Supplemental information

Atypically small temperature-dependence of the direct band gap in the metastable semiconductor copper nitride Cu_3N

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Figure 1: Temperature-dependent x-ray diffraction of Cu₃N. Mo and Cu anodes used respectively between 100 to 280 K and 4.2 through 100 K. Temperature dependent background fitted with splines and subtracted. Reflection possibly associated with Cu near 20° 2θ Mo $K\alpha$ (labeled 1). Preferential (m00) orientation and beryllium lines (labeled 2) seen at (49 through 52° 2θ) at 4.2 K.

1. X-ray diffraction patterns

For the XRD work with Mo $K\alpha$, several micrograms of Cu₃N crystallites were removed (via scalpel) from the film and fixed to the staging fiber with high vacuum grease (Dow Corning). With the sample temperature set by a nitrogen Cryojet (Oxford Instruments), phi scans ($0 \le \phi < 360^{\circ}$) were collected with a sample-detector distance of 120 mm, dark exposures of 120 s and 1x1 pixel binning; the resultant 2D images were integrated into $6 < 2\theta \le 57^{\circ}$ powder patterns by *CrysAlis Pro* 38.41. Before investigating Cu₃N with this instrument, the vacuum grease was scanned at 100 and 200 K to determine whether this adhesive contributed additional reflections. Crystallinity was found to develop in the grease at 200 K; however, reflections were avoided by quenching the grease below this temperature. The work with Cu $K\alpha$ covered $20 \le 2\theta < 71.5^{\circ}$ and studied the film as-deposited with a 2 mm entrance slit and a closed-cycle helium cryostat (Institut Laue-Langevin) with Joule-Thomson jet and beryllium windows. After an initial broad scan of 2 min per 0.035^{\circ} 2\theta step at 4.2 K, a series of narrow scans targeted only the most significant reflections at higher resolution to achieve satisfactory signal-to-noise with the point detector, given the instrument time available.

2. Structural investigations

To evaluate potential distortions or structural phase transitions (away from the well-known Pm3m anti-ReO₃ structure) which may develop as a function of time or temperature, the Cu₃N structure was treated as unknown and the 100 K pattern was indexed after fitting the background with a 13-coefficient Chebyschev polynomial in *GSAS-II*;¹ three solutions with minimal volume and convincing M20 figures-of-merit² were found as detailed below

Space grp.	M20	Lattice param. (Å)	Vol. (Å ³)
Pm3m	65.3	3.81657	55.59
P4/mmm	132.7	3.81860, 3.80607	55.50
Pmmm	367.2	3.803 07, 3.818 39, 3.814 13	55.39

The M20 statistic improves, perhaps expectedly, with increased parameter freedom. The patterns generated by the Pm3m and P4/mmm structures are sufficiently close to cubic Pm3m that a favored lattice is not discernible by eye. Rietveld refinement³ of structures in the P4/mmm and Pmmm space groups in *FullProf 2k*⁴ (v5.70) failed to find preferred solutions away from Pm3m. For example, P4/mmm was tried with N at (0,0,0) and Cu in the Wyckoff (*b*, *f*) or (*d*, *f*) positions, similar to Pm3m Cu₃N respectively either compressed along the *c*-axis or with one Cu displaced to the body-center position. Each attempt showed deteriorating R_{wp} and χ^2 statistics: supporting the Pm3m structure.

Rietveld refinement was initially preferred over extrapolation methods for structural evaluation: as full-pattern approaches exploit greater information to select the most appropriate systematic corrections.⁵ Perhaps expectedly (due to the borosilicate substrate), the Cu $K\alpha$ patterns showed significant (m00) orientations, which were not fitted acceptably using the models in *FullProf 2k*. The Rietveld fit to the 4.2 K pattern, the dotted line in Fig. 3a in the article (offset vertically for clarity), shows significant discrepancies in the (100) and (111) reflection amplitudes. The Pawley-like code utilized the Levenberg–Marquardt non-linear least-squares algorithm and composed the pattern from a single pseudo-Voigt lineshape with conventional { U, V, W, η, X } linewidth parameters,⁶ while incorporating corrections for sample displacement and zero error. Prior to each fit, the continuous x-ray background, which evolved somewhat as a function of temperature, was fitted with splines and subtracted. All spectra where fitted using the Pawley-like code to a cubic lattice with good statistics, mean reduced χ^2 of 1.2(1), mean degrees of freedom 3060 (Mo $K\alpha$), 883 (Cu $K\alpha$).

