

Phase transition and negative thermal expansion in copper pyrophosphate $\text{Cu}_2\text{P}_2\text{O}_7$ studied by neutron total scattering and the reverse Monte Carlo method

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The phase transition in copper pyrophosphate, $\text{Cu}_2\text{P}_2\text{O}_7$, has been studied using neutron total scattering and the reverse Monte Carlo method. The results show the growth of disorder of the orientations of the PO_4 tetrahedra and of the positions of the copper atoms along the long O–Cu–O linkage in the CuO_6 octahedra distorted by the Jahn–Teller effect. These two types of disorder are coupled, and neither show the preference for distinct sites of partial atomic occupancy in the high-temperature phase. The origin of the negative thermal expansion identified in $\text{Cu}_2\text{P}_2\text{O}_7$ can be understood as arising from the ordering of the copper atoms leading to one Cu–O bond expanding more than the other contracts.

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I. INTRODUCTION

Copper pyrophosphate, $\text{Cu}_2\text{P}_2\text{O}_7$, and a number of isomorphous crystals have attracted a lot of interest [1–12] because they show a large negative volumetric thermal expansion [13–18], and at the same time they are easy and inexpensive to synthesize. Furthermore, they are robust for potential high-performance applications. While initially the NTE in $\text{Cu}_2\text{P}_2\text{O}_7$ was suggested [19] as arising from a phonon mechanism known as the ‘tension effect’ [13,15], it has now been clearly demonstrated that its NTE originates from the structural phase transition [20]. Some issues around this contention are discussed in more detail in the Appendix.

The phase transition in $\text{Cu}_2\text{P}_2\text{O}_7$ is between two phases that both have monoclinic symmetry [21,22]. Their crystal structures are shown in Fig. 1, drawn using the crystal structure data refined here (as discussed in Sec. II), and reported in Table I and in the Supplemental Material (SM) [23]. The crystal structure of the high-temperature β phase has space group $C2/m$, with two formula units in the conventional unit

cell [22]. The parent structure for $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ is the mineral thortveitite, $\text{Sn}_2\text{Si}_2\text{O}_7$ [25]. It has layers of edge sharing octahedra parallel to the (001) plane, which are connected by pairs of tetrahedra, which in $\text{Cu}_2\text{P}_2\text{O}_7$ are the pyrophosphate, P_2O_7 , units. The nonbridging oxygens form the vertices of the octahedra. The CuO_6 octahedra in $\text{Cu}_2\text{P}_2\text{O}_7$ are significantly deformed by a Jahn–Teller distortion, leading to four shorter Cu–O distances, of around 1.94 Å, which form a square coordination, and two longer distances of around 2.60 Å in the two directions normal to the square. The long and short bonds are differentiated in the drawings of the crystal structures in Fig. 1.

The refinement of the crystal structure of the high-temperature β phase indicated the existence of considerable motion of the bridging oxygen atom within each pyrophosphate unit [22], thereby suggesting the presence of dynamic structural disorder, which would be associated with orientational disorder of the PO_4 tetrahedra. In some ways this might be reminiscent of the orientational disorder of SiO_4 tetrahedra in the high-temperature β phase of cristobalite, SiO_2 [26,27], not least because a structure refinement without the disorder in both cases would suggest linear P–O–P and Si–O–Si bond linkages. The refinement of the crystal structure of $\beta\text{-Cu}_2\text{P}_2\text{O}_7$ modeled the large-amplitude motions of the bridging oxygen by using two sites to describe the positions of this atom, with 50% occupancy of each [22]. One might also argue that the copper atom could have disorder along the two long Cu–O bonds, but this was not considered in the refinements of the crystal structure.

The transition to the low-temperature α phase, which has space group $C2/c$ with four formula units in the conventional

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TABLE I. Crystal structures of the two phases of $\text{Cu}_2\text{P}_2\text{O}_7$ obtained from our own Rietveld refinement using the data described in Sec. II. a, b, c, β are the lattice parameters, x, y, z are the fractional coordinates, and U_{iso} is the isotropic atomic displacement parameter. Standard deviations for all refined quantities are given in brackets for the last significant figures. For Cu1 and O1 sites in the β phase, the U_{iso} values are averaged from the anisotropic values, and hence are indicative values and standard deviations are not given. Crystal structure data for all temperatures are given in the Supplemental Material [23].

	a (Å)	b (Å)	c (Å)	β (deg)
α phase (10 K)	6.9251(8)	8.1147(2)	9.184(1)	109.804(3)
β phase (600 K)	6.864(2)	8.1323(3)	4.5822(8)	109.325(3)
α phase (10 K)				
atomic site	x	y	z	$1000 \times U_{\text{iso}}$ (Å ²)
Cu	−0.0223(2)	0.3133(2)	0.5093(2)	2.3(2)
P	0.1963(2)	0.0079(3)	0.2076(2)	2.8(3)
O1	0	0.0561(3)	1/4	8.6(5)
O2	0.3741(2)	0.0013(3)	0.3638(2)	5.1(3)
O3	0.2224(3)	0.1565(2)	0.1122(2)	4.7(4)
O4	0.1701(3)	−0.1474(2)	0.1202(2)	10.3(5)
β phase (600 K)				
atomic site	x	y	z	$1000 \times U_{\text{iso}}$ (Å ²)
Cu	0	0.31296(19)	0	18.6
P	0.30155(26)	1/2	0.5840(5)	8.1(3)
O1	1/2	1/2	1/2	69.7
O2	0.12664(29)	1/2	0.2749(4)	13.4(4)
O3	0.20010(25)	0.15355(17)	0.2281(3)	24.9(3)

unit cell [21,28], involves doubling of the c lattice parameter, giving a change in the translational symmetry. The phase transition involves symmetry-breaking tiltings of the two PO_4 tetrahedra in the pyrophosphate units, which might be seen as ordering of the position of the bridging oxygen. It also

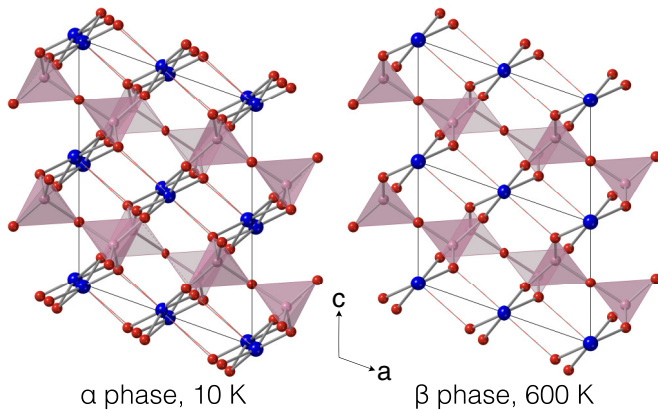


FIG. 1. Crystal structures of the two phases of $\text{Cu}_2\text{P}_2\text{O}_7$, originally reported by Robertson [21,22] but drawn using the atomic structure refined here and reported in Table I as well as in the Supplemental Material [23]. The images are viewed down the [010] axes, and aligned with the [001] axes in the vertical direction in the plane of the diagram. The c axis has been doubled in the picture of the β phase (right) to aid comparison with that of the α phase (left). The copper, phosphorous, and oxygen atoms are shown as blue, pink, and red colors respectively, with the PO_4 tetrahedra shown with translucency. The four shorter Cu–O bonds are shown as the thicker connecting cylinders, and the two longer Cu–O bonds are shown as thinner banded lines. The images were generated using CrystalMaker® [24].

involves separating the two long Cu–O bonds into a pair of longer and shorter bonds, of distances around 3.07 and 2.27 Å respectively, again possibly representing an ordering of the position of the copper atom. These changes in the crystal structure can be seen in Fig. 1. This paper is focused on understanding the nature of this disorder in the two phases of $\text{Cu}_2\text{P}_2\text{O}_7$, particularly in terms of the local atomic structure.

