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Atomic motions in the layered copper pseudochalcogenide CuNCN indicative of a quantum spin-liquid scenario

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Abstract

We explore the thermodynamic properties of the layered copper(II) carbodiimide CuNCN by heat-capacity measurements and investigate the corresponding thermal atomic motions by means of neutron powder diffraction as well as inelastic neutron scattering. The experiments are complemented by a combination of density-functional calculations, phonon analysis and analytic theory. The existence of a soft flexural mode—bending of the layers, characteristic for the material structure—is established in the phonon spectrum of CuNCN by giving characteristic temperature-dependent contributions to the heat capacity and atomic displacement parameters. The agreement with the neutron data allows us to extract a residual—on top of the lattice—presumably spinon contribution to the heat capacity $\propto T^2$, speaking in favor of the spin-liquid picture of the electronic phases of CuNCN.

Keywords: copper carbodiimide, flexural vibrations, atomic displacement parameters, heat capacity, neutrons, POWGEN, entropy

 Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

The phase dubbed copper carbodiimide (CuNCN) is a layered (figure 1) transition-metal pseudochalcogenide in which NCN^{2-} anions play a role similar to common chalcogenide (O^{2-} , S^{2-} or Se^{2-}) anions. This material is a temperature-independent (quasi-Pauli) paramagnet at room temperature, while at lower temperatures its magnetic susceptibility exhibits approximately activated (quasi-Arrhenius) behavior implying the presence of a spin gap in the ground state.

These features can be put in agreement with the absence of a magnetic order established in polarized neutron scattering experiments [1] by assuming either 2D spin-liquid (resonating valence bond, RVB) or unusual spin-glass electronic phases [2, 3], both of which have been proposed to determine the physics of this, at a first glance, very simple material [4, 5]. Structural studies over a range of temperatures reveal anomalies in the thermal expansion of CuNCN in the *a* and *c* crystallographic directions at about 100 and 40 K, respectively. Incidentally, the magnetic response

switches from the quasi-Pauli to the quasi-Arrhenius (gapless to gapped one) regime at ca. 100 K as well, thereby providing further experimental support to the spin-liquid scenario. Temperature-induced transitions between various spin-liquid phases accompanied by structure manifestations [6–8] naturally arise. The alternative scenarios of spin glass [3] and spin liquid can be distinguished by the amount of degeneracy in their ground state. The latter is quantified by residual entropy/heat capacity (HC) as exemplified, for instance, in the layered material NiGa_2S_4 , featuring a spin-liquid phase [9] with vanishing residual entropy. The residual entropy in its turn is obtained by integrating the residual HC, which remains after the lattice contribution to the heat capacity (LHC) is subtracted from the measured values. This procedure could not be directly repeated for CuNCN since no chemical analogue of CuNCN, without unpaired spins, which could be used to independently estimate the LHC and to single out the residual HC, is available. Thus, here we took a different approach: first, we determined the phonon spectrum of CuNCN from the neutron scattering data and made a comparison with the density-functional result and then calculated the LHC which allowed us to extract the residual HC. Its characteristic low-temperature quadratic dependence contributes to resolving the spin-glass/spin-liquid dilemma. The paper is organized as follows. In section 2 we present results and in section 3 their discussion while section 4 provides a conclusion. Some more detailed account of the methods used is given in section 5.

2. Results

2.1. Calculated and observed crystal structure

The crystal structure and the atomic motions in CuNCN were computed by spin-polarized density-functional theory (DFT) using the generalized gradient approximation (GGA) + U with parameters described in [1]. In addition, the D2 dispersion correction [10] was added because calculations with the pure Perdew–Burke–Ernzerhof (PBE) functional [11] overestimate the lattice parameter b by about 0.5 Å. The DFT-optimized lattice parameters and atomic positions together with the experimentally determined values from neutron diffraction [6], which served as a starting point for the calculations, are given in table 1 and depicted in figure 1. In fact, multiple calculations were carried out adjusting the DFT-related parameters such as the type of XC functional, the Hubbard U and dispersion corrections, taking the dynamical stability as a correctness criterion, the other one being the reproduction of the lattice parameters in order to have a reasonable setup for our studies.

2.2. Phonon spectrum and atomic displacement parameters

2.2.1. Phonon density of states. Figure 2 depicts the atom-resolved density of phonon states (DPS), calculated theoretically by the combination of the software packages VASP and PHONOPY as described in section 5. No imaginary frequencies appear in the vibrational spectrum, indicating the

Table 1. Structural parameters of CuNCN from DFT compared to that obtained from neutron diffraction at 17 K [6].

	Calculations (DFT)	Experiment	Δ	Δ (%)
a (Å)	2.9873	2.9891(1)	−0.0018	−0.06
b (Å)	5.9842	6.1420(2)	−0.1578	−2.64
c (Å)	9.4599	9.4009(3)	+0.0590	+0.62
y_N	0.3773	0.3804(1)	−0.0031	−0.82
z_N	0.3802	0.3804(1)	−0.0002	−0.05
y_C	0.3847	0.3860(3)	−0.0013	−0.34
$d(\text{Cu–N})_{\text{short}}$ (Å)	2.014	2.0093(6)	+0.0047	+0.23
$d(\text{Cu–N})_{\text{long}}$ (Å)	2.526	2.5930(10)	−0.0670	−2.65
$d(\text{C–N})$ (Å)	1.232	1.2264(8)	+0.0056	+0.45
N–C–N (°)	175.9	176.80(13)	−0.9000	−0.51

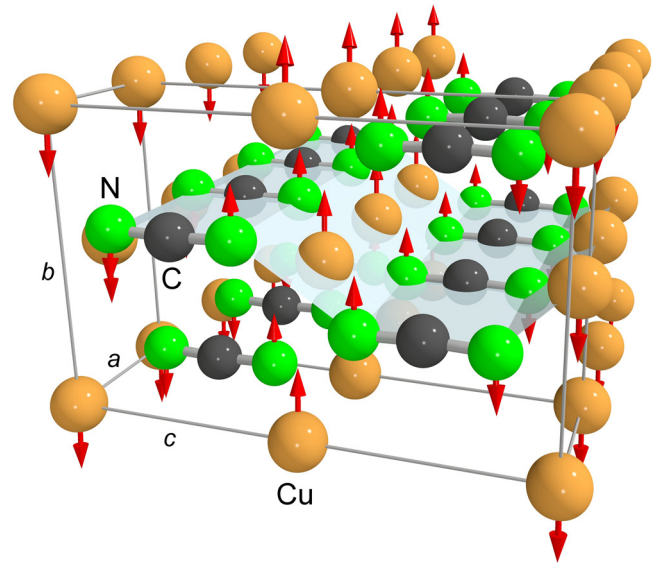


Figure 1. The crystal structure of CuNCN with Cu in dark-orange, C in black and N in green. The half-transparent surface is an eye guide to highlight the layered structure of the material. Γ point eigenvectors of the vibration at 0.8 THz (see below) are depicted by arrows. These eigenvectors are clearly dominated by the rotations of NCN^{2-} moieties around the a axis accompanied by the parallel motions of the Cu atoms. Contributions in the c direction are small and no a components are present.

obtained structure to be dynamically stable, therefore being at least a local energy minimum. The DPS separates into the low-frequency part below ca. 14 THz, where the copper atoms contribute to the vibrational modes, and the rather sharp signals above, exclusively caused by intra-molecular vibrations of the NCN^{2-} units. The atom-resolved DPS shows that the vibrations at about 17, 19 and 60 THz contain contributions of nitrogen and carbon atoms while at 39 THz only the nitrogen atoms are moving.

In order to obtain a deeper insight into the vibrational behavior below 14 THz, the phonon band structures along the high-symmetry directions $\Gamma \rightarrow X$, $\Gamma \rightarrow Y$, and $\Gamma \rightarrow Z$ are all depicted in figure 3. For clarity, the bands relate to the conventional orthorhombic setup of space group $Cmcm$ and not to the primitive-cell representation. The acoustic modes span up to about 7 THz in the X and up to about 2.5 THz in the Y

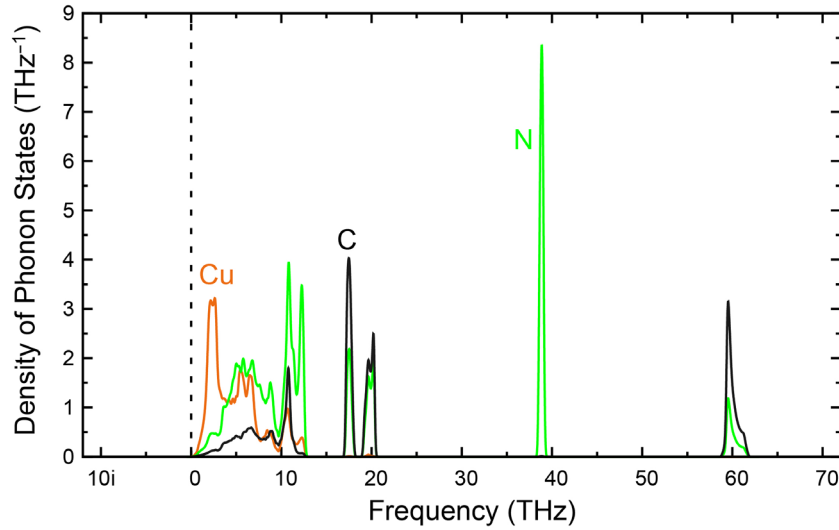


Figure 2. Atom-resolved DPS of CuNCN as derived from the VASP/PHONOPY procedure.