To evaluate the thermal expansion, a model is first fitted to the set of lattice parameters; this approach gives resilience to statistical extrema in individual lattice parameters and allows estimation of the thermal expansion away from the experimental datapoints. Here a Debye–Einstein–Grüneisen model is used, loosely based on the model of Sayetat et al.⁷ Aside from being a slightly less arbitrary treatment of thermal expansion (in comparison to a polynomial), this quasi-harmonic model estimates the Debye temperature, heat capacity, zero Kelvin lattice parameter, and an average Grüneisen pa-

rameter. The approach is 'quasi-harmonic' as no thermal expansion would be seen with the Debye model alone, i.e. with only harmonic vibrations. Instead, the anharmonicity of the lattice vibrations is approximated by combining the Debye and Einstein models of the lattice heat capacity with the semiempirical Grüneisen relation, which relates a material's vibrational modes to its volume. We start with the Grüneisen relation between the thermal (volume) expansion coefficient α_V and the isochoric heat capacity C_V ,

$$\alpha_V = \gamma \, C_V K / V \tag{1}$$

where K, V and γ are respectively the isothermal compressibility, the crystal volume and the average Grüneisen parameter. The heat capacity is modeled as the sum of the Debye and Einstein heat capacities (characterized by the temperatures θ_D and θ_E), with the Einstein term weighted by a factor (r - 1), with r the number of atoms in the crystal basis.⁸ Multiplying (1) by volume V and integrating with respect to temperature gives a system in the parameters V(0), γ , K, θ_D and θ_E .

$$V(T) = V(0) + \gamma K \int_0^T C_V(\theta_D, \theta_E) \, \mathrm{d}T'$$
⁽²⁾

In the right-hand side of (2) the Grüneisen parameter γ , isothermal compressibility K, zero Kelvin lattice parameter [or equivalently the volume V(0)], and the Debye and Einstein temperatures θ_D and θ_E are then fitted by least-squares regression to the volumes V(T) associated with the lattice parameters resulting from the Pawley analysis. The thermal expansion in Cu₃N as determined by (2), along with the thermal (linear) expansion coefficient as given by (1) and the relation between the linear α_L and volume α_V expansion coefficients ($\alpha_V = 3 \alpha_L$), are plotted in Figure 3b in the main article.

Our implementation differed somewhat from that of Sayetat et al.,⁷ who fitted the product of the isothermal compressibility and the Grüneisen parameter as a single parameter; instead, the Cu₃N bulk modulus *B* (the inverse of the compressibility, B = 1/K) was set to a predicted ^{9,10,11,12} (and typical) value of 110 GPa, and the Grüneisen parameter was solved for directly. Various limitations of the Sayetat et al. approach are discussed in the original paper; while the fit statistics for such a model are acceptable without an Einstein heat capacity term, the computed Debye temperature of 930(230) K is somewhat larger than the mean (and standard deviation) values 390(50) K predicted ^{10,13,14} for Cu₃N. The Debye model is essentially conceived for the acoustic phonon regime, i.e. for rather low temperatures or for monatomic crystals with one atom per unit cell. While the Debye heat capacity should be an accurate model ¹⁵ for temperatures well below $0.1 \theta_D$, most of the points in main article Fig. 3b lie above this limit even with an overestimated Debye temperature. In Cu₃N, with four atoms per unit cell, optical modes may contribute significantly at medium temperatures, as perhaps supported by the anisotropic thermal displacement parameters determined in Rietveld refinements (discussed shortly). This led to the introduction of the Einstein heat capacity in (2), leading to a lattice heat capacity written in Debye and Einstein terms, $C_V(\theta_D, \theta_E)$. As parameter freedom with separate Einstein θ_E and

Debye θ_D temperatures led to results which were not physically acceptable, the Einstein temperature was set to be 1.5 times the Debye temperature: a reasonable magnitude seen in semiconductor phonon dispersion relations, e.g. see Yu et al.¹⁶ or main article Fig. 4(b).