The phase transition in $\text{Cu}_2\text{P}_2\text{O}_7$ was recently characterized using a combination of diffraction data using both neutron and synchrotron radiation beams [5]. These data have been interpreted within the context of the underpinning theories of phase transitions [29–32], giving results for spontaneous strains, order parameters from the crystal structure, and measurement of the order parameter from integrated intensities of superlattice reflections [20]. We showed that NTE is associated with a single strain in the set of principal axes, which lies approximately normal to the layers of atoms in the crystal structure close to the [101] direction [20]. All together the data were shown to give a consistent interpretation of the phase transition as a continuous tricritical phase transition [29–31]. It was also found that the high-pressure behavior was fully consistent with this interpretation. In contrast, most examples of this family of materials show continuous second-order phase transitions [33] or discontinuous first-order phase transitions [34,35]; this can be tuned by changing chemical composition.

The significance of the phase transition being tricritical is that the spontaneous strains, which do not break the symmetry and thus are proportional to the square of the order parameter [29–31] (a derivation is given in the SM [23]), will vary with temperature as $\epsilon \propto (T_c - T)^{1/2}$, and in the case of $\text{Cu}_2\text{P}_2\text{O}_7$ there is a positive coefficient. It follows that the linear thermal expansion will follow as $\alpha = \partial\epsilon/\partial T \propto -(T_c - T)^{-1/2}$,

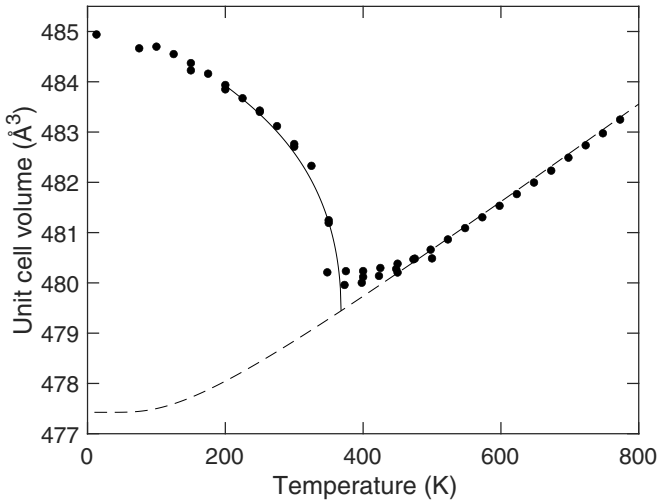


FIG. 2. Measurements of the volume of the unit cell of $\text{Cu}_2\text{P}_2\text{O}_7$ as compiled from different sources [20], with the volume for the high-temperature β phase multiplied by a factor of 2 to put all the data into a common scale. Data are shown as the black filled circles. The dashed curve is fitted to the high-temperature data and extrapolated down to low temperatures, accounting for saturation effects as described previously [20]. The continuous black curve represents an added strain of the form $\epsilon_V \propto (T_c - T)^{1/2}$ consistent with the tricritical phase transition and quadratic coupling between the order parameter and strain.

which diverges to a value of $-\infty$ at the phase transition. This explains the remarkably-large thermal expansivity seen in diffraction measurements at temperatures close to the phase transition [5]. We highlight this in Fig. 2, which shows the data for volume as a function of temperature with a superimposed form of the volumetric strain $\epsilon_V \propto (T_c - T)^{1/2}$. This is different from the large values claimed for $\text{Cr}_2\text{P}_2\text{O}_7$ [34] and $\text{Zn}_2\text{P}_2\text{O}_7$ [35], which appear to be associated with the thermal smearing of expansivity—possibly due to temperature gradients, hysteresis, or the effects of internal interfaces—seen at the discontinuous first-order phase transitions in these materials.

One issue that was not properly resolved in the recent analysis of the phase transition [20] is the reason why the spontaneous strain associated with the phase transition is positive. It was pointed out that if the dominant effect was from the rotations of the PO_4 tetrahedra, this should give the more-normal behavior of negative strain from the phase transition. Instead we can anticipate that the positive strain arises from the asymmetry in the two longer Cu–O bonds in the two phases.

It is our purpose in this paper to identify the nature of the ordering of the copper and bridging oxygen atoms through the phase transition in $\text{Cu}_2\text{P}_2\text{O}_7$ in order to better understand the origin of the phase transition and of the NTE. Our approach is to study the local structure using neutron total scattering, and to build configurations of atoms using the reverse Monte Carlo method (RMC) [36,37]. This approach has proven to be useful for a wide range of studies of phase transitions and local structural disorder in crystalline phases [38–41]. We will see that the RMC configurations show that the ordering of the

PO_4 orientations and distribution of Cu atoms along the long O–Cu–O linkage are coupled, in that both show the onset of continuous disorder and neither shows preferences for disorder between identifiable sites in the crystal structure. Analysis of the local structure demonstrates that the positive sign of the spontaneous strains associated with the phase transition in $\text{Cu}_2\text{P}_2\text{O}_7$, and hence the reason for the NTE, arises from the ordering of the copper atoms within the CuO_6 octahedra distorted by the Jahn–Teller effect causing one Cu–O bond to extend more than the other bond contracts.

II. METHODS

The method used to prepare the sample has been described in detail elsewhere [5]. For the neutron total scattering measurements, the sample was contained within a thin-walled vanadium can of internal diameter 9 mm, which was held within a cryofurnace mounted within the instrument. The measurements were performed using the Multi-Physics Instrument [42,43] at the China Spallation Neutron Source. Each measurement took four hours. Data were obtained for seven temperatures over the range 10 to 600 K, with two measurements performed in the high-temperature phase. The total scattering data were processed using in-house software to give normalization, and to correct for the scattering from the background from the instrument and from the sample environment.

It is useful to define the scattering function and pair distribution function (PDF) used in this work [44,45]. The scattering function is given as

$$i(Q) = S(Q) - \sum_m c_m b_m^2 = 4\pi\rho \int \sum_{mn} c_m c_n \bar{b}_m \bar{b}_n r^2 [g_{mn}(r) - 1] \frac{\sin Qr}{Qr} dr, \quad (1)$$

where Q is the scattering vector, $S(Q)$ is the measured scattering function in absolute units (rather than normalized), obtained after correction for background, attenuation, multiple scattering, incoherent scattering, effects from inelasticity etc., ρ is the total number density, c_m is the fractional concentration of atom type m , and b_m and $\bar{b}_m$ are the corresponding total and coherent neutron scattering lengths, respectively. $g_{mn}(r)$ is the partial PDF function, defined such that the number of atoms of type n lying in a thin spherical shell of radius r and thickness dr is equal to $4\pi r^2 c_n \rho$.

