Entangled quantum systems can exhibit correlations that cannot be explained on the basis of classical laws. Since the birth of quantum theory, such correlations have been used to highlight a number of counter-intuitive phenomena, such as the Einstein-Podolsky-Rosen paradox [2] or quantum non-locality [4] - the conflict between quantum mechanics and local realism as quantified by violation of Bell’s inequalities. In recent years entanglement was realized to be a crucial resource that allows for powerful new communication and computational tasks that are not possible classically [5].

The existence of quantum entanglement is generally not seen beyond the atomic scale. Only very recently entanglement experiments were realized with increasingly complex objects, either by entangling more and more systems with each other [6, 7, 8, 9], or by entangling systems with a larger number of degrees of freedom [10]. Moving towards demonstration of entanglement at even larger scales will tackle the question on limits on mass, size and complexity of systems that still can contain entanglement. The usual arguments against seeing entanglement on macroscopic scales is that large objects contain large number of degrees of freedom that can interact with environment thus inducing decoherence that ultimately lead to a quantum-to-classical transition.

Remarkably, macroscopic entanglement in solids, that is, entanglement in the thermodynamical limit of infinite large number of constituents of solids, was theoretically predicted to exist even at moderately high temperatures [11, 12, 13, 14, 15]. Recently, it was demonstrated that entanglement can even affect macroscopic thermodynamical properties of solids [13, 14, 17, 18, 19, 20], such as its magnetic susceptibility or heat capacity, albeit at very low temperature (few millikelvin) and only for a special material system - the insulating magnetic salt LiHo$_2$Y$_{1-x}$F$_4$ [20]. This extraordinary result shows that entanglement can have significant macroscopic effects.

Nevertheless, it is an open question whether or not there are macroscopic thermodynamical quantities that are entanglement witnesses for broader classes of solid state systems. Entanglement witnesses are observables which have positive expectation values for separable states and negative ones for some entangled states [22]. Finally, a direct experimental demonstration of entanglement, in the form of a determination of correlations between microscopic constituents of solids, remains an experimental challenge.

Here we show that bulk properties of solids can be entanglement witnesses. We use already published experimental results of both microscopic structure and macroscopic properties of the spin-1/2 alternating bond antiferromagnet CN (Cu(NO$_3$)$_2$2.5D$_2$O), to demonstrate the existence of entanglement in this type of solid. In the first approach we analyse experimental results of neutron scattering measurement of CN obtained in 2000 [2] and show that they provide, for the first time, a direct experimental demonstration of macroscopic entanglement in solids. The experimental characterization of the dynamic spin correlations for next neighbouring sites enables us to determine concurrence [21] - a measure of bipartite entanglement - and show the existence of entanglement at moderately high temperatures (as high as 5 Kelvin). In the second, parallel, approach we show that magnetic susceptibility at zero magnetic field is a macroscopic thermodynamical entanglement witness for the class of solid states systems that can be modeled by strongly alternating spin-1/2 antiferromagnet chain. We then show that the measured values for magnetic susceptibility of CN in 1963 [1] imply presence of entanglement in the same temperature range (below 5 Kelvin).

CN is an accurate realization of strongly alternating one-dimensional antiferromagnetic Heisenberg spin chain. The corresponding spin Hamiltonian is given by

$$H = \sum_j (J_1 S_{2j} \cdot S_{2j+1} + J_2 S_{2j+1} \cdot S_{2j+2}),$$

representing pairs of spins that are alternately coupled by strong intradimer $J_1 \approx 0.44$ meV and weak inter-
dimer $J_2 \approx 0.11$ meV coupling \footnote{23}. This can be described by a model of antiferromagnetically coupled spin pairs - dimers - which are themselves coupled by weaker antiferromagnetic interaction. The model has a highly entangled nontrivial spin-0 ground state \footnote{24,25} and for all $0 \leq J_2/J_1 < 1$ has a gap of the order of $\Delta \approx J_1$ to the first excitation, which is a band of spin-1 excitations (magnons). However, because here $J_2/J_1 \approx 0.24$ \footnote{26,27}, it is useful to think of CN as a chain of uncoupled spin dimers. Each dimer then has a singlet ground state and the triplets are the degenerate excited states. The existence of the energy gap gives the first estimate for persistence of entanglement for temperature range below $T \approx J_1/k \approx 5K$, where $k$ is the Boltzmann constant.