While the lattice parameters are determined most reliably by the above Pawley analysis, a Rietveld refinement of the Mo $K\alpha$ patterns (for which preferential orientation was less of a concern) offers potential insights. Such a refinement in *FullProf 2k* determined lattice parameters in agreement with those of the Pawley analysis, with fractional differences well below 5×10^{-5} . Refinement of the 200 K Mo $K\alpha$ pattern was complicated by the proximity of grease reflections: excluding the most significant Cu₃N (100) reflection and the leading grease reflections gave a 200 K lattice parameter of 3.8180(9) Å, possibly perturbed by residual grease contributions and further supporting the Pawley approach.

Thermal displacement parameters resulting from the Rietveld analysis indicated respective isotropic and anisotropic displacements for the nitrogen and copper atoms, with copper displacements perpendicular to the N-Cu-N axis growing in magnitude above 150 K. Small improvements in the fit were seen with phase admixtures of Cu_3N with either Cu_4N or Cu_3N_2 ; however, these were not sufficient to discriminate a favored composition, the improved statistics likely resulting from increased parameter freedom in the fit.

In all patterns, a small intensity excess is found amid the Cu₃N (111) and (200) reflections (at 20.15° $2\theta \text{ Mo } K\alpha \text{ or } 44.5^{\circ} 2\theta \text{ Cu } K\alpha$). This feature (see Fig 3a in the main article) does not match the reflections of Cu, Cu₂O, CuO or H₂O, but is in the vicinity of the (111) reflection of metallic copper (at 19.6° 2θ Mo $K\alpha$ or 43.3° 2θ Cu $K\alpha$), yet is perhaps too distant for a copper association to be held with much confidence. While copper (111) reflections are frequently seen in diffraction patterns from Cu₃N,^{17,18,19} no such feature was reported in a survey of over thirty Cu₃N papers reporting x-ray diffraction. While the feature could result from strained copper nano-crystallites under an effective 3% lattice parameter reduction, such contractions would differ to thermal expansion and shape effects seen previously in copper nano-crystallites.²⁰ Explorative structural work with simulated XRD patterns of Cu₃N supercells, e.g. employing FCC sub-lattices offset by half a lattice constant and comprising Cu, N, O₂, N₂ or Ar atoms, failed to develop evidence for such a reflection, but tentatively suggested that the feature could be related to a proposed oxygen-terminated surface layer.^{21,22,23} Further work including XRD with improved signal-to-noise is necessary to further assess the feature.

Further details of our x-ray diffraction investigations are discussed in reference 24.



Figure 2: Temperature-dependent FTIR reflection/transmission spectra, pre and post-processing



Figure 3: Temperature dependence of Cu_3N band gap and sample fitted FTIR absorption onsets. Shows selected fitted absorption edges and residuals for the 4.2 K trace. The inset shows a feature in the reflectivity and transmissivity at 78 meV associated with the three-fold degenerate Γ_{15} IR-active phonon mode.

3. Processing of optical spectra

The 0.37 to 3.1 eV spectral range was chosen primarily to evaluate any evolution in the fundamental absorption onset, with prior theoretical and experimental reports suggesting indirect and direct absorption onsets between 0.6 through 2.2 eV, and initial examinations which showed a long transmission edge starting below 1 eV and spanning some 0.8 eV. Two instrumental configurations were necessary to capture the entire absorption edge from baseline, each with different detectors; a silicon detector was used above 1.1 eV, while a liquid-nitrogen cooled mercury cadmium telluride (MCT) detector was selected for lower photon energies.

The FTIR reflectivity and transmissivity spectra as determined by the silicon and MCT detectors were first joined in the overlapping spectral region near 1.15 eV. Various systematic contributions were carefully considered in this procedure as discussed in reference 24. As a result of this work, the asmeasured reflection and transmission spectra (see Figure 2, top) were corrected to give spectra which were suitable for conversion to absorption spectra (see Figure 2, bottom), as discussed in Section 4.