The pair distribution function $D(r)$ is thus defined as

$$D(r) = 4\pi\rho r \sum_{mn} c_m c_n \bar{b}_m \bar{b}_n [g_{mn}(r) - 1] \quad (2)$$

such that

$$Qi(Q) = \int D(r) \sin(Qr) dr. \quad (3)$$

$D(r)$ can then be obtained from the experimentally measured $i(Q)$ from the reverse sine transform,

$$D(r) = \frac{2}{\pi} \int Qi(Q) \sin(Qr) dQ. \quad (4)$$

The integral should span the range of Q from 0 to ∞ , but in practice we only ever have a finite range of values of Q . The

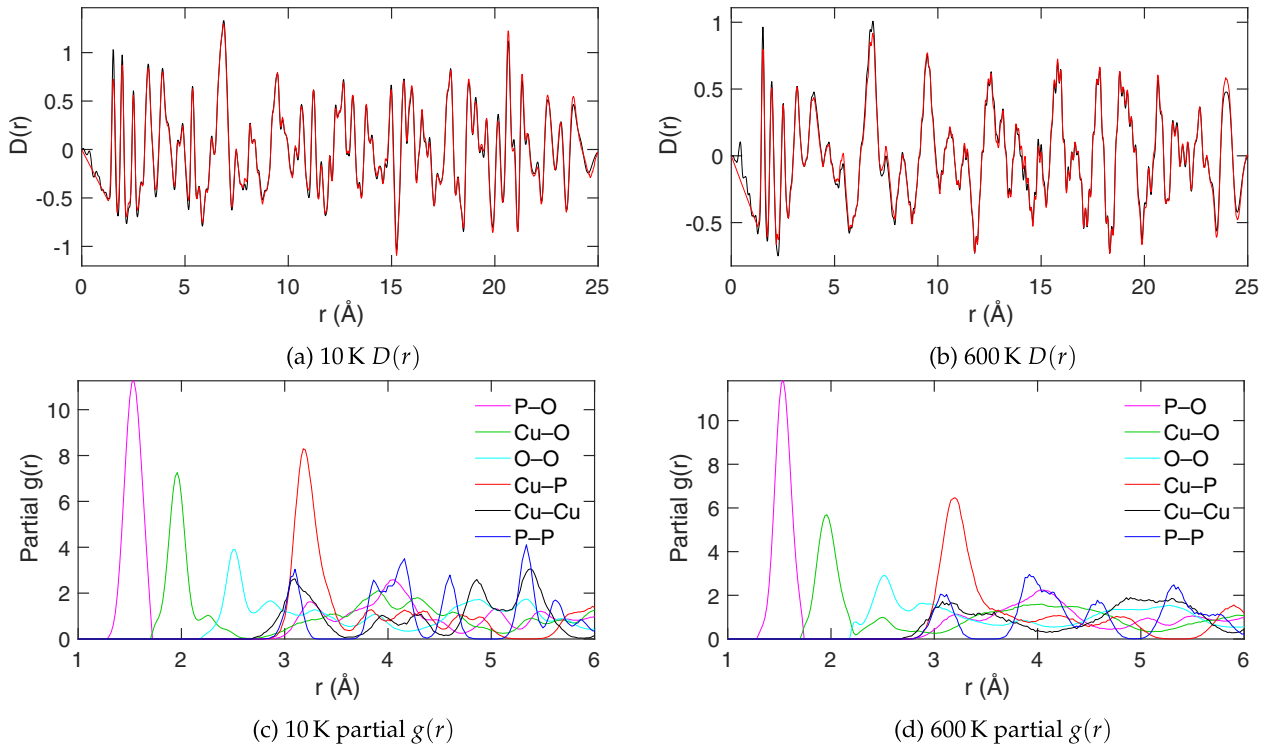


FIG. 3. (a), (b) Examples of two PDFs obtained in this study (black data) and the corresponding fit using RMC (red data) for $\text{Cu}_2\text{P}_2\text{O}_7$ at the two extreme temperatures of 10 K (a) and 600 K (b). (c), (d) Partial $g(r)$ PDFs corresponding to the data in (a) and (b), obtained from the RMC configurations, and shown for a limited range of r .

scattering function below the low- Q range of data was added by extrapolation. Truncation of the data at $Q = Q_{\text{max}}$ was handled by multiplying the experimental data by the Lorch window function, $M(Q) = \sin(\pi Q/Q_{\text{max}})/(\pi Q/Q_{\text{max}})$.

The PDF was actually formed from the total scattering data using a new method to merge data from different banks of detectors, which handles, and removes, the different resolution functions [46]. The same approach also handles uncertainties in the total scattering associated with the effects of inelasticity and unknown errors introduced into the corrections for background scattering. It thereby enables consistent merging of the scattering functions from different banks of detectors into a single function making use of all the data. PDFs for 10 and 600 K are shown in Figs. 3(a) and 3(b), respectively.

The first peaks in the PDF are for the nearest neighbor P–O, Cu–O, and O–O distances, in order, as can be seen by inspection of the partial $g(r)$ functions shown in Figs. 3(c) and 3(d) obtained from the RMC refinements (discussed below). Visually the full and partial PDFs from the two temperatures are similar, with the main visual difference being the broadening of the peaks in the PDF at higher temperature, which lead to reductions of the peak heights in a nonuniform way, and the amplitudes of the oscillations in the PDFs. The major visual differences in the partial PDFs are for the Cu–O distributions. Although overall the differences between the two temperatures are slight, we will see that the RMC method was capable of modeling the small changes in structure across the range of temperatures.

The crystal structure was refined from the diffraction data using GSAS II [47]. Results are given in the SM [23].

The RMC modeling was performed using the RMCPROFILE code [36,37]. The original configurations for each temperature were constructed from the refined crystal structures, using a supercell of size $8 \times 7 \times 6$ relative to the crystal structure of the α phase, using the DATA2CONFIG software [48]. The box size had edge lengths of around 55 Å. The RMC was performed using the total scattering function $i(Q)$ [Eq. (1)], pair distribution function $D(r)$ [Eq. (2)], and the Bragg profiles extracted by GSAS II for its data sources. For each temperature we ran 10 independent RMC simulations to enable us to obtain good statistical accuracy from the configurations. Each configuration gave identical distribution functions within the levels of statistical noise. Sample fits to the data for each temperature are given in the SM [23].

The ten atomic configurations generated for each temperature were used to extract distances between atoms, orientations of bonds, and angles between bonds, to generate the data given in Figs. 3–10, using a combination of the CrystalMaker® [24] and DATA2CONFIG [48] software tools.

All data for the Rietveld refinement, formation of the PDFs, and the RMC simulations are available from Ref. [49], together with all ten configurations analyzed for each temperature.