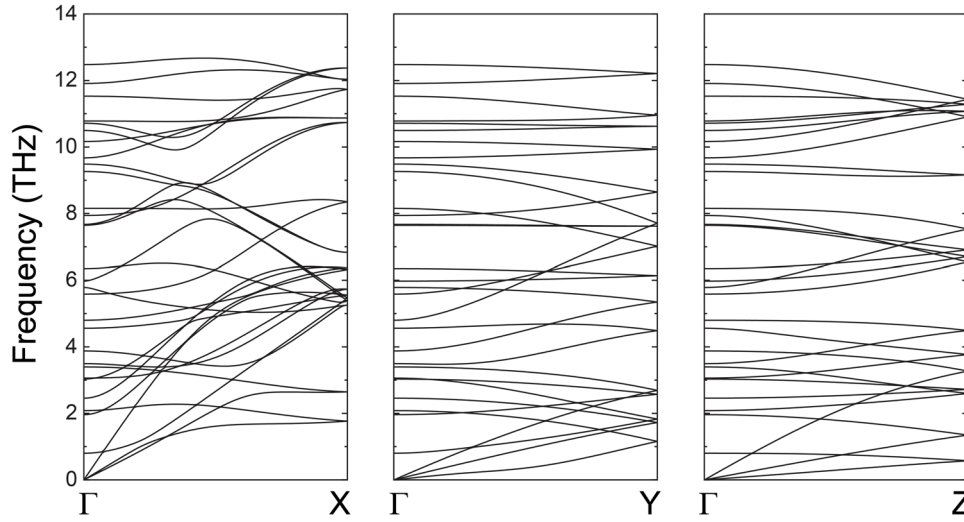


Figure 3. Phonon band structure of CuNCN as derived from the VASP/PHONOPY procedure along the high-symmetry directions $\Gamma \rightarrow X$, $\Gamma \rightarrow Y$ and $\Gamma \rightarrow Z$ in the conventional orthorhombic setup. Along the reciprocal a -axis, that is, parallel to $\Gamma \rightarrow X$, there is a rather strong dispersion compared to the other high-symmetry directions.

and Z directions. Across the Brillouin zone (BZ) these modes intersect with numerous optical modes emerging above ca. 0.8 THz. The strong dispersion and consequent overlap of the phonon modes suggests that the Q -averaged phonon spectrum is rather flat and should lack whatever sharp features, which reasonably holds for the frequency range 3–10 THz.

The low-frequency (acoustic) contribution to the DPS fairly reconstructs from the nonvanishing elastic moduli characteristic for the orthorhombic medium coming from VASP: $c_{11} = 1966$, $c_{22} = 594$, $c_{33} = 2294$, $c_{44} = 47$, $c_{55} = 317$, $c_{66} = 218$, $c_{12} = 392$, $c_{13} = 721$, $c_{23} = 208$ kBar (subscripts follow the standard Voigt notation of the elasticity theory). The first of two maxima at 2.5 THz of the theoretical DPS (figure 2) fairly coincides with that of the purely acoustic Born–von Kármán DPS (aDPS) derived in supplementary materials section S1 (figure S1.2 (stacks.iop.org/JPhysCM/29/235701/mmedia)), whereas its further features are absorbed in the ‘fence’ DPS region (see below).

2.2.2. Atomic displacements—experimental situation. In order to investigate the atomic displacement parameters (ADP), neutron powder diffraction experiments using the POWGEN instrument were performed. The derived ADPs are represented in figure 4 together with similar values calculated theoretically by the procedure implemented in PHONOPY [12, 13]. Three eigenvalues u_i , i.e. the main axes of the thermal ellipsoids, are shown. The corresponding eigenvectors (the thermal ellipsoid axes) were found to be temperature-independent within the error bars. For symmetry reasons those for the C atom are always directed along the crystallographic axes while for the other atoms only one of these axes always coincides with the crystallographic a axis; other eigenvectors tilt away from the b axis by 25° for Cu and by 10° for N, respectively, with the remaining ones determined by the orthogonality condition.

The amount of disagreement between theory and experiment is quantified by the similarity index $S_{12} = 100 \cdot (1 - R_{12})\%$,

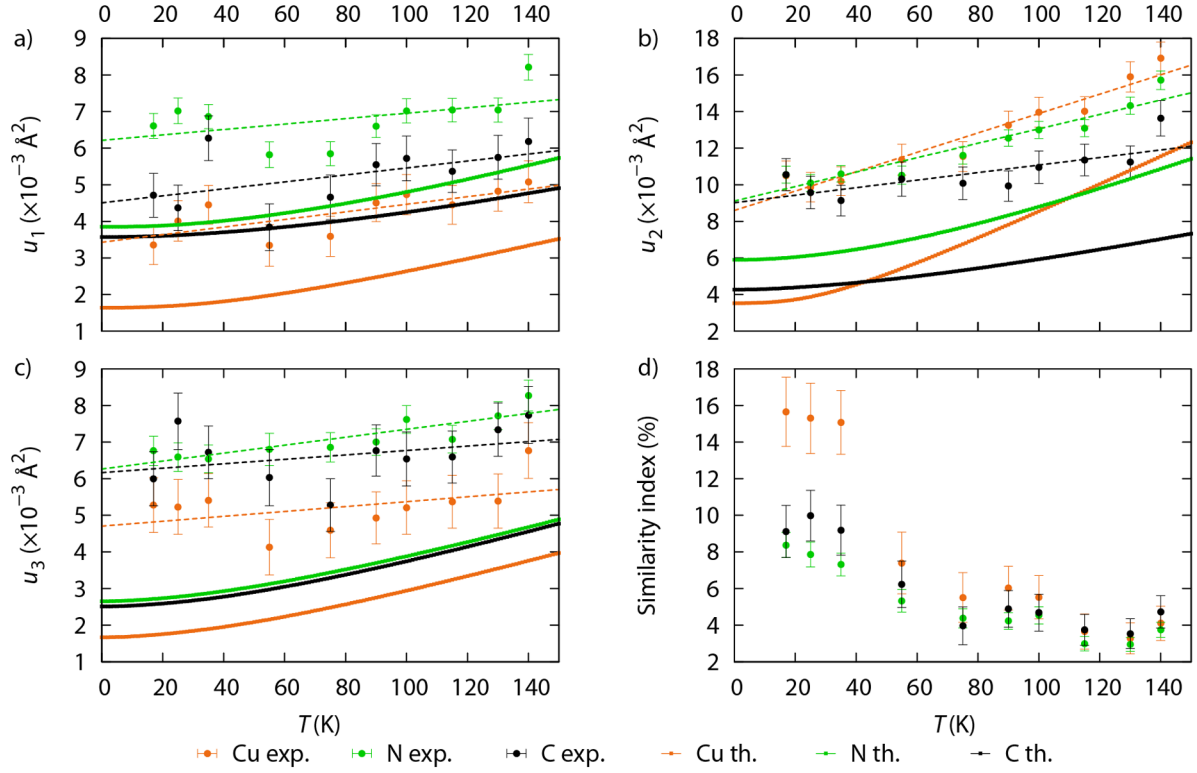


Figure 4. Comparison of the displacements along the main axes of the thermal ellipsoids u_i ($i = 1-3$) and the computed similarity index (lower right panel) as a measure for the overall quality of the agreement of the measured and calculated U_{ij} matrices. Solid lines are the theoretical values obtained using the DFT based phonon spectrum. Dotted lines are linear fits of the experimental values.

indicating the percentage of the volume outside the common part of two overlapping thermal ellipsoids (theoretical and experimental) [14] as recently introduced [15]. In contradiction with the usual behavior, the difference between experiment and theory comes out significantly larger at *lower* temperatures than that at higher ones. This is unexpected because theoretical harmonic ADPs typically fall behind experimental ones at higher temperatures because here the vibrations are no longer harmonic. In the present CuNCN case, however, the density-of-phonon states as calculated via DFT is underestimated at low frequencies, and so are the amplitudes of the low-temperature vibrations along *b* and/or *c*. More quantitatively, we computed the mass-weighted sum of the linearly extrapolated experimental values of u_i to 0 K, left part in equation (1), and compared this with the numerical integral of the DPS divided by frequency (right part) which has to obey the sum rule [16]:

$$\sum_{\nu} M_{\nu} \sum_i u_{ii}(\nu) = \frac{\hbar}{4\pi} \int_0^{\infty} \frac{g(\nu)}{\nu} d\nu. \quad (1)$$

Puzzingly, the experimental value on the left (about $7.6 \text{ Da} \cdot \text{\AA}^2$)⁸ overshoots the theoretical value on the right (ca. $3.6 \text{ Da} \cdot \text{\AA}^2$) as extracted from the numerical DPS by a factor of more than two. This discrepancy is far too large and indicates serious problems for the description of the phonon spectrum at lower frequencies and the related low-temperature

physics. This is visible in figure 4 as the deviation between the theoretical low-temperature limit (solid lines) and the linear extrapolation of the experimental values (dotted lines).