To estimate uncertainties in the correction process, the corrected and uncorrected spectra were each used in subsequent band gap calculations: with the differences between parameters used to evaluate the error bars in main article Figure 2b; the 175 K error bar vanished after this process so was set to the next smallest magnitude.

The ellipsometric model specified in *CompleteEASE* v5.08 comprised a film upon a 1.1 mm glass substrate, and the fit employed corrections for depolarization, internal reflections, angular discrepancies and sample roughness (20 Å fitted). The Cu₃N refractive index was modeled as a B-spline with a 50 meV interval, giving 89 points across the data range. Whilst the ellipsometric model suggested a 1000(4) nm film thickness (with mean-squared error of 11.8 for the fit), the claimed uncertainty was considered to significantly overestimate the precision of the thickness determination. The magnitude of the ellipsometric mean-squared error perhaps suggests possible further complications in the ellipsometric fit. Given reports of Cu oxide layers protecting the Cu₃N film surface, nanometre-thick layers of these have been used in prior ellipsometric work:²³ yet no significant improvement was found here for models incorporating such layers.

The fitting of direct transitions to the absorption onset, as described by Equation (4) in the main article, proceeded between 492 and 1798 meV with a baseline evaluated for each spectrum using the average absorption coefficient in the transparent region between 492 and 723 meV. Constraints were set to ensure the solution converged to physically reasonable values. The direct gap and Urbach energy $E_{\rm U}$ where constrained to lie respectively between 1.4 and 1.8 eV and below 0.5 eV, while the absorption strength was constrained to be positive.

4. Absorption correction via a self-consistent intrinsic reflectivity

Algebraic relations for absorption spectra $\alpha(\hbar\omega)$ are typically written in the intrinsic reflectivity $R_0(\hbar\omega)$ which is the reflectivity seen by light at a planar boundary between the vacuum and a semi-infinite expanse of the material under investigation. Consider the reflectivity R_{tot} and transmissivity T_{tot} of a single-layer of incoherent material of thickness d with parallel faces²⁴

$$R_{\text{tot}} = R_0 \left[1 + \frac{(1 - R_0)^2 e^{-2\alpha d}}{1 - R_0^2 e^{-2\alpha d}} \right] \quad \text{and} \quad T_{\text{tot}} = \frac{(1 - R_0)^2 e^{-\alpha d}}{1 - R_0^2 e^{-2\alpha d}} \tag{3}$$

Experiments do not directly measure the reflectivity $R_0(\hbar\omega)$; instead, the total reflectivity R_{tot} is seen, which includes contributions from internal reflections at each face. Typically, workers assume strong absorption so that $R_0 \approx R_{tot}$, yet this can lead to errors²⁴: particularly for absorption strengths below 10^4 cm^{-1} . In incoherent media (without interference oscillations), R_{tot} should always satisfy $R_{tot} \geq R_0$, due to contributions from internal reflections. When R_{tot} differs significantly from R_0 , equations (3) are not satisfied under the assumption $R_0 \approx R_{tot}$. Our approach then is to solve (3) self-consistently, starting from the guess $R_0 = R_{tot}$. Some rearrangement of (3) gives

$$\frac{1}{T_{\text{tot}}} \left(\frac{R_{\text{tot}}}{R_0} - 1\right) - \exp\left(-\alpha d\right) = 0 \tag{4}$$

While the transmissivity (3) is quadratic in the absorption coefficient, giving

$$\alpha = -\frac{1}{d} \log \left[\frac{-(1-R_0)^2 + \sqrt{(1-R_0)^4 + 4T_{\text{tot}}^2 R_0^2}}{2T_{\text{tot}} R_0^2} \right]$$
(5)