III. RESULTS

A. Distributions of P–O and shorter Cu–O bond lengths, and of phosphate tetrahedral angles

As we noted in the Introduction, the changes in the crystal structure through the phase transition concern the orientations of the PO_4 groups, and the distribution of copper atoms within

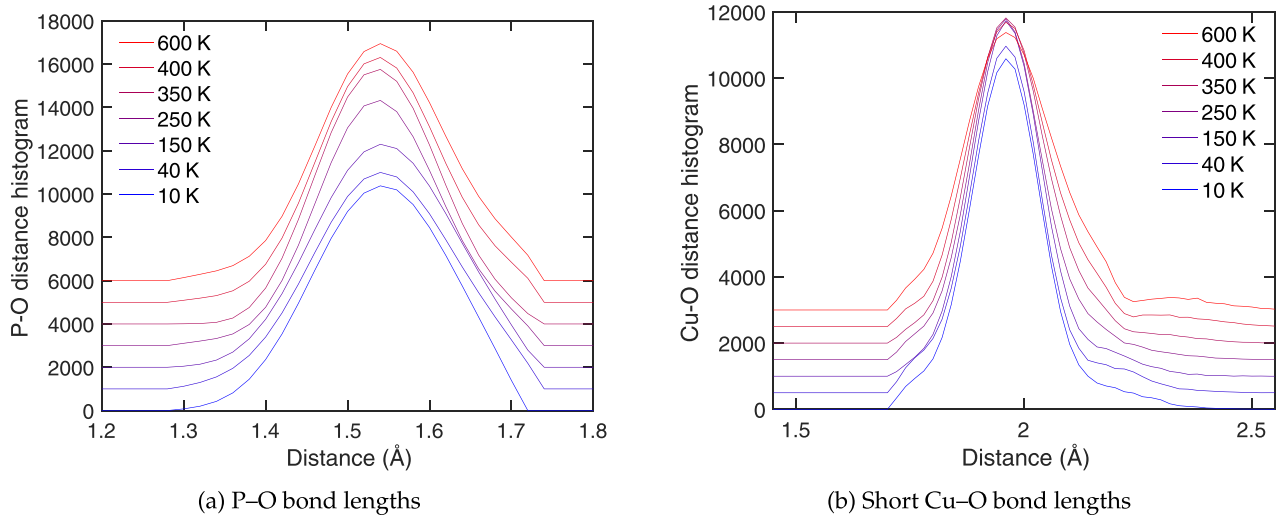


FIG. 4. Distribution functions for the (a) P–O distances and (b) short Cu–O distances. Data for different temperatures are systematically shifted vertically.

the axis of the two long Cu–O bonds. The integrity of the PO_4 tetrahedra and distributions of the shorter Cu–O bonds are not expected to change through the phase transition, so we first report the analysis of these quantities.

The distribution functions for the P–O bond lengths are shown in Fig. 4(a). These distribution functions include both the nonbridging and bridging P–O bonds, which in the average crystal structure at low-temperature have bond lengths that differ by as much as 0.1 Å. This difference will contribute to the width of the distribution function at low temperature, and so the width of the distribution function shows a smaller variation with temperature than would a single bond. The thermal expansivity of the mean P–O bond is $1.7 \times 10^{-6} \text{ K}^{-1}$, comparable to that for the Si–O bond in silica [50].

The distribution functions for the short Cu–O bond lengths are shown in Fig. 4(b). They also show little variation with temperature, but again, at low temperature the variation in the bond length of the average structure is 0.08 Å. The thermal

expansivity of the mean shorter Cu–O bond is $18 \times 10^{-6} \text{ K}^{-1}$, significantly larger than for the P–O bond.

The distribution functions for the tetrahedral O–P–O bond angles are shown in Fig. 5(a). These are centered around the ideal tetrahedral angle of 109.5° for all temperatures. It can be seen that the distribution functions broaden on raising temperature, with the variance of the angles being 40 deg^2 at low temperature and rising linearly to 70 deg^2 at 600 K.

B. Pyrophosphate linkages

The distribution functions for the bridging P–O–P angles are shown in Fig. 5(b). At low temperatures they are peaked around 153° , which reflects the natural bending of the pyrophosphate group around the bridging oxygen. On heating the distribution functions broaden and their mean value shifts to larger angles, reaching a value of around 165° in the high-temperature β phase. Because we are not weighting

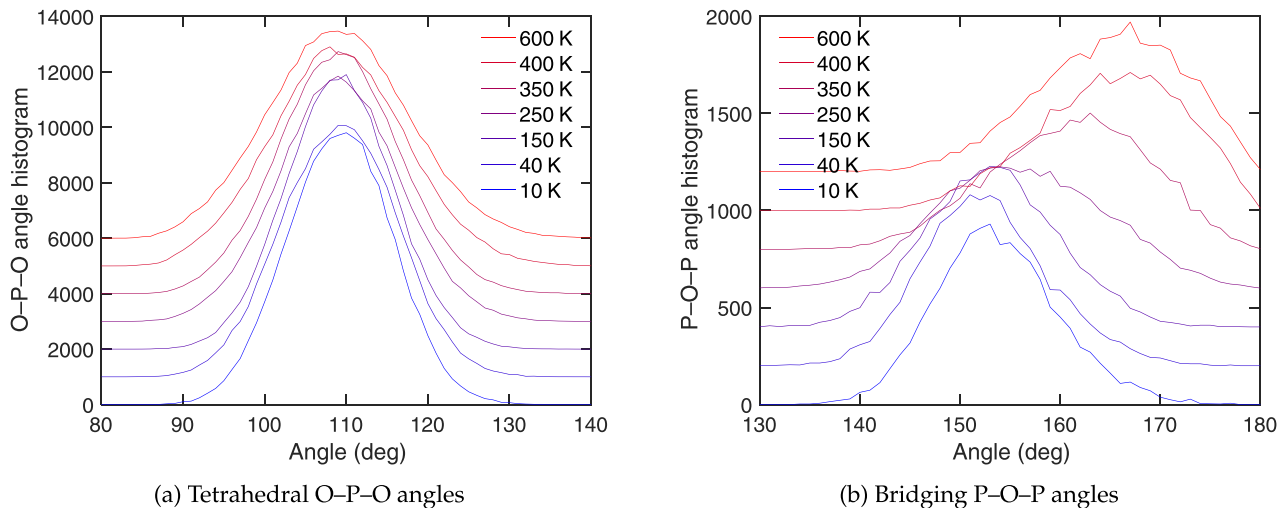


FIG. 5. Distribution functions for the (a) tetrahedral O–P–O angles and (b) bridging P–O–P angles. Data for different temperatures are systematically shifted vertically.