2.2.3. Acoustic contributions to ADPs and anisotropy of their temperature-dependent anomaly. In order to clarify the differences between experimental and theoretical ADPs we notice, first, that different parts of the phonon spectrum contribute differently to the ADPs. The phonon spectrum above ca. 3 THz comprises intramolecular and/or optical modes, so it contributes only to the temperature-independent background of the ADPs or CFADs (correlation function of the atomic displacements). In order to grasp the most spectacular feature, namely the temperature dependence of the ADPs, we analyze the low-frequency modes. To start with, we estimated the acoustic contribution to the ADPs. As explained in the supplementary material section S2, it can be interpolated by (figure 5):

$$U_{\gamma\gamma}^{(T)}(\text{acoust}) = d_{\gamma\gamma}^2 \sqrt{1 + \left(\frac{T}{T_{0\gamma}}\right)^2} \quad (2)$$

The interpolation works perfectly for the entire studied temperature range with $T_{0a} \approx 43$; $T_{0b} \approx 29$; $T_{0c} \approx 38$ K; $d_{aa}^2 = 0.36 \cdot 10^{-3}$; $d_{bb}^2 = 0.67 \cdot 10^{-3}$; $d_{cc}^2 = 0.53 \cdot 10^{-3} \text{\AA}^2$. We subtracted the acoustic contributions calculated by equation (2) and derived the quantities $Y_{\gamma\gamma}^{(T)}(\nu) = U_{\gamma\gamma}^{(T)}(\nu) - U_{\gamma\gamma}^{(T)}(\text{acoust})$, which are shown in figure 6 and table 2.

⁸ Dalton (Da); 1 Da = 1822.888 486 192(53) $m_e = \frac{1}{12} m_{12C}$.

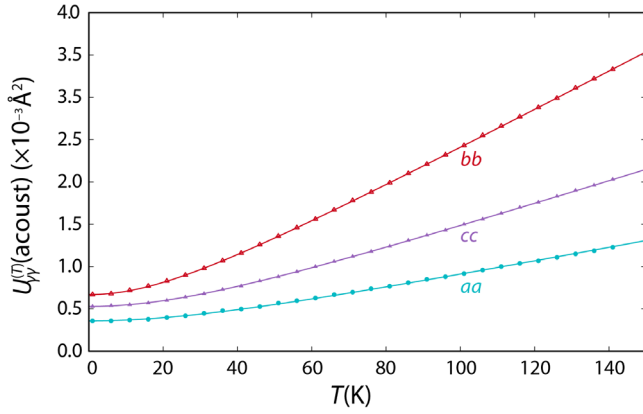


Figure 5. Acoustic contribution $U_{\gamma}^{(T)}(\text{acoust})$ to the ADPs versus temperature equal for all atoms in the unit cell. Points represent numerical values obtained, as explained in section S2, lines are the interpolations by equation (2).

In figure 6 we see that the quantities $Y_{\gamma}^{(T)}(\nu)$ which represent the CFADs cleaned of the acoustic contribution are not temperature independent in general but only along two of three lattice parameters (a and c) in the entire studied temperature range 17–140 K. By contrast, $Y_{bb}^{(T)}(\text{Cu})$, $Y_{bb}^{(T)}(\text{N})$ and $Y_{bc}^{(T)}(\text{Cu})$, $Y_{bc}^{(T)}(\text{N})$ show a discernible (well beyond the error bars) temperature trend whereas $Y_{bb}^{(T)}(\text{C})$ exhibits apparently irregular deviations from the average mostly within the error bars. Also, the quantities $Y_{\gamma}^{(T)}(\nu)$ for $\gamma = b$ are significantly larger than those for $\gamma = a, c$ already at the lowest explored temperatures. This represents quite a sophisticated combination of features, which we are going to interpret.

The nontrivial temperature dependence of the ADPs not covered by the acoustic modes populated at arbitrary low temperature suggests the presence of soft-vibrational modes. In the frequency range below 2 THz (100 K) one clearly sees three acoustical and three optical branches. The lowest optical band with the minimum at 0.8 THz is somewhat suspicious. Although it is included in the theoretical ADP estimate shown in figure 4, it apparently does not suffice to explain either the observed ADP magnitude or their temperature dependence. One could interpret the motions along b in terms of strong anharmonicity but such an effect should then also manifest in the thermal expansion of CuNCN.

This is, however, not the case. By contrast, although the thermal expansion constants characteristic for the b direction and the ac plane differ noticeably ($\alpha_b \approx 3.1 \cdot 10^{-5} \text{ K}^{-1}$; $\alpha_a \approx 5.3 \cdot 10^{-6} \text{ K}^{-1}$; $\alpha_c \approx 5.2 \cdot 10^{-6} \text{ K}^{-1}$ [2, 6]), which one would expect for a layered structure, the values themselves do not indicate any anomalous anharmonicity. In fact, they manifest a remarkable *isotropy* in the ac plane already seen from the angular dependence of the sound velocities depicted in figure S1.1.

2.3. Inelastic neutron scattering and flexural phonons

2.3.1. Experimental observations. Due to the observed discrepancies in the low frequency/temperature behavior of the ADP along b , inelastic neutron scattering (INS) measurements on the CuNCN crystalline powder probing the required frequency range were performed. The measurement was performed on the time-of-flight spectrometer FOCUS [17] at Swiss spallation source SINQ. Two setups of the instrument were employed. The setup with incoming neutron energy $E_i = 28 \text{ meV}$ with a resolution of 2 meV at the elastic line allows to review high-energy excitations. The setup with $E_i = 8 \text{ meV}$ with a resolution of 0.4 meV at the elastic line, focuses at low-energy signal. The data reduction included empty can and vanadium measurements, necessary for subtraction of background and detector calibration, respectively [18, 19]. An overview of the measured reduced data for the two setups at two temperatures $T = 1.5$ and 130 K are shown in figures 7 and 8. Two strong, well peaked, bands of scattering are observed at 4.6 meV and 10 meV. They disperse from the Q -positions corresponding to the nuclear Bragg peaks and increase in intensity with temperature, so we attribute these bands to a powder averaged set of optical and acoustic phonon excitations. Integration of the experimental energy spectra has been performed over the accessible Q -ranges for the respective energies (0.5–3.5 $\text{\AA}^{-1}$ for $E_i = 8 \text{ meV}$ and 1–6.5 $\text{\AA}^{-1}$ for $E_i = 28 \text{ meV}$, respectively) provide an insight into the optical bands. The anomaly at 4.6 meV could be fitted by a single Gaussian line yielding full width at half maximum (FWHM) of 0.51(5) meV, which is relatively close to instrumental resolution for the low-energy setup. On the other hand, the anomaly at 10 meV requires two Gaussian lines centered at 9.4 and 11.4 meV with corresponding widths of 1.6(2) meV, which is again close to the experimental resolution for the high-energy setup. The existence of several anomalies in the INS spectrum indicates complex phonon contributions.

Comparing the measured intensities (circles in panels (b) and (e) of figures 7 and 8) with the calculated DPS (figures 9 and S1.2) we see that the higher-energy feature falls in a frequency range abundant of phonon bands (figure 9). The low-energy feature, however, is not reproduced at all. One could attempt to attribute it to the calculated lowermost optical band at 0.8 THz but there is only a very weak shoulder at 4.2–4.5 meV (0.8 THz) in the theoretical DPS (figure 9). This is not surprising as this branch obviously has only one negative eigenvalue as a quadratic function of wave-vector components (k_c^2 enters with the negative coefficient as seen in the $\Gamma \rightarrow Z$ panel of figure 3), so it makes a van Hove singularity of the S_1 type [20, 21] at the Γ point. Such a singular point is expected to generate a root-like dependence of the DPS with only a flat contribution to it, but it cannot explain the rather sharp feature in the experimental spectra. On the other hand, the low-energy feature cannot be attributed to the magnetic excitations of a 2D spin-liquid RVB state of CuNCN, since one would expect