With a known film thickness d, equations (4) and (5) are easily solved for the absorption coefficient $\alpha(\hbar\omega)$ and intrinsic reflectivity $R_0(\hbar\omega)$ using a non-linear least squares method (such as the Levenberg–Marquardt implementations in Python or MATLAB: see below). In each iteration, our guess for R_0 is used first in (5) and the resulting α creates a residual in the left-hand side of (4) which is the minimized quantity.

```
function Main() % TODO: set sFileNameWavenumRT, iNumHeaderRows, iColumnR, iColumnT, iColumnWavenum, fThicknessM
global mxExprWavenumRT iThisRow fThicknessM fAlphaPerM;
mxExprWavenumRT=dlmread(sFileNameWavenumRT,'\t',iNumHeaderRows,0);
mxAbsorptionPerMetre=[];
for iThisRow=1:size(mxExprWavenumRT,1)
    fIntrinsicR=fsolve(@FitIntrinsicReflectivity,fIntrinsicR);
    mxAbsorptionPerMetre=[mxAbsorptionPerMetre; mxExprWavenumRT(iThisRow, iColumnWavenum), fAlphaPerM];
end % finished: now save [mxAbsorptionPerMetre]
end
function y=FitIntrinsicReflectivity(fIntrinsicR) % TODO: implement SolveAbsorption()
    global mxExprWavenumRT iThisRow fThicknessM fAlphaPerM;
    fAlphaPerM=SolveAbsorption(fIntrinsicR,mxExprWavenumRT(iThisRow,iColumnT),fThicknessM);
    y=(mxExprWavenumRT(iThisRow,iColumnR)/fIntrinsicR-1)/mxExprWavenumRT(iThisRow,iColumnT)-exp(-fAlphaPerM*fThicknessM);
end
```

The correction gives impressive results for incoherent single layers²⁴; with the assumption of a specific substrate refractive index, the method may be extended for double-layers.

5. Direct absorption edges and the Urbach tail

Consider the absorption coefficient $\alpha(\hbar\omega)$ at a direct onset²⁴

$$\alpha(\hbar\omega) = \frac{A}{\hbar\omega} \cdot \sqrt{\hbar\omega - E_{\rm g}} \tag{6}$$

where $E_{\rm g}$ and A are respectively the band gap and a material constant. Without high-quality material, absorption onsets in the form of (6) are rarely seen. Instead, static and dynamic effects (i.e. disorder due to impurities, defects and phonons^{25,26}) lead to an exponentially decaying Urbach tail²⁷ which joins the direct absorption edge smoothly and continuously at some energy $E_{\rm g} + E_{\rm U}$. The absorption due to the Urbach tail is then

$$\alpha_{\rm U}(\hbar\omega) = B \exp\left(\gamma \left\{\hbar\omega - E_{\rm g} - E_{\rm U}\right\}\right) \tag{7}$$



Figure 4: Urbach tails and direct onsets. The tails shown join the direct edge at up to 16 meV above E_g .

where *B* and γ are additional material constants. To attach the Urbach tail smoothly the gradients of (6) and (7) are needed with respect to photon energy. Differentiating gives

$$\frac{\mathrm{d}\alpha}{\mathrm{d}(\hbar\omega)} = -\frac{A}{(\hbar\omega)^2} \sqrt{\hbar\omega - Eg} + \frac{A}{2\hbar\omega} \frac{1}{\sqrt{\hbar\omega - Eg}} \quad \text{and} \quad \frac{\mathrm{d}\alpha_{\mathrm{U}}}{\mathrm{d}(\hbar\omega)} = \gamma \,\alpha_{\mathrm{U}} \tag{8}$$

Equating (6) and (7) for continuity at the intersection energy $\hbar\omega=E_{\rm g}+E_{\rm U}$ gives

$$B = \frac{A}{E_{\rm g} + E_{\rm U}} \sqrt{E_{\rm U}} \tag{9}$$

Equating the equations (8) for smoothness at $\hbar \omega = E_g + E_U$ and using (9) gives

$$\gamma A \sqrt{E_{\rm U}} = -\frac{A}{E_{\rm g} + E_{\rm U}} \sqrt{E_{\rm U}} + \frac{A}{2} \frac{1}{\sqrt{E_{\rm U}}} \longrightarrow \qquad \gamma = \frac{1}{2E_{\rm U}} - \frac{1}{E_{\rm g} + E_{\rm U}} \tag{10}$$

Thus the tail may be written in a new form, with only one free parameter $E_{\rm U}$ (see Figure 4).