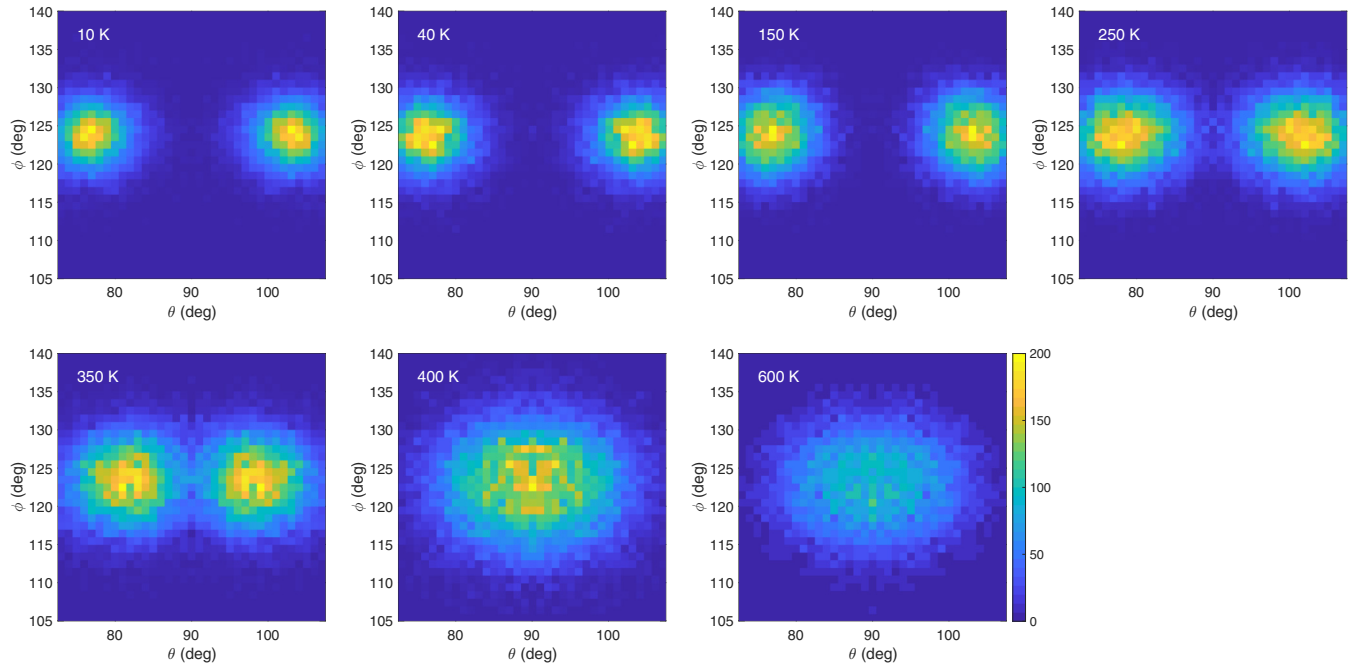


FIG. 6. Distribution functions for the bridging P–O bond orientations. The polar angles θ and ϕ are defined relative to the [010] and [001] crystal axes, respectively.

this distribution function by the arcsine of the angle, which would have accounted for the growing size of the solid angle when the angle increases, the distribution function necessarily falls to a value of zero at 180° . However, when we plot the corresponding distributions as functions of the cosines of the bridging P–O–P angles, thereby accounting for the

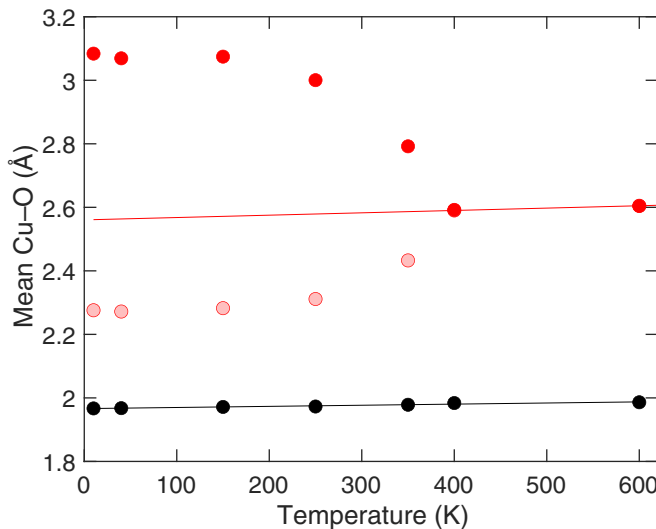


FIG. 7. Mean Cu–O bond lengths as a function of temperature. The black points show the mean of the four short Cu–O distances, which form the square coordination. The black line is a fit to the data, and shows a slight positive slope suggesting positive thermal expansion of the short Cu–O bonds. The two sets of red circles show the shorter and longer Cu–O distances. The straight red line is the extrapolation from the high-temperature phase and indicates that the longer bond expands more than the shorter bond contracts.

two-dimensional nature of the solid angle, this does have its peak at $\cos(180^\circ) = -1$ for the two temperatures in the high-temperature β phase. This suggests that the distribution itself is peaked around the linear angle rather than having a bimodal distribution.

To illustrate this point, we show two-dimensional representations of the distributions of orientations of the corresponding P–O bonds in Fig. 6, where θ is the polar angle, defined with respect to the crystallographic [010] axis, and ϕ is the azimuthal angle, with the [001] axis defining the direction for $\phi = 0^\circ$. We show the orientations of two symmetrically

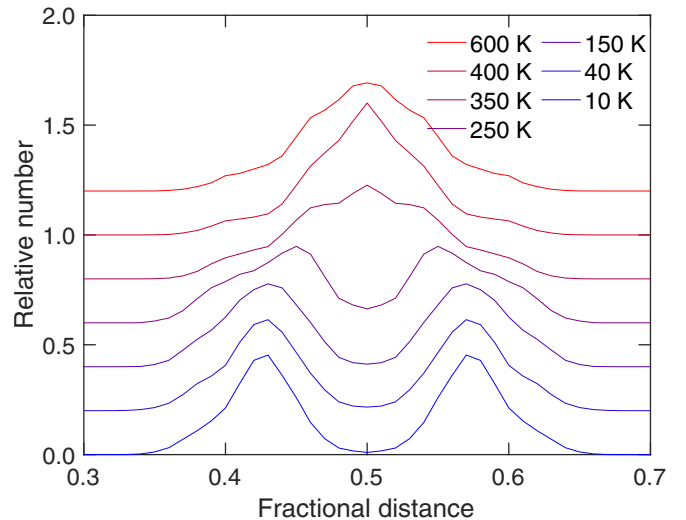


FIG. 8. Distributions functions for the relative position of Cu along the long O–Cu–O line. Data for different temperatures are systematically shifted vertically.

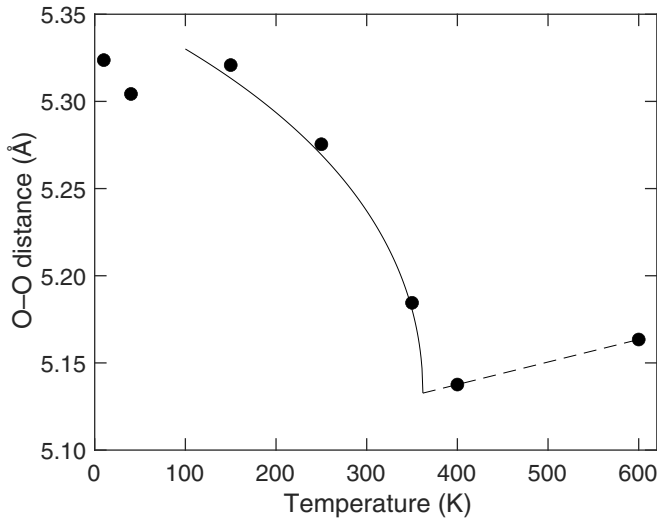


FIG. 9. Mean length of the O–O separation. The dashed curve is the line connecting the two points in the high temperature phase, and shows normal positive thermal expansion. The solid curve is described in the text, and represents the form expected when the distance expands in line with ordering associated with a tricritical phase transition.

related bonds to highlight the change in symmetry on heating through the phase transition. There is a mirror symmetry about $\theta = 90^\circ$, which reflects the (010) reflection symmetry in the space group symmetry. We have averaged over this symmetry in order to improve statistical analysis. Representing the angular distributions onto a flat two-dimensional surface will lead to some distortion of the distribution function, but we have chosen the axes, and show a restricted range of angles around $\theta = 90^\circ$, in order to minimize this distortion.