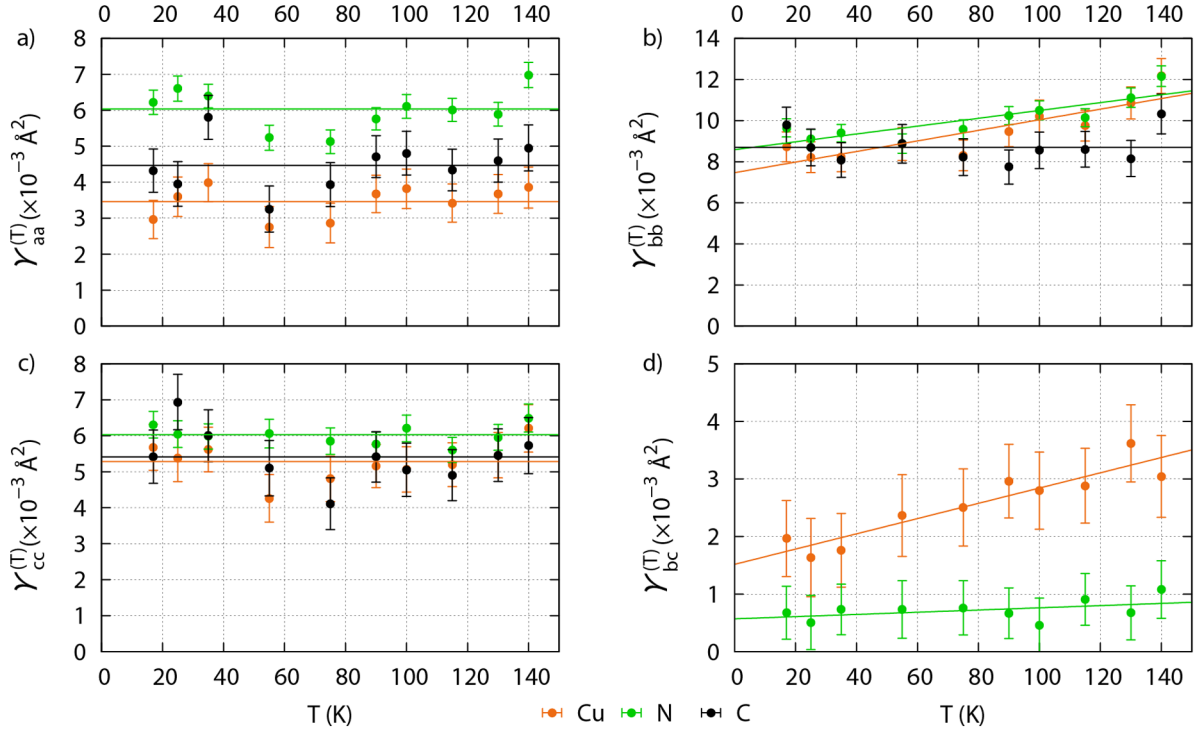


Figure 6. The ADPs after subtracting the acoustic contributions versus temperature. Note the different scale of the ordinate axis in plots (a) and (c) to plot (b) as well as to (d). For plot (d) the absolute values are plotted and the acoustic contributions of b and c are subtracted according to the temperature-independent eigenvectors contribution to these components. Solid lines in (a) and (c) show the average values, stressing the absence of any regular temperature dependence. In (b) and (d) the solid lines result from the linear fit and show a remarkable difference in behavior of the Cu and N atoms on one hand and of the C atoms on the other.

a temperature dependence of such features between 1.5 and 130 K.

2.3.2. Flexural phonons and the INS spectrum. In order to resolve the above contradiction, we re-iterate the CuNCN structure as being composed of 2D layers parallel to the ac plane (figure 1). Such structural feature manifests in the appearance of the flexural vibrations [22–26], that is, bending of layers. The characteristic dispersion law for the flexural phonons derives from elasticity theory [27] and reads, for an isolated layer, as

$$-\sigma \frac{\partial^2 \zeta}{\partial t^2} = D \Delta^2 \zeta, \quad (3)$$

where σ is the areal mass density of the layer, ζ is the position-dependent flexural displacement of the layer along its normal, D is the flexural stiffness of the layer, producing the squared characteristic frequency $\alpha^2 \omega_{\perp}^2 = D/\sigma$ of the flexural deformation. In the solid-state context, this notation proves to be useful, as shown right below.

The key specific of the above equation is that the Laplacian (Δ) of the flexural displacement enters in the second power, making the entire equation of fourth order with respect to the spatial partial derivatives. This produces an unusual dispersion law for the flexural phonons $\omega_f \propto k^2$ [27], in which k is the length of a 2D wave vector in the layer, —an extra soft mode/branch in addition to the three acoustic modes with the dispersion law $\omega_a \propto k$ corresponding to the relative motions of the non-deformed unit cells.

Table 2. Size of the ADPs cleaned from the acoustic contributions including those extrapolated to zero temperature $Y_{\gamma\gamma}^{(0)}(\nu)$ (10^{-3} Å^2) and its slopes versus temperature $Y'_{\gamma\gamma}(\nu)$ ($10^{-5} \text{ Å}^2 \text{ K}^{-1}$).

	aa	bb	cc	bc
$Y_{\gamma\gamma}^{(0)}(\text{Cu})$	3.460	7.464	5.283	1.517
$Y_{\gamma\gamma}^{(0)}(\text{N})$	6.034	8.585	6.028	0.570
$Y_{\gamma\gamma}^{(0)}(\text{C})$	4.469	8.701	5.413	0
$Y'_{\gamma\gamma}(\text{Cu})$	0	2.576	0	1.33
$Y'_{\gamma\gamma}(\text{N})$	0	1.907	0	0.19

For the solid state, the above description of flexural vibrations must be modified by taking into account (i) the interaction of the layers, (ii) a small contribution proportional to the Laplacian itself, rather to its square, and (iii) the discrete (atomistic) character of the vibrating layers in contrast with the continual equation (3). The atomistic character of the propagation medium for the flexural waves is taken into account by discretizing the equations coming from elasticity theory, that is, by going from the partial derivatives to finite differences of the respective order. Combining the required modifications, we arrive at the dispersion law

$$\omega^2 = \omega_{\perp}^2 \left(\alpha^2 \left(\sin^2 \frac{k_a a}{2} + \sin^2 \frac{k_c c}{2} \right)^2 + w^2 \left(\sin^2 \frac{k_a a}{2} + \sin^2 \frac{k_c c}{2} \right) + \sin^2 \frac{k_b b}{2} \right) \quad (4)$$

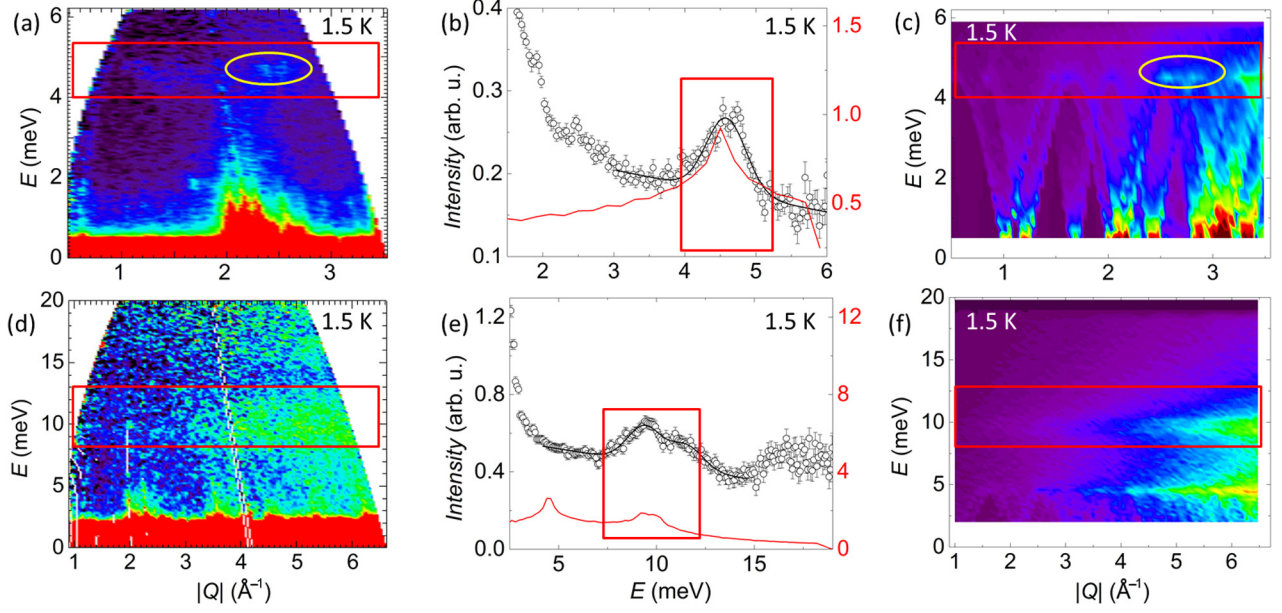


Figure 7. Powder-averaged inelastic neutron spectra recorded at 1.5 K with the incoming neutron energy $E_i = 8$ meV (a) and $E_i = 28$ meV (d). In (b) and (e) the energy spectra integrated over all experimentally accessible Q -range are shown (black circles). Black solid lines are fits to a single (b) and two (e) Gaussians. Red solid lines in (b) and (e) are the simulated flexural (see section 2.3.2) contribution to the Q -integrated intensities; (c) and (f) are the simulated flexural contributions to the powder-averaged inelastic neutron spectra in the respective ranges of Q and E . We note that the difference between the experimental and simulated panels results from acoustic modes, which are not included in the simulations.

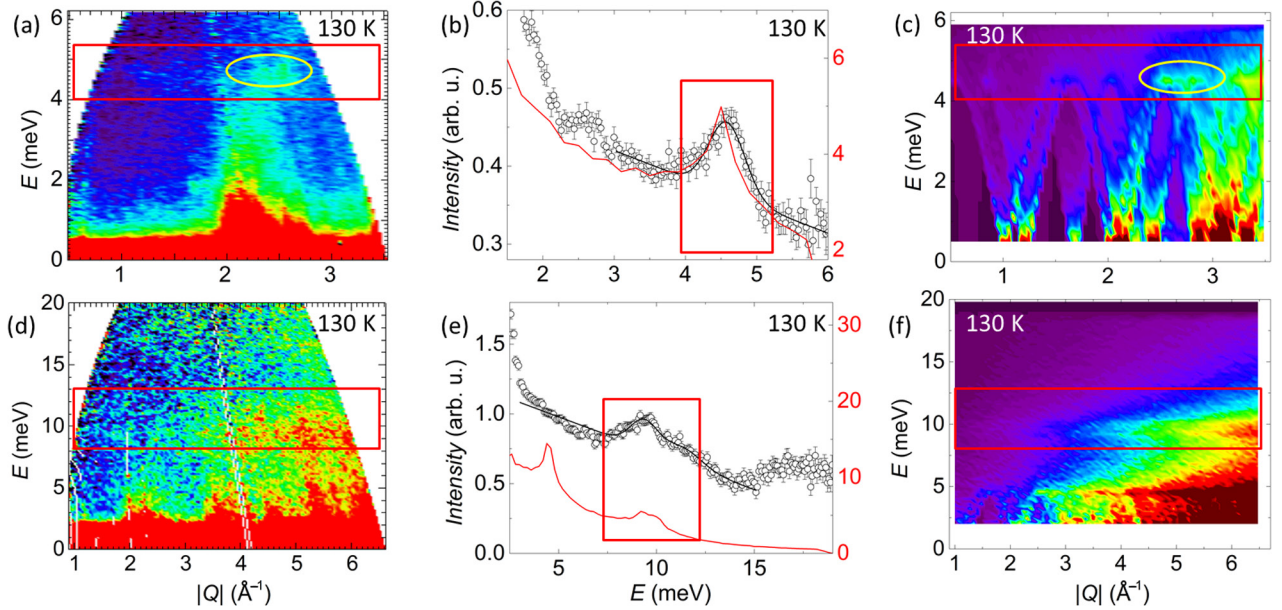


Figure 8. Same as in figure 7, but here the data is for 130 K.

for the flexural mode. Its characteristic frequency in terms of an individual layer is given as a product between the frequency $\omega_{\perp}$ characterizing the interlayer interaction and an anisotropy parameter α , whereas w scales the contribution linear in the Laplacian. The scaling parameters are subject to the condition: $w \ll 1 < \alpha$. Through the discretization, the dispersion law for the flexural waves becomes characteristic for the wave propagation in a crystal. The critical points of ω as function of the wave vector k lead to singularities in the flexural DPS, dubbed fDPS (figure 10).