$$\alpha_{\rm U}(\hbar\omega) = \frac{A\sqrt{E_{\rm U}}}{E_{\rm g} + E_{\rm U}} \exp\left\{\frac{\left(\hbar\omega - E_{\rm g} - E_{\rm U}\right)\left(E_{\rm g} - E_{\rm U}\right)}{2E_{\rm U}\left(E_{\rm g} + E_{\rm U}\right)}\right\} \quad \text{for} \quad \hbar\omega \le \left(E_{\rm g} + E_{\rm U}\right) \tag{11}$$

Various relations are seen in the literature, with up to three parameters^{28,29,30}. Typically $\alpha(\hbar\omega) = A \exp(B\{\hbar\omega - C\})$, where *C* is often (but not always³¹) the zero Kelvin band gap³², while *B* sometimes has a temperature dependence^{28,29}, $B = D/k_{\rm B}T$ (as in Urbach's original work²⁷). Tails typically broaden with increasing temperature³² (see Tropf et al.²⁸).

Appendix: band gap temperature dependence

The temperature-dependence of a semiconductor's band gap results from contributions from thermal expansion of the lattice, as well as effects from the electron–phonon interaction, written generally as³³

$$\left(\frac{\mathrm{d}E_{\mathrm{g}}}{\mathrm{d}T}\right)_{P} = \left(\frac{\partial E_{\mathrm{g}}}{\partial T}\right)_{TE} + \left(\frac{\partial E_{\mathrm{g}}}{\partial T}\right)_{EP} \tag{12}$$

where on the left-hand side $(dE_g/dT)_P$ denotes the isobaric band gap change as seen for example in temperature-dependent optical measurements, while the terms on the right-hand side require further explanation. The thermal expansion term may be written as³³

$$\left(\frac{\partial E_{g}}{\partial T}\right)_{TE} = \left(\frac{\partial E_{g}}{\partial V}\right)_{P} \left(\frac{\partial V}{\partial T}\right)_{P}$$
(13)

where $(dV/dT)_P$ is the isobaric thermal (volume) expansion, as determined for example in x-ray diffraction. Alternatively, the chain rule allows the thermal expansion (13) to be formulated for pressure-dependent work

$$\left(\frac{\partial E_{g}}{\partial T}\right)_{TE} = \left(\frac{\partial E_{g}}{\partial p}\right)_{T} \left(\frac{\partial p}{\partial V}\right)_{T} \left(\frac{\partial V}{\partial T}\right)_{P}$$
(14)

which is often written in terms of the bulk modulus B and thermal (volume) expansion coefficient α_V

$$\left(\frac{\partial E_{g}}{\partial T}\right)_{TE} = -\alpha_{V}B\left(\frac{\partial E_{g}}{\partial p}\right)_{T}$$
(15)

The second term in (12) arises from the treatment of the electron–phonon interaction in perturbation theory, which creates further contributions (so-called renormalizations) to the band gap temperature dependence^{33,34}

$$\left(\frac{\partial E_{g}}{\partial T}\right)_{EP} = \frac{\partial}{\partial T} \sum_{b,\mathbf{q}}^{B.Z.} \frac{\partial E_{g}}{\partial n_{b,\mathbf{q}}} \left(n_{b,\mathbf{q}} + \frac{1}{2}\right) \tag{16}$$

where the sum is taken over the entire Brillouin zone and $n_{b,q}$ is the Bose–Einstein factor for the phonon mode with energy $E_{b,q}$ and wavevector **q** in branch *b*

$$n_{b,\mathbf{q}} = \left[\exp\left(\frac{E_{b,\mathbf{q}}}{k_{\mathrm{B}}T}\right) - 1 \right]^{-1} \tag{17}$$

The term $\partial E_{\rm g}/\partial n_{b,{\bf q}}$ in equation (16) includes contributions from two dominant electron–phonon processes. Phonon emission followed by successive absorption (and vice versa) are considered in the self-energy (SE or Fan³⁵) process; while the Debye–Waller (DW) diagram treats the simultaneous emission and absorption of two phonons.³⁶ These interactions are considered in perturbation theory³⁷ to respectively second and first orders. Each of the DW and SE terms is second degree in the root-mean square atomic displacements^{38,39} $\sqrt{\langle x^2 \rangle}$, which leads to a proportionality to the Bose–Einstein factor $n_{b,{\bf q}}$, which is exploited in Bose–Einstein fits to the band gap temperature-dependence.

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