At low temperature we see that there are two orientations of the P–O vector. The angular separation in this plot is 27° , which corresponds exactly with the mean P–O–P angle of

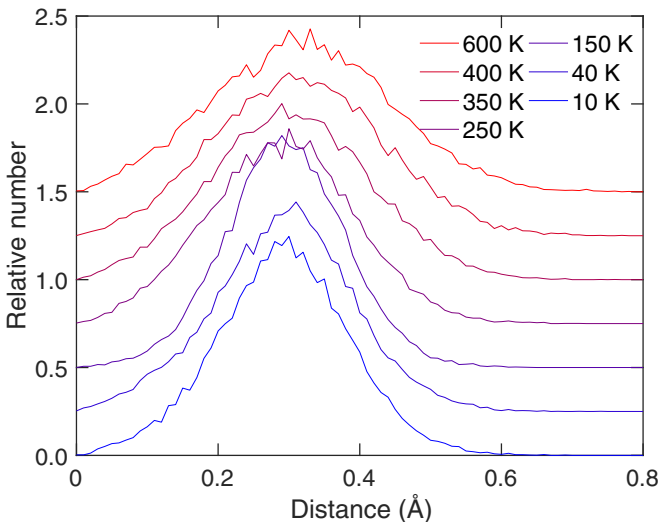


FIG. 10. Distribution functions for the lateral displacements of Cu atoms from the O–O line. Data for different temperatures are systematically shifted vertically.

153° shown in the plot of P–O–P angles, Fig. 5(b). On heating the distributions initially broaden, then, consistent with the distribution functions shown in Fig. 5(b), the peaks in the two-dimensional plot move towards $\theta = 90^\circ$. At high temperature the distribution is centered around $\theta = 90^\circ$, but is quite broad. At 600 K, the two perpendicular widths of the peak (determined as twice the standard deviation) are $\Delta\theta = 14.7^\circ$ and $\Delta\phi = 10.4^\circ$. These were determined using strips of widths of 2° along and perpendicular to $\theta = 90^\circ$.

As we discussed in the Introduction, the distribution in θ had previously been handled using a split site for the oxygen atom, with a site–P–site angle of 20.4° at 400 K. But what is clear is that there are not in fact two sites for the O atom. As suggested in our recent paper on $\text{Cu}_2\text{P}_2\text{O}_7$ [20] the actual distribution associated with each site in the crystal structure refinement is simply a mathematical way to represent the broad distribution of atomic positions [20]. Also it is clear that the O atoms do not lie on an annulus as they appear to do in β -cristobalite [27].

The rotations of the PO_4 groups that give rise to the spread of the transverse position of the bridging oxygen atom in the P–O–P linkage is directly connected with the disorder of the copper along the two long Cu–O bonds, which we discuss next.

C. Long Cu–O bonds

As discussed in the introduction, the Jahn–Teller distortion of the CuO_6 octahedra leads to the existence of four short Cu–O bonds that form a square coordination and have near-equal length, with the distribution of bond lengths having been shown in Fig. 4(b). The other two Cu–O bonds form longer bonds at low temperature, of which one is longer than the other, and these become of equal length, on average, on heating through the phase transition. From the distribution of bond lengths, we have obtained the three distinct mean Cu–O distances, and show these in Fig. 7. We have discussed the thermal expansion of the shorter bonds above.

The two longer Cu–O bond lengths are very different at low temperature, but coalesce on heating into the high-temperature phase. By extrapolating the mean Cu–O distance downwards in temperature from the data for two temperatures in the high-temperature phase we see that the longest Cu–O distance expands more than the other distance contracts.

To get a sense of the distribution of Cu positions, we have projected the position of the Cu atom onto the vector connecting the two oxygen atoms. The distribution functions for the relative positions along these vectors, represented as fractional coordinates ranging from 0 to 1, are shown in Fig. 8. This distribution function includes both the shorter and longer of the long Cu–O bonds. At low temperature we see tight distributions around the long and short distances, and thus is bimodal at lower temperatures. On heating the centres of the two peaks in the distribution function move closer to the center. In the high-temperature phase there is one broad peak at the center. This suggests considerable disorder associated with the Jahn–Teller distortion in the high-temperature phase, but without disordering between two distinct distances.

The greater expansion of the longer long Cu–O bond than the contraction of its shorter partner on cooling below the

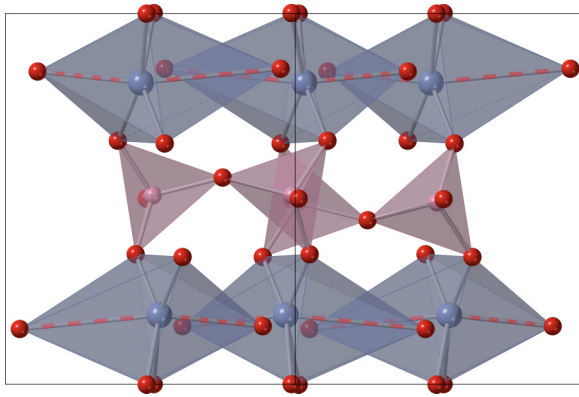
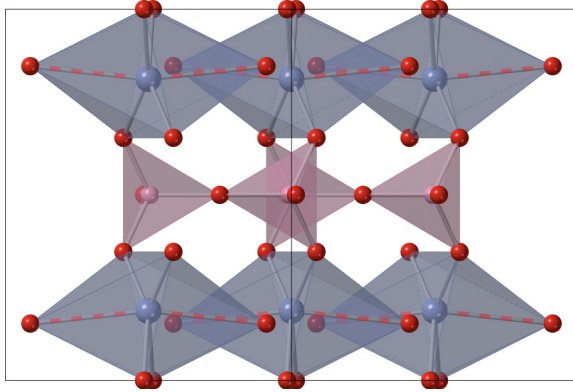
(a) Low-temperature α phase of $\text{Cu}_2\text{P}_2\text{O}_7$ (b) High-temperature β phase of $\text{Cu}_2\text{P}_2\text{O}_7$

FIG. 11. Representations of the crystal structures of both phases of $\text{Cu}_2\text{P}_2\text{O}_7$ viewed down the common $[101]$ axes, with the unit cell of the high-temperature phase doubled along the c axis to enable direct comparison. The distorted CuO_6 octahedra are shown as sea gray, and the PO_4 tetrahedra are shown as pink, with the oxygen atoms shown as red spheres. The longer Cu–O bonds are shown with two alternating colors. The important point to note is the coupling of the rotations of the PO_4 tetrahedra within each pyrophosphate group coupled with the change in the lengths of the two longer Cu–O bonds.

phase transition suggests there will be a commensurate expansion of the O–O distance. The variation of the mean value of this distance is shown in Fig. 9. It can be seen that this distance shows positive expansion in the high-temperature phase (but unfortunately we only have two points in this phase), then the distance expands considerably on cooling into the low-temperature phase. In this figure we have added a curve of the form $a_0(T) + \alpha(T_c - T)^{1/2}$ to reflect the expected variation with the phase transition, which has tricritical character. The background function $a_0(T)$ has been extrapolated from the two points in the high-temperature phase, and the value of $T_c \simeq 362$ adjusted to give a reasonable fit. This is consistent with our analysis of the spontaneous strains associated with the phase transition in our earlier work [20].

There is also a lateral displacement of the Cu atoms from the O–O vector of about 0.3 Å. The distribution of lateral displacements is shown in Fig. 10. The mean lateral displacement corresponds to about 5% of the O–O distance. It can

be seen that the mean lateral displacement does not change significantly with temperature, but the distribution functions show considerable broadening on heating.