We simulated the contribution of the flexural phonons to the INS as prescribed [28] by taking $\hbar\omega_{\perp}$ as the position of the low-energy feature and using the values of the vibration amplitudes $e_b(N, f)$, $e_b(Cu, f)$ as resulting from DFT (see section 2.3.3). The anisotropy parameter α was plausibly estimated either as the ratio of thermal expansion coefficients for the b and c axes or as the ratio of the sound velocities in the same directions, both giving a similar magnitude of about two (see supplementary material section S1 for details). The results are presented in figures 7 and 8. The simulated

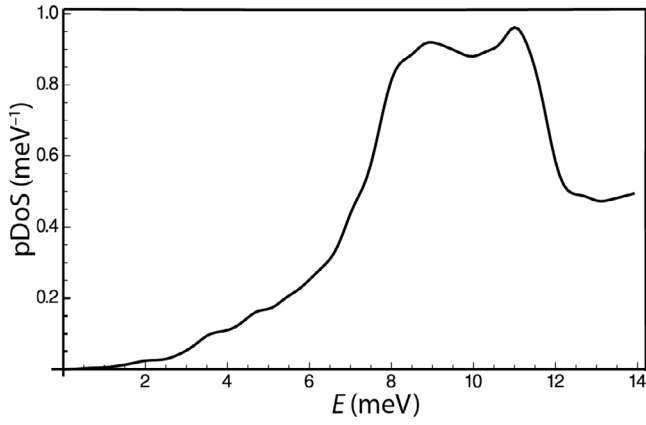


Figure 9. The low-frequency theoretical DPS of CuNCN.

powder-averaged scattering spectra (panels (c) and (f)) fairly match the experimental ones. Particularly informative are the low-energy spectra reproducing the contribution of the Y flexural phonons. As one could expect, the form of the Q -integrated INS spectra (panels (b)) is in reasonable agreement with the fDPS depicted in figure 10 with a sharp feature at 4.6 meV ($= \hbar\omega_{\perp}$). The 9.41 meV feature is then contributed by the flexural phonons between two S_2 -type critical points X and R with the fDPS plateau between $\hbar\alpha\omega_{\perp}$ and $\hbar\omega_{\perp}\sqrt{1+\alpha^2}$. Also, the acoustic DPS having a maximum at this energy (see figure S1.2 in section S1) and other phonons from the bottom of the ‘fence/spaghetti’ range shown in figure 9 contribute here. The values of the acoustic and flexural contributions to the PDS at this energy (ca. 10 meV) relate as 3:1, thus the flexural contribution to this feature is at best 25%. This explains the quite noisy experimental spectra for higher-temperature measurements (panels (d) in figures 7 and 8) as well as the scale used in panels (e) of these figures. By contrast, the intensity at 4.6 meV has only the flexural modes as its source, which justifies the scale used in the (b) panels.

2.3.3. Flexural contribution to ADP's. The soft mode in the phonon spectrum not reproduced by the numerical methodology, but observed in the INS as the 4.6 meV feature (that is, the flexural mode), must produce a temperature-dependent contribution to the ADPs as well. Taking the general relation (supplementary material section S2, equation (S2.1)) with an additional assumption that the atomic displacement vectors $e(\nu;f)$ in the flexural mode are $\mathbf{k}$ -independent so that the normal vibrations have the form: $e(\nu;f)\exp(i\mathbf{k}\mathbf{r})$, we derive the flexural contribution for the ν -th atom:

$$Y^{(Tf)}(\nu) = \frac{\hbar}{2M_{\nu}} e(\nu;f) \otimes e^*(\nu;f) \int_0^{\infty} \frac{d\omega}{\omega} \coth\left(\frac{\hbar\omega}{2k_B T}\right) g_f(\omega) \quad (5)$$

Possible temperature dependence enters through the integral over frequencies. Its direct calculation with the above parameters $\omega_{\perp}$, α harmonized with the INS spectrum and anisotropy estimates and plausible $w = 0.1$ yields the temperature dependence of the integral in equation (5) as depicted in figure 11. It is perfectly linear in the entire concerned temperature range (unlike the acoustic contribution showing quadratic temperature dependence at lower temperatures).

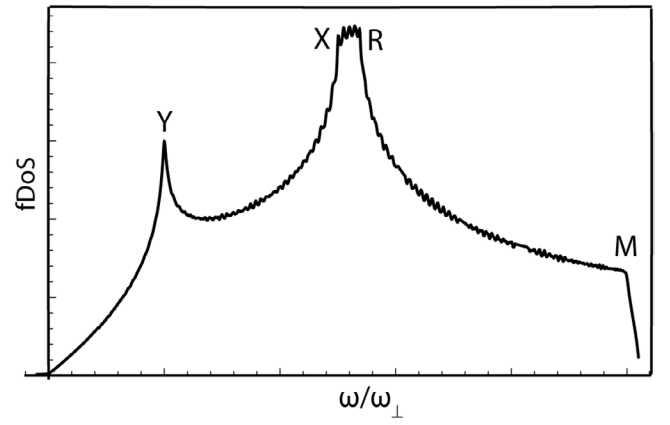


Figure 10. The density of flexural phonon states (fDPS) as a function of relative frequency $\omega/\omega_{\perp}$ in which the van Hove singularities have been marked by the indices of the critical points in the BZ contributing to them. The energies (frequencies) and the wave vectors corresponding to different singularities are, first, $Y = (0, \pi/b, 0)$ with a logarithmic peak at $\omega = \omega_{\perp}$. In addition, there is a wide peak in the middle as the superposition of the S_1 -type critical point $X = (\pi/a, 0, 0)$ at $\alpha\omega_{\perp}$ and the S_2 -type one $R = (\pi/a, \pi/b, 0)$ at $\sqrt{1+\alpha^2}\omega_{\perp}$. Between X and R , fDPS is almost linear. The critical point $M = (\pi/a, 0, \pi/c)$ at $2\alpha\omega_{\perp}$ is of the S_2 -type and the upper boundary of the spectrum is at $\omega_{\perp}\sqrt{1+4\alpha^2}$ and corresponds to the corner of the BZ $A = (\pi/a, \pi/b, \pi/c)$.

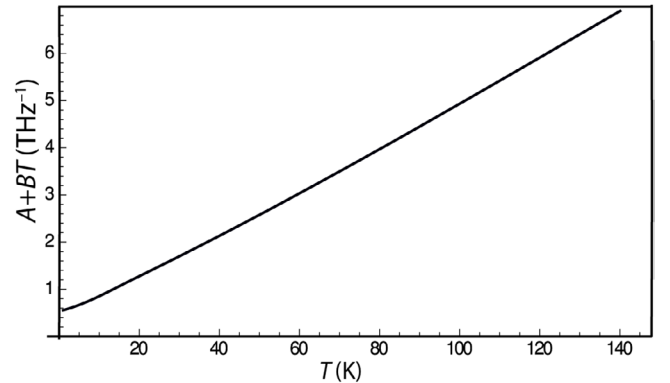


Figure 11. Temperature dependence of the integral in equation (5) calculated for the dispersion law equation (4) or equivalently fDPS (figure 10) with the parameters extracted from the INS spectrum.

