetic inter-dimer coupling $K$ derived from susceptibility measurements under pressure, cf. Fig. 4.

In the following we will argue that the auxetic behavior at $T_g$ and the huge magneto-elastic coupling of azurite is likely due to peculiarities of the molecular arrangement in this compound, in particular that of the Cu$_2$O$_6$ dimer units, cf. Fig. 6. As shown in Fig. 6b, CuO$_4$ monomer units (containing Cu1) are connected via O$_2$ ions to Cu$_2$O$_6$ dimers (containing Cu2 and marked by yellow planes in Fig. 6) to form chains along the $b$ axis. According to structural data at room temperature and 5 K, the structural parameters of the monomers, involving O1-Cu1 and O2-Cu1 bonds, change very little upon cooling and are very close to those values (1.90 - 1.93 Å) typically found in isolated Cu(II) complexes. This indicates a stable and rigid configuration of the CuO$_4$ monomer units. In contrast, the structural parameters of the Cu$_2$O$_6$ dimers are rather unusual. In particular the Cu$_2$-O$_2$ bonds, mediating the intra-dimer coupling $J_2$, are significantly longer (1.9947 Å and 1.9675 Å at 300 K) than those found in isolated dimer complexes, reflecting an unusually "stretched" arrangement. It is thus obvious to suspect that this dimer unit represents the flexible part in the structure which may accommodate itself accordingly when the surrounding structure is exposed to external stimuli. This is the case, e.g., when a $b$-axis strain is applied or, alternatively, upon cooling through $T_g$ which is accompanied by a significant contraction of the $b$ axis (large positive anomaly in $\alpha_b$, cf. Fig. 2).

In fact, according to structural data (Table 1), the structural parameters of the dimers may alter the relationship between the exchange coupling constant and the dimers' structural parameters $\eta$, such as the inter-atomic distances or bonding angles, and with it the generalized derivatives $\partial J / \partial \eta$. According to Crawford et al., who investigated various stable hydroxo-bridged dimer complexes, there is a linear correlation between the intra-dimer

| atom 1-atom 2 | distance [Å] at 300 K ($d_{300K}$) | distance [Å] at 5 K ($d_{5K}$) | $d_{300K} - d_{5K}$ [Å] |
|---------------|----------------------------------|-----------------|------------------|
| O3-Cu2        | 1.93850                          | 1.93320         | 0.00530          |
| Cu2-O4        | 1.93990                          | 1.93910         | 0.00080          |
| Cu2-Cu2       | 1.99470                          | 1.98820         | 0.00650          |
| Cu2-O2        | 1.96750                          | 1.96420         | 0.00330          |
| Cu2-Cu2       | 2.98510                          | 2.99220         | -0.00710         |
| O2-O2         | 2.60560                          | 2.58320         | 0.02240          |
| O3-O3         | 6.20180                          | 6.19130         | 0.01050          |

TABLE I: Structural data of the Cu$_2$O$_6$ dimer units of azurite at 300 K and 5 K taken from refs. The first column denotes the atoms involved with labels according to Fig. 6. The second (third) column gives the distance between these atoms at 300 K (5 K). The fourth column gives the difference in these distances upon cooling from 300 K to 5 K. The O2-O2 and O3-O3 distances, showing the strongest changes upon cooling and which are involved in the auxetic behavior, are printed in bold.
coupling and both the Cu-Cu distance as well as the Cu-O-Cu bond angle. All of these materials exhibit nearly the same typical Cu-O distances. It is likely that these relations may change significantly for a strongly stretched configuration, as realized for the dimer units in azurite. This may result in strongly enhanced derivatives $\partial J / \partial \eta$ such as the large magneto-elastic coupling constant $\partial J / \partial \delta \kappa$ revealed here. A microscopic theory, addressing the relationship between the coupling constants and the dimers’ structural parameters, is necessary to confirm this conjecture. Note that the presence of pre-stressed structural units in azurite is consistent with the fact that a hydrothermal synthesis technique operating at a pressure of about 0.350 GPa has to be applied for growing single crystals of this mineral.\(^\text{30}\)

IV. CONCLUSIONS

Measurements of the longitudinal elastic constant $c_{22}$ and the uniaxial thermal expansion coefficients $\alpha_i$ on single crystalline azurite reveal pronounced anomalies associated with the intra-dimer coupling constant $J_2$. From a quantitative analysis of the elastic constant data, an exceptionally large value of the magneto-elastic coupling $G = \partial J_2 / \partial \delta \kappa$, of $| G | \sim (3650 \pm 150) \, \text{K}$ has been derived. By lacking a microscopic theory, we tentatively assign this large value, exceeding corresponding magneto-elastic couplings for other low-dimensional quantum spin systems by two to three orders of magnitude, to structural peculiarities of azurite. We propose that it is the Cu$_2$O$_6$ dimer unit, which is incorporated in the structure in an unnaturally stretched manner, which is responsible for the exceptionally large magneto-elastic coupling in this system.

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