IV. DISCUSSION

In this paper we have reported a neutron total scattering study of the phase transition in $\text{Cu}_2\text{P}_2\text{O}_7$ with data analyzed using the RMC method, and have explored the implications of the nature of the phase transition for the existence of the NTE. One question is whether the local structure of $\text{Cu}_2\text{P}_2\text{O}_7$ in the high-temperature β phase retains characteristics of the order in the low-temperature α phase. In particular, we have investigated whether or not there is a bimodal distribution of the orientations of the P–O bonds for the bridging oxygen atom, and a bimodal distribution of the positions of the copper atoms along the long O–Cu–O linear linkage with the CuO_6 octahedra. These two processes are likely to be coupled, as can be seen in the projection of the crystal structure down the $[101]$ direction of the lattice of the low-temperature phase, Fig. 11. That is, if there is a bimodal distribution in one of these, say the orientations of the PO_4 tetrahedra, there will probably also be a bimodal distribution in the other, in this case the position of the copper atom. The corollary of this is that if there is a unimodal distribution in one, there will also be unimodal distribution in the other.

It was found that the functions show unimodal distributions of both the orientations of the PO_4 tetrahedra and positions of the copper atoms in the high-temperature β phase. Thus, it appears that the local structure of the high-temperature β phase reflects the average structure of this phase rather than the average structure of the low-temperature α phase. This is one of the key findings from this study, and it allows us to better understand the way in which the Jahn–Teller distortion is involved in the phase transition in $\text{Cu}_2\text{P}_2\text{O}_7$.

We showed before [20] that if the phase transition merely involved rotations of the PO_4 tetrahedra with bending of the bridging bonds in the pyrophosphate group, from purely geometric considerations this would lead to a negative spontaneous strain and hence no NTE. Instead, it is clear that the way that the two long Cu–O bonds respond to the ordering of the Jahn–Teller distortion, as seen in Fig. 7, with an overall lengthening of the long O–Cu–O distance, is the primary reason why the phase transition is accompanied, unusually, by a positive spontaneous strain. This is the second key finding of this work.

In conclusion, we have now quantified the disorder in $\text{Cu}_2\text{P}_2\text{O}_7$ on heating, which has given a picture of dynamic disorder rather than some degree of site-hopping quasistatic disorder. We believe that we now have a near-complete understanding of the phase transition and of the origin of the NTE in $\text{Cu}_2\text{P}_2\text{O}_7$. We presume that the findings here will apply to many of the other materials with the thortveitite structure having a phase transition. We also feel that we have demonstrated that the methods used in this study could usefully be employed in studies of other related materials.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [49].

APPENDIX: DISCUSSION OF WHY THE POSITIVE THERMAL EXPANSION OF THE HIGH-TEMPERATURE PHASE PRECLUDES THE POSSIBILITY THAT THE NEGATIVE THERMAL EXPANSION IN THE LOW-TEMPERATURE PHASE ARISES FROM A TENSION EFFECT

In this paper we have argued that the NTE in the low-temperature phase of $\text{Cu}_2\text{P}_2\text{O}_7$ is entirely due to the nature of the spontaneous strains that accompany the distortion of the lattice because of the phase transition. But is there a role for a classic tension-effect mechanism that could give rise to negative Grüneisen parameters, perhaps seen only in the low-temperature phase? We believe not, and we assert that when NTE is associated with a phase transition, if there is not a sufficiently large tension effect to give NTE in the high-temperature phase, it is almost certain that NTE in the low-temperature phase will not be driven by a tension effect. It is sometimes suggested—at least anecdotally—that since the low-temperature phase is a different phase, perhaps we should not make the comparison between the two phases. Here we will explain the argument in support of our assertion.

At the outset of this discussion we want to point out that there are other materials besides $\text{Cu}_2\text{P}_2\text{O}_7$ that undergo displacive phase transitions and show volumetric NTE in the low-temperature phase but not in the high-temperature phase. The materials we are aware of are ferroelectric PbTiO_3 [53–55], ammonium sulfate [56,57], and the pyrochlore $\text{Cd}_2\text{Re}_2\text{O}_7$ [58,59]. The latter material has the same type of chemical formula as $\text{Cu}_2\text{P}_2\text{O}_7$, but it has a very different crystal structure and a different phase transition. Furthermore, the phase transition in $\text{Cd}_2\text{Re}_2\text{O}_7$ is also tricritical, and so like $\text{Cu}_2\text{P}_2\text{O}_7$ it will show a divergence of the thermal expansivity at the transition temperature. This appears to be supported by diffraction data [58,59]. Actually the same appears to be the case for ammonium sulfate, but there the picture appears to be a little more complicated [57].

The crystal structure of the low-temperature phase following a displacive phase transition is a small distortion of that of the high-temperature phase. This involves small displacements of the atoms which do not break the chemical bonds, but which do lower the crystal symmetry, possibly, as in the case of $\text{Cu}_2\text{P}_2\text{O}_7$, also involving the loss of some of the

translational symmetry operations. These small displacements give the quantitative difference between the low-temperature and high-temperature phases, without any other distinctive new modifications of the structure on cooling below the phase transition. The size of the displacements taken together is characterized by the order parameter, often given the symbol Q [29–32].

The low-temperature phase will always have a lower internal energy than the high-temperature phase. This point, of course, merely follows from the statement that the low-temperature phase is the thermodynamically stable phase at low temperatures. Thus, the high-temperature phase must be stabilized by the entropic contribution to the free energy, which for displacive phase transitions will arise from the lattice dynamics. For this to be so, the phonon frequencies must have, on average, higher values in the low-temperature phase, since the entropy is larger with lower frequencies. This can be seen from the equation for entropy in the high-temperature limit, $k_B T > \hbar\omega_\lambda$, $S = \sum_\lambda k_B [1 + \ln(k_B T / \hbar\omega_\lambda)]$, where the sum is over all normal modes, denoted by the index λ .

The standard theory of displacive phase transitions [31] makes the reasonable assumption that the key anharmonic interactions are fourth order. It follows automatically that the phonon frequencies change with the value of the order parameter Q as

$$\omega^2 = \omega_0^2 + \frac{1}{2}\alpha Q^2. \quad (\text{A1})$$

If the potential energy around $Q = 0$ varies as $E(Q) = -\frac{1}{2}\kappa_2 Q^2 + \dots$, such that κ_2 determines the low-temperature imaginary value of the soft-mode frequency, it follows that the transition temperature is given as [31]

$$RT_c = \frac{2\kappa_2 \langle \omega \rangle^2}{3\langle \alpha \rangle}. \quad (\text{A2})$$

The averages $\langle \omega \rangle$ and $\langle \alpha \rangle$ can be formed in an appropriately weighted way to replace the full summations over all wave vectors in the Brillouin zone. The point is that this gives the constraint $\langle \alpha \rangle > 0$, supporting the argument that the values of the vibrational frequencies must increase on average when the system is in the low-temperature phase.