The constant A (zero-temperature limit of the integral) equals to 0.557 THz^{-1} , whereas its temperature slope B is $46 \cdot 10^{-3} \text{ THz}^{-1} \text{ K}^{-1}$ so that the sought flexural contribution to the correlation function of the atomic displacements (CFAD) of the ν -th atom (3×3 matrix) is:

$$Y^{(Tf)}(\nu) = \frac{\hbar}{2M_{\nu}} e(\nu;f) \otimes e^*(\nu;f) (A + BT) \quad (6)$$

Thus, the temperature-independent part of the flexural contribution to the ADPs is

$$Y_{bb}^{(0f)}(\nu) = \frac{\hbar}{2} \frac{e_b^2(\nu;f)}{M_{\nu}} A \quad (7)$$

whereas, the temperature slopes of the ADPs as contributed by the flexural motions are

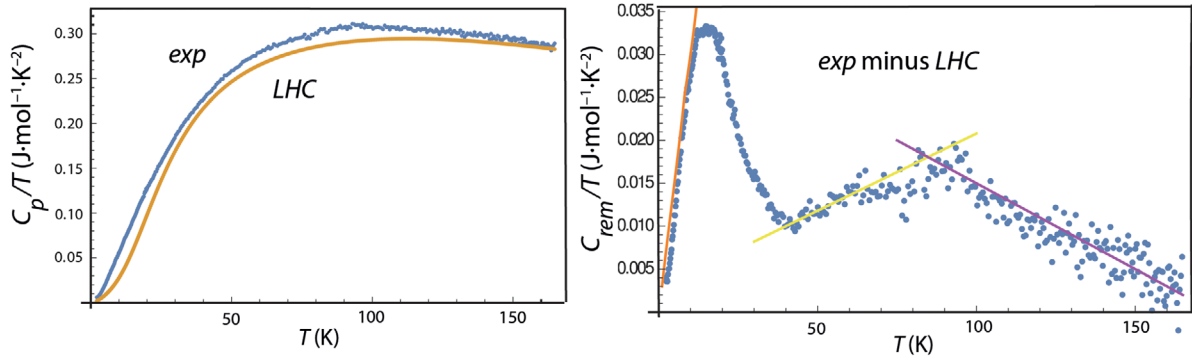


Figure 12. Left: The experimental data on C_p/T versus T (blue) and the total LHC calculated as described in the text (orange). Right: the residual—presumably magnetic—HC as extracted from the experimental data by subtracting the intramolecular, ‘fence’, acoustic, and flexural (obtained with the INS derived $\hbar\omega_{\perp} = 4.6$ meV, and plausible $\alpha = 2$, $w = 0.1$) contributions to the LHC. The straight lines serve as guides to the eye.

$$Y_{bb}^{(f)'}(\nu) = \frac{\hbar}{2} \frac{e_b^2(\nu, f)}{M_{\nu}} B, \quad (8)$$

both expressed through the b -component of the corresponding displacement vector and atomic masses. Combining the numerical values of A , B and the eigenvector components of the 0.8 THz branch, ($e_b(N, f) = 0.16$; $e_b(\text{Cu}, f) = 0.44$), we obtain $Y_{bb}^{(f)'}(\text{Cu}) = 7 \cdot 10^{-5} \text{ \AA}^2 \text{ K}^{-1}$ and $Y_{bb}^{(f)'}(N) = 4.2 \cdot 10^{-5} \text{ \AA}^2 \text{ K}^{-1}$. These values are correct to the order of magnitude (table 2). The possibility of using the form of the flexural mode shown in figure 1 while in failure with its frequency is discussed in section 3. On the other hand, we find $Y_{bb}^{(0f)}(\text{Cu}) = 0.85 \cdot 10^{-3} \text{ \AA}^2$, $Y_{bb}^{(0f)}(N) = 0.52 \cdot 10^{-3} \text{ \AA}^2$. These values are not as small as they may seem when compared with data of table 2. They show that ca. 10% of the zero temperature ADP’s $Y_{bb}^{(0)}(\text{Cu})$ and $Y_{bb}^{(0)}(N)$ cleaned from the acoustic contribution, whose total is given by the zero energy vibrations of all 45 non-acoustic modes, is provided by the flexural mode alone.

The temperature slope of the off-diagonal components of the CFAD tensors stripped of the acoustic contribution is:

$$Y_{bc}^{(f)'}(\nu) = \frac{\hbar}{2} \frac{e_c(\nu, f)e_b(\nu, f)}{M_{\nu}} B. \quad (9)$$

Comparing this with equation (8) yields the relation: $e_c(\nu, f)/e_b(\nu, f) = Y_{bc}^{(f)'}(\nu)/Y_{bb}^{(f)'}(\nu)$. The experimental values of the slopes $Y_{bc}'(N)$, $Y_{bb}'(N)$ (table 2) immediately yield $e_c(N, f)/e_b(N, f) \cong 0.1$. This is in fair agreement with our theoretical prediction, which gives $e_c(N, f) = 0.02$ for the 0.8 THz band explaining the above ratio although not the absolute value of the temperature slope. Similarly, the ratio of the slopes $Y_{bc}'(\text{Cu})/Y_{bb}'(\text{Cu})$ (table 2) yields: $e_c(\text{Cu}, f)/e_b(\text{Cu}, f) \cong 0.5$, which implies that a quarter of the squared amplitude of the Cu atom refers not to the b , but rather to the c direction. This reduces the above estimate of $Y_{bb}^{(f)'}(\text{Cu})$ 1.25 times and brings it closer to the experimental value (table 2). A tentative temperature slope $Y_{cc}^{(f)'}(\text{Cu})$ of $1.45 \cdot 10^{-5} \text{ \AA}^2 \text{ K}^{-1}$ which can be derived from this estimate of $e_c(\text{Cu}, f)$ ($\cong 0.2$), most probably, does not show up in the experiment because it is

masked by the more chaotic behavior of $Y_{cc}^{(T)}(\text{Cu})$ as seen in figure 6(c). Despite remaining uncertainties, the performed analysis fairly well interprets the temperature dependence of the ADPs obtained in our experiments (figure 6). Further analysis of remaining, temperature-independent contributions to the ADPs i.e. of the zero-energy vibrations of all remaining modes, requires detailed information about their forms at higher frequencies, which is not available at present.

2.4. Heat capacity

The HC measurements are performed on a high-purity sample as described in section 5.2.3. The results are depicted in figure 12. For the purpose of the present paper, these have to be corrected for the lattice contribution previously dubbed as LHC. In a standard way, the LHC is obtained by numerical integration of the contributions of independent oscillators in the body:

$$C_{\text{lat}} = \frac{R}{Z} \int E\left(\frac{\hbar\nu}{\theta}\right) g_{\text{tot}}(\nu) d\nu, \quad (10)$$

where $E\left(\frac{\hbar\nu}{\theta}\right)$ is the Einstein function, $\theta = k_B T$ (T is the temperature and k_B the Boltzmann constant, R is the universal gas constant and Z is the number of formula units in the unit cell).

The DPS $g_{\text{tot}}(\nu)$ is normalized to the number of degrees of freedom in the unit cell ($3NZ = 48$, where N is the number of atoms in the formula unit and $Z = 4$). Naively using the numerical DPS coming from DFT (figure 2) in equation (10), results in a strong overshoot of the calculated lattice heat capacity (LHC) over the measured one for the temperatures above 50 K, which is in contradiction to the second law of thermodynamics (see figure S3.1(a) in supplementary material section S3). This discrepancy appears since the numerical DPS is underestimated in the sensitive low-frequency region (the frequency of the flexural mode does not flow to zero as it should). Through the normalization of the DPS this defect translates into an overestimate at higher frequencies and thus also of the LHC at higher temperatures. To accommodate this fact we reconstructed the correct DPS using the information obtained from elastic and inelastic neutron scattering. For the purpose of the LHC calculation,

the reconstructed DPS $g_{\text{tot}}(\nu)$ is represented as the acoustic contribution calculated in the Born–von Kármán approximation from the elasticity moduli obtained from VASP. The intramolecular contributions are added as the delta functions placed at the characteristic frequencies of the dispersionless bands of the NCN intramolecular vibrations with the relevant spectral weights. Due to significant anisotropy of the material the Debye approximation, even with three separate Debye frequencies for these acoustic modes, is not sufficient in the sensitive temperature range (see figures S3.1(a) and (b) in supplementary material section S3), so that the interpolation of the numerical HC derived from the Born–von Kármán acoustic aDPS had to be used. The theoretical density in the ‘fence/spaghetti’ region is doubtful as well because of the incorrect treatment of the flexural mode, manifesting in the INS spectra and temperature dependence of ADP’s. Due to the integral character of the LHC we replace the unknown precise density in the ‘fence’ region by the uniform distribution, providing the following contribution to the LHC:

$$\frac{R}{Z} \frac{N_b}{\nu_h - \nu_l} \int_{\nu_l}^{\nu_h} E\left(\frac{h\nu}{\theta}\right) d\nu, \quad (11)$$

where N_b is the number of bands in the ‘fence’ range and ν_h, ν_l are its upper and lower boundaries, respectively. Details of the interpolation procedure in the ‘fence’ range can be found in supplementary material section S3.

The flexural modes produce a characteristic temperature-dependent contribution to the LHC [22, 24]. In the lowest temperature range between zero and *ca.* $\hbar\omega_l/k_B$ this contribution is proportional to T^3 ; then up to *ca.* $\hbar\omega_l/k_B$ it changes to the T^2 -dependence. Using the fDPS (figure 10) obtained numerically with the parameters derived from the INS spectrum we calculated this contribution to the LHC.

Once all the components (acoustic, intramolecular, flexural, and ‘fence’) of the LHC are assembled, one immediately sees some residual HC extending over the entire studied temperature range (figure 12, left). We stress here that the calculated lattice contribution was not subject to any general scaling and is a direct result of the theoretical model. Subtracting the LHC thus yields the residual HC depicted in figure 12 (right) bringing to light its rather rich structure.