Next we describe the main experimental results of Ref. [2]. We will follow the discussion given there. CN has a monoclinic crystal structure with space group $I12/c1$ and with low-temperature parameters $a = 16.1A$, $b = 4.9A$, $c = 15.8A$, and $\beta = 92.9^\circ$. The vector connecting dimers center to center is $u_0 = [111]/2$ for half the chain, and $u_0' = [1\bar{T}1]/2$ for the other half. The corresponding intradimer vectors are $d_{1} = [0.252, \pm 0.027, 0.228]$, respectively. In the experiment the neutron scattering intensity was measured in the temperature range $0.31K < T < 7.66K$ (i.e. $0.06J_1 < kT < 1.5J_1$) as a function of energy transfer $\omega$ and wave vector transfer $Q$. Count rates were normalized to incoherent elastic scattering from the sample to provide absolute intensity $I(Q, \omega) = |\frac{1}{2}F(Q)|^2S(Q, \omega)$. Here $g = \sqrt{(g_{\perp}^2 + g_{c}^2)^{1/2}} = 2.22$ with $g_{\perp} = 2.31$ and $g_{c} = 2.11$ that show small anisotropy of $g$-factor along and perpendicular to the crystallographic direction $b$ \footnote{23}. $F(Q)$ is the magnetic form factor for Cu$^{2+}$ \footnote{26}, and $S(Q, \omega)$ is the scattering function \footnote{27}.

The direct link between the microscopic structure as given by the correlation function between spins and the intensity of inelastic neutron scattering is given by an exact sum rule (the first $\omega$-moment of scattering cross section) \footnote{28}

$$\hbar \omega(Q) \approx \hbar^2 \int_{-\infty}^{+\infty} S(Q, \omega) d\omega$$

$$= \frac{1}{3} \sum_{d} J_d \langle S_{0} \cdot S_{d}\rangle (1 - \cos Q \cdot d), \quad (2)$$

where $\{d\}$ is the set of all bond vectors connecting a spin to its neighbours, $S_{Q}(Q, \omega)$ is single site normalized and $\langle S_{0} \cdot S_{d}\rangle \equiv \langle S_{0}^{x} S_{d}^{x}\rangle + \langle S_{0}^{y} S_{d}^{y}\rangle + \langle S_{0}^{z} S_{d}^{z}\rangle$ is the sum over correlations for three orthogonal directions $x$, $y$ and $z$.

The intradimer correlation $\langle S_{0} \cdot S_{d}\rangle$ between next neighbouring spins was extracted from the global fits of the following phenomenological form for $S_{Q}(Q, \omega)$ to the complete data set at each of temperatures (it was used more than 1000 data points per parameter):

$$S(Q, \omega) = \frac{\hbar \omega(Q)}{\epsilon(Q)} \frac{1}{1 - \exp[-\beta \epsilon(Q)]} f[\hbar \omega - \epsilon(Q)]. \quad (3)$$

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FIG. 1: The temperature dependence of spin correlation function $\langle S_{0} \cdot S_{d}\rangle$ for neighbouring sites in CN. The figure is taken from Ref. [2]. The open circles correspond to the temperatures at which measurements were performed, the solid black line were obtained from fits in Ref. [2]. The solid red line is from this work. It distinguishes temperature ranges with and without entanglement in CN. The critical temperature is around $T_{c}^{exp} \approx 5K$ and 0.25 on the y-axis is the maximal value for $\langle S_{0} \cdot S_{d}\rangle$ achievable with separable states. For $T > T_{c}^{exp}$ concurrence is given by $C = -2\langle S_{0} \cdot S_{d}\rangle - (1/2)$ and has the same functional dependence on temperature as given in the figure. For $T \geq T_{c}^{exp}$, $C$ vanishes.

Here $\beta = 1/(kT)$, $\epsilon(Q)$ is a normalized spectral function and $\epsilon(Q)$ is the dispersion relation. Equation (4) represents the "single mode approximation" which is valid for sufficiently low temperatures \footnote{23, 24}. The dispersion relation is used in the variational form based on the first order perturbation theory \footnote{30}.

$$\epsilon(Q) = J_1 - \frac{1}{2} \sum_{u} J_u \cos Q \cdot u, \quad (4)$$

where the vectors $\{u\}$ connect neighbouring dimers center to center both within and between the chains.