3. Discussion

The purpose of the present work was to single out the residual heat capacity of CuNCN in order to eventually establish the amount of the degeneracy of its ground state. As usual (see, e.g. [9]), this requires a separation of the lattice contribution, which is not an easy task for CuNCN. The approach taken in this paper is based on the energy calculations of CuNCN performed with use of VASP. However, this has to be taken cautiously, because the software [12, 13] routinely employed to evaluate the phonon spectrum further used for estimating the LHC and ADP’s underestimates the DPS at low frequencies. In the case of CuNCN, this clearly manifests in the discrepancy between the calculated and measured ADP’s and the huge values of the (dis)similarity measure in figure 4 (lower right panel) at lower temperatures. We were able to explain

this discrepancy and to interpret the major part (up to 95% of the measured amount) of the HC of layered CuNCN analyzing the lattice contributions coming from various types of phonons: acoustic, intra- and intermolecular optic, and flexural ones occupying overlapping frequency ranges.

The flexural vibrations of the layers running parallel to the *ac* planes feature a large amplitude in the *b* direction partially explaining the observed anisotropy of the ADP’s (figure 4) whereas their population at lower temperatures, contrary to those predicted by the standard method, explains the observed temperature dependence of ADP’s. The reason, why ω_f calculated numerically remains finite (0.8 THz) instead of approaching zero when $k \rightarrow 0$, stems from the procedure [29] used in PHONOPY for calculation of the dynamical matrix. In it, the force constants are derived from the forces emerging when individual atoms are one by one shifted from their equilibrium positions by a small finite amount along each coordinate. It is, however, known [23] that in order to reproduce the collective character of flexural motion one needs the force constants for simultaneous displacements of several atoms. This has been recently stressed in the context of the flexural modes of graphene [30], where at least four atoms had to be displaced simultaneously to correctly reproduce this motion. This can be understood from the discretization point of view. Equation (3) coming from the elasticity theory and describing the flexural modes involve spatial partial derivatives of the fourth order. Its finite difference version requires the values of the sought function in at least five points (including one remaining at rest) to estimate the fourth derivative, which in the solid state context translates into a simultaneous shift of (at least) four atoms. Our assumption is that the frequencies of the flexural modes of the CuNCN layers are overestimated by the standard procedure because of lack of the many-particle shifts and thus the corresponding density of states has to be estimated separately, from independent experimental data, as we did. One may ask, how is it possible to reproduce the form of the flexural mode (figure 1), being in failure with its frequency. The answer is that the dynamical matrix available within the PHONOPY is a zero approximation to the exact one and its difference with the exact one is a perturbation. Thus, the squared frequencies of the normal modes are going to be affected by the said perturbation in the first order eventually bringing the 0.8 THz minimum to zero whereas the eigenvectors (the *forms* of the normal modes) will be affected only in the second order with respect to this perturbation. Thus, we conclude that the depicted motions are at least close enough to the correct ones. With this in mind, we notice in figure 1 that the NCN units indeed perform rotational (librational) motions in the *bc* planes. This is in a perfect agreement with our analysis of the ADPs refined from neutron diffraction patterns.

The residual HC, remaining after subtracting all lattice contributions, can be used to estimate the degeneracy of the (electronic) low-temperature phase of CuNCN. We established the quadratic course of the residual HC at the lowest available temperatures. This together with two other independent evidences (the absence of magnetic signal in the polarized neutron scattering [1] and the absence of coherent

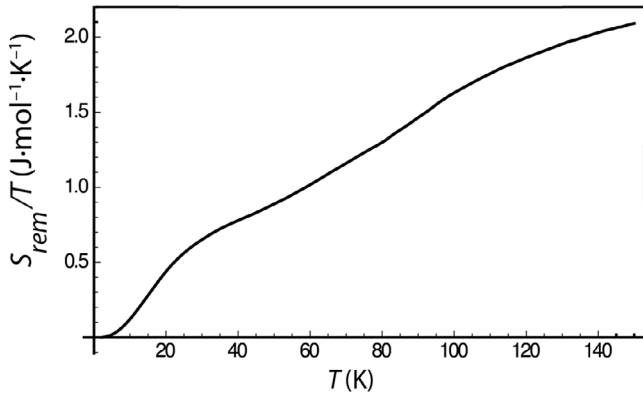


Figure 13. Spinon entropy of CuNCN as obtained by integrating the residual HC extracted from experimental data.

oscillations in the muon spin relaxation [3]) proves that the system lacks long-range magnetic order even at the lowest accessible temperatures which implies a spin-liquid state [31]. The quadratic dependence of the residual HC suggests also gapless and linearly dispersive 2D magnetic excitations like those observed in a spin-liquid phase of NiGa_2S_4 [9]. The result of numerical integration of the residual HC extracted from experimental data, which should reflect the spinon entropy contribution, is shown in figure 13.

The bump at *ca.* 20 K indicates some degeneracy of the electronic phase existing in this temperature range. Nevertheless, the amount of degeneration is rather modest since the entropy value is only slightly larger than $\frac{1}{10}R \ln 2$ in this temperature range. Moreover, even at the highest studied temperature this entropy contribution does not reach the paramagnetic value of $R \ln 2$. The remaining entropy is likely released at higher temperatures, since the magnetic exchange amounts to several hundred kelvin [3, 7], thus indicating that a highly correlated phase, tentatively similar to a spin-liquid, persist at least up to 150 K (the highest temperature accessed throughout the HC measurements). A part of the missing entropy could also be associated with the magnetism below the lower temperature limit of the HC experiment.

The observed features in the residual HC are attributable to the variations of the magnetic behavior of CuNCN [3] and accompanied by the structure manifestations [2, 6]. Specifically, the change of the magnetic susceptibility from the quasi-Pauli to quasi-Arrhenius one occurs at a temperature of *ca.* 90–100 K. This transition structurally manifests in an odd behavior of the *a* lattice parameter which starts to increase instead of decreasing with temperature below this temperature [2, 6]. We see a broad maximum in the residual HC at about the same temperature. At a lower temperature of *ca.* 35–40 K another reliably documented structure effect [6], namely, the reverse of the temperature course of the *c* lattice parameter takes place. Again, almost at this temperature we observe a peak in the residual HC.

Finally, the spinons should in principle manifest also in the INS data. The spin-liquid scenario [7] predicts two features. The first (temperature independent) at *ca.* 125 meV is, clearly, out of our experimental range. The second must manifest well below the transition between the gapless and gapped regime

(100 K—that is in the 1.5 K experiments—figure 7(d)) at *ca.* 14 meV (the number is determined from analysis of the magnetic susceptibility [7]). This second peak is, however, difficult to identify due to limited sensitivity of our INS experiment, so we currently cannot confirm or reject its presence.

The features in the residual HC can be put in correspondence with the transitions between the proposed spin-liquid (*alias*, resonating valence bond—RVB) states [7]. Indeed, the transition from the high-temperature quasi-one-dimensional RVB (*Q1D*-RVB) featuring Pauli paramagnetism to a transient two-dimensional RVB (*t2D*-RVB) phase accompanied by opening of a pseudogap in the quasiparticle spectrum, is expected to manifest itself in the HC, which may correspond to the broad maximum at higher temperature. The anomaly in the temperature behavior of the lattice parameter *c* at *ca.* 35–40 K [6] was attributed to a second RVB transition—this time from the *t2D*-RVB to the stable 2D-RVB (*s2D*-RVB)—presumably, the ground state phase [7, 32]. Both transitions are accompanied by corresponding temperature evolution of the RVB order parameters, thus they also must manifest in the residual HC of CuNCN as observed. The strong temperature dependence of the residual HC below 10 K represented by the orange line in figure 12 (right) can be as well caused by that of the RVB order parameters in the lowest temperature range, which is not known for the time being.

4. Conclusions

In the present paper, we successfully merged available data on the nuclear motions in the layered transition metal pseudo-chalcogenide CuNCN and were able to use this information for the analysis of its thermodynamic properties, namely, for extracting the residual heat capacity. The hypothesis of flexural vibrations of the CuNCN layers turned out to be very productive, since it helped to integrate the results of the elastic and inelastic neutron scattering experiments into the general picture by identifying the low-energy peak in the INS spectrum with the logarithmic singularity characteristic for the density of the flexural phonons (fDPS). Our analysis of the phonon calculations confirms the bending-like (flexural) motion of atoms in the mode coming from the DFT based procedure as the lowest optical one (figure 1). With use of the reconstructed phonon density of states, we were able to exhaustively describe the results of the neutron diffraction experiments with respect to the temperature dependence of the ADP. These latter as well stem from the various types of phonons and the puzzling *trends* (not *irregularities*), namely the linear temperature dependence of *only* Cu and N mean square displacements *only* in the *b* direction, observed in the measured ADPs after cleaning out the acoustic contribution, could be understood.

The LHC obtained from the DPS reconstructed from the neutron scattering data when subtracted from the measured HC reveals a rich structure of the residual HC with the features corresponding to those obtained in the magnetic and structural studies of CuNCN over the range of the temperatures. They are presumably attributable to the transitions between various

spin-liquid phases whose existence had been conjectured in this material.

Two major issues remain to be addressed: (i) the visible irregularities in the temperature course of the ADPs eventually also related with the RVB transitions occurring at approximately the same temperatures where our previous studies position them; (ii) the detailed temperature dependence of the residual HC so far has been interpreted only qualitatively. For a more detailed analysis one needs the exact temperature dependence of the RVB order parameters close to the phase transitions, which is not available at present.