At $T = 0.3K$ they used $f(E) = \delta(E)$ and obtained the global fit with an overall factor and four exchange coupling constants ($J_1, J_2$ and the constants $J_L$ and $J_R$ for coupling between the chains $\footnote{2}$) in Eq. (4) as the only fit parameters. The fit gives $\langle S_{0} \cdot S_{d}\rangle = -0.9(2)$ in agreement with the value of -3/4 for dimers in the singlet state. To perform the fit at higher temperatures the spectral function was replaced by a normalized Gaussian with half-width-half-maximum $\Gamma(\tilde{\omega}) = \Gamma_0 + \frac{L_0}{2} \cos \tilde{\omega}$, where $\tilde{\omega} = Q \cdot u_0$ is wave vector transfer along the chain.

Also, the dispersion relation \footnote{31} was replaced by the form $\epsilon(Q) = J_1 - n(T) \frac{1}{2} \sum_{u} J_u \cos Q \cdot u$, where renormalization factor $n(T)$ was introduced to account for finite temperatures. The prefactor for global fits at each temperature yields the intradimer spin correlations $\langle S_{0} \cdot S_{d}\rangle$ as given in Fig. 1. The correlations decreases with temperature increase due to mixing of the triplets with the singlet state of each dimer.

We will now show that the values estimated for the correlation function can only be explained if entanglement is present in the solid. We first show that $\langle S_{0} \cdot S_{d}\rangle$ is
an entanglement witness. The proof is based on the fact that for any product state of a pair of the spins one has

\[ |⟨S_0 \cdot S_{d_1}⟩| = |⟨S_0^x S_d^x⟩ + ⟨S_0^y S_d^y⟩ + ⟨S_0^z S_d^z⟩| \leq |S_0||S_{d_1}| \leq 1/4. \]  

(5)

Here and throughout the paper we choose units to be consistent with those of Ref. [2]; spin is expressed in units of $1/2$; $h = 1$. The upper bound was found by using the Cauchy-Schwarz inequality and knowing that for any state $|S|=\sqrt{(S_x^2)+(S_y^2)+(S_z^2)} \leq 1/2$. The proof is also valid for any convex sum of product states of two spins (separable states): $\rho = \sum_k w_k \rho_k \otimes \rho_k$ with $\sum_k w_k = 1$. In Fig. 1A the value of 1/4 for $|⟨S_0 \cdot S_{d_1}⟩|$ distinguishes temperatures ranges with and without entanglement in CN. The critical temperature is found to be $T_c^{exp} \approx 5K$.

The reported error in the correlation function ($\Delta = 0.2$ at $T = 0.3K$ [2]) implies an error of around $\Delta T \approx 1K$ in the critical temperature.

Within the model of uncoupled dimers the isotropy of Heisenberg interaction in spin space ensure that $⟨S_0^x S_{d_1}⟩ = ⟨S_0^y S_{d_1}⟩ = ⟨S_0^z S_{d_1}⟩$ and concurrence is given by $C = 2\max\{0, (|⟨S_0 \cdot S_{d_1}⟩| - 1/4)\}$. Similarly, Bell's parameter - the quantum value of Bell's expression in the Clauser-Horne-Shymony-Holt inequality [31] - is given by $(8\sqrt{2}/3)|⟨S_0 \cdot S_{d_1}⟩|$. It is higher than the local realistic limit 2 at temperatures below $T_c^{exp}$. Apart from rescaling both the temperature dependency of concurrence and of Bell's parameter have the same functional form as the correlation function in Fig. 1B.

The temperature dependence of $⟨S_0 \cdot S_{d_1}⟩$ in Fig. 1A is in a good agreement with a model of uncoupled dimers for which $⟨S_0 \cdot S_{d_1}⟩ = -(3/4)\Delta n(\beta J_1)$, where $\Delta n(\beta J_1) = (1 - e^{-\beta J_1})/(1 + 3e^{-\beta J_1})$ is the singlet-triplet population difference [2]. Within the model the theoretical temperature dependence of concurrence is given by $C = \max\{0, (1 - 3e^{-\beta J_1})/(1 + 3e^{-\beta J_1})\}$, as first obtained in Ref. [11, 12]. The theoretical value for the critical temperature $T_c^{th} = J_1/(k ln 3) = 4.6K$ is in excellent agreement with the value estimated from the experiment.

We now proceed with our second approach. We will analyse experimental results of a magnetic susceptibility measurement of CN [11 to show that the values measured at low temperatures cannot be explained without entanglement being present in the system. This will be based on a general proof that magnetic susceptibility of any strongly alternating antiferromagnetic spin-1/2 chain is a macroscopic thermodynamical entanglement witness.