5. Methods

5.1. Computational methods

Computations based on DFT were carried out within the framework of the projector augmented-wave (PAW) method [33] as implemented in the Vienna *ab initio* simulation package (VASP) [34, 35]. Plane wave basis sets with a kinetic energy up to 500 eV were used. Exchange and correlation were accounted for by the GGA parametrization of Perdew, Burke, and Ernzerhof [11]. BZ sampling on $17 \times 8 \times 5$ grids of reciprocal space points after the Monkhorst–Pack [36] scheme was chosen. The strongly correlated 3d electrons were considered by the GGA + *U* method [37] with an effective *U* of 4 eV. Also, the dispersion correction following the D2 method was applied [10]. The electronic structure was optimized until the energy difference between two iterative steps was below 10^{-8} eV per simulation cell; the structural optimization was carried out to a difference below 10^{-6} eV per simulation cell between two atomic configurations. The antiferromagnetic setup dubbed ‘AFM1’ (ferromagnetic in the *ab* plane alternating the direction of the momenta along the *c* direction every half period) produces the most stable crystal structure compared to other setups discussed previously [4], and also more stable than the non-magnetic case [1]. This was used as a basis for numerical estimates, though this magnetic setup cannot describe the complicated magnetic behavior of CuNCN [3], since it provides the most convenient starting point for the numerical analysis performed in this work.

Phonon properties were calculated using the program PHONOPY [12, 13] which is based on the small-displacement method [29]. $6 \times 3 \times 2$ super cells related to the unit cell in the orthorhombic setup were constructed and displacements of 0.01 Å were applied for the force calculations carried out with VASP. Total and atom-resolved densities of phonon states (DPS), ADP and the constant volume heat capacity C_V were computed on a $34 \times 17 \times 11$ mesh of reciprocal space points.

5.2. Experimental methods

5.2.1. Neutron diffraction. A detailed description of the neutron-powder diffraction experiments on the POWGEN diffractometer (at 17 K, Bank 2) used for determination of the

ADPs presented herein is given in [6]. The comparison of the experimental values [6] to the theoretical ones is carried out using the displacements along the main axis of the thermal ellipsoids, i.e. from the eigenvalues u_i of the U_{ij} matrices. Therefore, the dimensionless β_{ij} values refined from the experimental data were first, transformed to their U_{ij} representation with respect to the orthorhombic space group including a Gaussian error propagation. From those, the respective 3×3 eigenproblems were solved to yield the eigenvalues and eigenvectors while again the Gaussian error propagation was carried out for the experimental data.

5.2.2. Inelastic neutron scattering (INS). INS measurements were performed in the temperature range between 1.5 K and 130 K on the time-of-flight spectrometer FOCUS at SINQ, Paul Scherrer Institute, Switzerland, using incident neutron energies of 28 meV and 8 meV. To subtract the background and to correct for the detector efficiency the empty can and vanadium standard were measured.

5.2.3. Heat capacity. A high purity sample of CuNCN was measured in zero-field in two separate calorimeters. Above ~15 K the measurements were carried out in an adiabatic Nernst-type calorimeter (sample mass ~85 mg) and between 2 and 20 K a very small sample (~1 mg) was measured in a relaxation-type calorimeter (PPMS, Quantum Design).

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References

- [1] Xiang H, Liu X and Dronskowski R 2009 Theoretical reinvestigation of the electronic structure of CuNCN: the influence of packing on the magnetic properties *J. Phys. Chem. C* **113** 18891–6
- [2] Tchougréeff A L, Liu X, Müller P, van Beek W, Ruschewitz U and Dronskowski R 2012 Structural study of CuNCN and its theoretical implications: a case of a resonating-valence-bond state? *J. Phys. Chem. Lett.* **3** 3360–6
- [3] Zorko A, Jeglič P, Potočnik A, Arčon D, Balčytis A, Jagličić Z, Liu X, Tchougréeff A L and Dronskowski R 2011 Unconventional magnetism in a nitrogen-containing analog of cupric oxide *Phys. Rev. Lett.* **107** 047208
- [4] Liu X, Dronskowski R, Kremer R K, Ahrens M, Lee C and Whangbo M H 2008 Characterization of the magnetic and structural properties of copper carbodiimide, CuNCN, by neutron diffraction and first-principles evaluations of its spin exchange interactions *J. Phys. Chem. C* **112** 11013–7
- [5] Liu X, Wankeu M A, Lueken H and Dronskowski R 2005 A novel method for synthesizing crystalline copper carbodiimide, CuNCN. Structure determination by x-ray rietveld refinement *Z. Naturforsch. B* **60** 593
- [6] Jacobs P, Houben A, Tchougréeff A L and Dronskowski R 2013 High-resolution neutron diffraction study of CuNCN: new evidence of structure anomalies at low temperature *J. Chem. Phys.* **139** 224707
- [7] Tchougréeff A L and Dronskowski R 2013 Low-temperature structure anomalies in CuNCN. Manifestations of RVB phase transitions? *J. Phys.: Condens. Matter* **25** 435602
- [8] Tchougréeff A L and Dronskowski R 2015 Spin-liquid states in a copper-based material: the mysterious quantum phase CuNCN *Quantum Matter* **4** 63–8
- [9] Nakatsuji S, Nambu Y, Tonomura H, Sakai O, Jonas S, Broholm C, Tsunetsugu H, Qiu Y and Maeno Y 2005 Spin disorder on a triangular lattice *Science* **309** 1697–700
- [10] Grimme S 2006 Semiempirical GGA-type density functional constructed with a long-range dispersion correction *J. Comput. Chem.* **27** 1787–99
- [11] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple *Phys. Rev. Lett.* **77** 3865–8
- [12] Togo A, Oba F and Tanaka I 2008 First-principles calculations of the ferroelastic transition between rutile-type and CaCl₂-type SiO₂ at high pressures *Phys. Rev. B* **78** 134106
- [13] Togo A and Tanaka I 2015 First principles phonon calculations in materials science *Scr. Mater.* **108** 1–5
- [14] Whitten A E and Spackman M A 2006 Anisotropic displacement parameters for H atoms using an ONIOM approach *Acta Crystallogr. B* **62** 875–88
- [15] Deringer V L, Stoffel R P, Togo A, Eck B, Meven M and Dronskowski R 2014 *Ab initio* ORTEP drawings: a case study of N-based molecular crystals with different chemical nature *CrystEngComm* **16** 10907–15
- [16] Willis B T M and Pryor A W 1975 *Thermal Vibrations in Crystallography* (Cambridge: Cambridge University Press)
- [17] Mesota J, Janssen S, Holitzner L and Hempelmann R 1996 Focus: Project of a space and time focussing time-of-flight spectrometer for cold neutrons at the spallation source SINQ of the Paul Scherrer Institute *J. Neutron Res.* **3** 293–310
- [18] Paul Scherrer Institut, FOCUS Team, FOCUS Characteristics www.psi.ch/sinq/focus/parameters
- [19] Paul Scherrer Institut, FOCUS Team, FOCUS Manuals & Guides www.psi.ch/sinq/focus/manuals
- [20] Böttger H 1983 *Principles of the Theory of Lattice Dynamics* (Mostbach: Physik Verlag)
- [21] Maradudin A A, Montroll E W E W and Weiss G H G H 1963 *Theory of Lattice Dynamics in the Harmonic Approximation* (New York: Academic)
- [22] Landau L D, Pitaevskii L P and Lifshitz E M I 1980 *Statistical Physics* (Oxford: Heinemann)
- [23] Косевич А М 1972 *Основы Механики Кристаллической Решетки* (Moscow: Наука)
- [24] Лифшиц И М 1952 О тепловых свойствах цепных и слоистых структур при низких температурах *Журнал экспериментальной и теоретической физики* **22** 475
- [25] Тарасов В В 1945 К теории низкотемпературной теплоёмкости линейных макромолекул *Доклады Академии наук СССР* **46** 22
- [26] Тарасов В В 1950 Теория теплоёмкости цепных и слоистых структур *Журнал физической химии* **24** 111
- [27] Landau L D and Lifshitz E M 1970 *Theory of Elasticity* (Oxford: Pergamon)
- [28] Serrano J, Manjón F J, Romero A H, Ivanov A, Cardona M, Lauck R, Bosak A and Krisch M 2010 Phonon dispersion relations of zinc oxide: Inelastic neutron scattering and *ab initio* calculations *Phys. Rev. B* **81** 174304
- [29] Parlinski K, Li Z Q and Kawazoe Y 1997 First-principles determination of the soft mode in cubic ZrO₂ *Phys. Rev. Lett.* **78** 4063–6
- [30] Jiang J-W, Wang B-S, Wang J-S and Park H S 2015 A review on the flexural mode of graphene: lattice dynamics, thermal conduction, thermal expansion, elasticity and nanomechanical resonance *J. Phys.: Condens. Matter* **27** 083001
- [31] Balents L 2010 Spin liquids in frustrated magnets *Nature* **464** 199
- [32] Tchougréeff A L and Dronskowski R 2014 Mean-field RVB ground states of lattice models of CuNCN *Low Temp. Phys.* **40** 73–83
- [33] Blöchl P E 1994 Projector augmented-wave method *Phys. Rev. B* **50** 17953–79
- [34] Kresse G and Furthmüller J 1996 Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set *Phys. Rev. B* **54** 11169–86
- [35] Kresse G and Joubert D 1999 From ultrasoft pseudopotentials to the projector augmented-wave method *Phys. Rev. B* **59** 1758–75
- [36] Monkhorst H J and Pack J D 1976 Special points for Brillouin-zone integrations *Phys. Rev. B* **13** 5188–92
- [37] Dudarev S L, Botton G A, Savrasov S Y, Humphreys C J and Sutton A P 1998 Electron-energy-loss spectra and the structural stability of nickel oxide: an LSDA + *U* study *Phys. Rev. B* **57** 1505–9