When the system is in thermal equilibrium under a certain temperature $T$, its state is $\rho = e^{-H/kT}/Z$, where $Z = Tr(e^{-H/kT})$ is the partition function and $H$ is the Hamiltonian. The magnetic susceptibility along the direction $α$ is defined as $χ_α ≡ \langle \partial (M_α)/\partial B \rangle = (g^2μ_B^2/kT)(\langle(M_α)^2⟩ - \langle M_α \rangle^2)$, where $⟨M_α⟩$ is magnetization along $α$, $M_α = \sum_j S_j^α$, $B$ is external magnetic field, $g$ is $g$-factor and $μ_B$ is the Bohr magneton. Because of the isotropy of the Hamiltonian in spin space magnetization at zero-field vanishes for any temperature. This implies the following form for magnetic susceptibility at zero-field: $χ_α = (g^2μ_B^2/kT)(\langle M_α \rangle^2)/(\langle(M_α)^2⟩ - \langle M_α \rangle^2) \approx (g^2μ_B^2N/kT)(1/4 + \langle S_0^2 \rangle / (∑_i S_i^2))$. Here we assume that correlations between all spins that are not nearest neighbors are negligible compared with $⟨S_0^2 S_{d_1}⟩$. This approximation is valid for our case of strongly alternating spin chains at low temperatures. It is important to note that apart from the weak anisotropy in the $g$ factor, the magnetic susceptibility at zero-field is isotropic, i.e. $χ_x = χ_y = χ_z ≡ χ$. Thus, if we sum the values of magnetic susceptibilities over the three orthogonal directions $x$, $y$ and $z$ in space we obtain $χ = (g^2μ_B^2N/kT)(1/4 + (∑_i S_i^2)/ (∑_i S_i^2))$, where the mean value (…) is taken over the thermal state at $B=0$. However, because one has $|⟨S_0 \cdot S_{d_1}⟩| \leq 1/4$ for any separable state (Eq. (5)), the magnetic susceptibility for such states is limited as given by

$$χ \geq \frac{g^2μ_B^2N}{kT} \cdot \frac{1}{6}. \quad (6)$$

Thus, a violation of this inequality necessarily detects entanglement in the system. In Ref. [11] magnetic susceptibility of CN was measured on single crystal in 0.4 $-$ 4.2K and 14 $-$ 20K ranges of temperature. The measurement method was based on a mutual inductance bridge working at 275 Hz. The susceptibility was found to have a rounded maximum at 3.2K dropping very rapidly below this temperature approaching zero at vanishing temperatures, as given in Fig. 2A. Such behaviour is typical for alternating spin chains. Thermodynamical entanglement witness [10] is represented by the red solid line in Fig. 2A. The measured values of magnetic susceptibility below the intersection point of the curve representing the witness and the experimental curve cannot be described without entanglement. The critical temperature is around $T_c^{exp} \approx 5K$. This is in excellent agreement with the value estimated from the neutron scattering experiment in spite the fact that different samples were used (authors of Ref. [11] noted possible variations of the physical state of the sample due to high hygroscopy of CN), the two experimental methods test entirely different physical quantities and are almost 40 years apart (we note that no experimental error of magnetic susceptibility measurement was reported in Ref. [11]).

In conclusion, we show that neutron scattering experiments [3] directly and measurement of magnetic susceptibility [11] indirectly demonstrate presence of macroscopic quantum entanglement in a solid (cooper nitrate). We believe our results indicate that entanglement may play a broad generic role in macroscopic phenomena.

The question of having macroscopic entanglement is not only fascinating in its own right but it also has a fundamental significance as it pushes the realm of quantum physics well into the macroscopic world, thus opening the
possibility to test quantum theory versus alternative theories well beyond the scales on which theirs predictions coincide. It also has important practical implications for implementation of quantum information processing. If the future quantum computer is supposed to reach the stage of wide commercial application, it is likely that it should share the same feature as the current (classical) information technology and be based on solid state systems. It will thus be important to derive the critical values of physical parameters (e.g. the high-temperature limit) above which one cannot harness quantum entanglement in solids as a resource for quantum information processing.

We consider our work to imply that many experiments performed in the past may still hide new and interesting physics. Experiments of Berger et al. [1] from 1963 and Xu et al. [2] from 2000 used here are exemplary. Interestingly, the 1963 experiment was performed long before any serious attempts to measure entanglement begun in the seventies. It is not even impossible that we are able to find a result from which we can infer the existence of entanglement and which appeared well before this concept was conceived by Schrödinger in 1935.

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