The appropriate form of the mode Grüneisen parameters, written in terms of linear rather than volume strain, is

$$\gamma_{\lambda,j} = -\frac{1}{\omega_\lambda} \frac{\partial \omega_\lambda}{\partial \epsilon_j} = -\frac{1}{2\omega_\lambda^2} \frac{\partial \omega_\lambda^2}{\partial \epsilon_j}, \quad (\text{A3})$$

where ϵ_j is a component of the second-rank strain tensor written using Voigt notation, and the second form, using ω_λ^2 , is more appropriate for our argument. The values of ω_λ^2 are the eigenvalues of the dynamical matrix. This is a Hermitian matrix, and the most sensitive eigenvalues for small perturbations of a Hermitian matrix are those with the lowest eigenvalues [60]. It thus follows that the frequencies most affected by a small strain will be those with lowest values of ω_λ^2 . That is, the largest absolute values of $\partial \omega_\lambda^2 / \partial \epsilon_j$ will be for modes with the smallest values of ω_λ^2 . This effect is further enhanced by the multiplicative factor of ω_λ^{-2} , again emphasizing the role of low values of the frequency.

The point is that if the frequencies increase as a result of the phase transition, it is almost certain that the abso-

lute values of the mode Grüneisen parameters will decrease. Thus, if there is no significant tension effect in the high-temperature phase leading to NTE in that phase, it is almost certain that the NTE in the low-temperature phase will not be associated with a tension effect. It will follow from this that any tension effect present in the high-temperature phase—presumably some modes will have negative values of their mode Grüneisen parameters—will be seen only in the extrapolation of the lattice parameters to low temperature, which will remain dominated by the same modes that dominate in the high-temperature phase.

A counter argument can be proposed, but it can be explained why it is not relevant. We have recently demonstrated that disorder in a crystal structure can limit the size of NTE, so that a material with flexibility to show NTE

can actually show PTE [61]. Given that high-temperature phases can be more disordered than their corresponding low-temperature phases, it might be suggested that with less disorder in the low-temperature phase, that might enable the NTE to be ‘liberated’. However, this is unlikely to be the case here, as indeed it is not found to be the case in other systems showing phase transitions, because the static distortions in the low-temperature phase are exactly the distortions that occur as dynamic fluctuations in the high-temperature phase. In the case of $\text{Cu}_2\text{P}_2\text{O}_7$ we even do not need to make this counter argument—the RMC results presented in this paper show that the disorder of the high-temperature phase appears to be large-amplitude motion about the atomic positions in the average structure of the high-temperature phase.

- [1] C. Calvo, The crystal structure and phase transitions of $\beta\text{-Zn}_2\text{P}_2\text{O}_7$, *Can. J. Chem.* **43**, 1147 (1965).
- [2] N. S. Rao and O. G. Palanna, Phase transition in copper(II) pyrovanadate, *Bull. Mater. Sci.* **16**, 37 (1993).
- [3] H. Wang, M. Yang, M. Chao, J. Guo, Q. Gao, Y. Jiao, X. Tang, and E. Liang, Negative thermal expansion property of $\beta\text{-Cu}_2\text{V}_2\text{O}_7$, *Solid State Ionics* **343**, 115086 (2019).
- [4] B. H. K. Pogorzelec-Glaser, A. Pietraszko, and M. Połomska, Structure and phase transitions in $\text{Cu}_2\text{P}_2\text{O}_7$, *Phase Transitions* **79**, 535 (2006).
- [5] N. Shi, A. Sanson, Q. Gao, Q. Sun, Y. Ren, Q. Huang, D. O. de Souza, X. Xing, and J. Chen, Strong negative thermal expansion in a low-cost and facile oxide of $\text{Cu}_2\text{P}_2\text{O}_7$, *J. Am. Chem. Soc.* **142**, 3088 (2020).
- [6] N. Shi, A. Sanson, A. Venier, L. Fan, C. Sun, X. Xing, and J. Chen, Negative and zero thermal expansion in $\alpha\text{-(Cu}_{2-x}\text{Zn}_x\text{)V}_2\text{O}_7$ solid solutions, *Chem. Commun.* **56**, 10666 (2020).
- [7] N. Shi, A. Sanson, Q. Sun, L. Fan, A. Venier, D. Oliveira de Souza, X. Xing, and J. Chen, Strong negative thermal expansion of Cu_2PVO_7 in a wide temperature range, *Chem. Mater.* **33**, 1321 (2021).
- [8] N. Shi, A. Sanson, A. Venier, L. Fan, Y. Ren, D. O. de Souza, L. Olivi, Y. Song, X. Xing, and J. Chen, Tuning thermal expansion from strong negative to zero to positive in $\text{Cu}_{2-x}\text{Zn}_x\text{P}_2\text{O}_7$ solid solutions, *Scr. Mater.* **207**, 114289 (2022).
- [9] K. Takenaka, M. Kano, R. Kasugai, K. Takada, K. Eto, Y. Kadowaki, Y. Yokoyama, N. Katayama, and Y. Okamoto, Structural phase transition and negative thermal expansion in $\text{Cu}_{1.8}\text{Zn}_{0.2}\text{V}_{2-x}\text{P}_x\text{O}_7$ solid solutions, *Appl. Phys. Express* **15**, 025504 (2022).
- [10] Y. Xiang, X. Hao, X. Liu, M. Wang, J. Tian, C. Kang, E. Liang, W. Zhang, and Y. Jia, Tailoring thermal expansion of $(\text{LiFe})_{0.5x}\text{Cu}_{2-x}\text{P}_2\text{O}_7$ via codoping LiFe diatoms in $\text{Cu}_2\text{P}_2\text{O}_7$ oxide, *Inorg. Chem.* **61**, 1504 (2022).
- [11] N. Shi, X. Kong, A. Sanson, N. Wang, A. Venier, D. O. de Souza, and J. Chen, Observation of near-zero thermal expansion in CrVMoO_7 , *Scr. Mater.* **235**, 115597 (2023).
- [12] N. Shi, L. Fan, Y. Xu, W. Yin, H. Chen, B. Yuan, C. Zhou, and J. Chen, Significant enhancement of negative thermal expansion under low pressure in $\text{Cu}_2\text{P}_2\text{O}_7$, *Small* **20**, 2312289 (2024).
- [13] G. D. Barrera, J. A. O. Bruno, T. H. K. Barron, and N. L. Allan, Negative thermal expansion, *J. Phys.: Condens. Matter* **17**, R217 (2005).
- [14] J. Chen, L. Hu, J. Deng, and X. Xing, Negative thermal expansion in functional materials: Controllable thermal expansion by chemical modifications, *Chem. Soc. Rev.* **44**, 3522 (2015).
- [15] M. T. Dove and H. Fang, Negative thermal expansion and associated anomalous physical properties: Review of the lattice dynamics theoretical foundation, *Rep. Prog. Phys.* **79**, 066503 (2016).
- [16] K. Takenaka, Progress of research in negative thermal expansion materials: Paradigm shift in the control of thermal expansion, *Front. Chem.* **6**, 267 (2018).
- [17] N. Shi, Y. Song, X. Xing, and J. Chen, Negative thermal expansion in framework structure materials, *Coord. Chem. Rev.* **449**, 214204 (2021).
- [18] E. Liang, Q. Sun, H. Yuan, J. Wang, G. Zeng, and Q. Gao, Negative thermal expansion: Mechanisms and materials, *Front. Phys.* **16**, 53302 (2021).
- [19] Y. Mochizuki, K. Nagamatsu, H. Koiso, T. Isobe, and A. Nakajima, Mechanism of negative thermal expansion in monoclinic $\text{Cu}_2\text{P}_2\text{O}_7$ from first principles, *J. Phys. Chem. Lett.* **15**, 156 (2024).
- [20] M. T. Dove and N. Shi, The phase transition in copper pyrophosphate, $\text{Cu}_2\text{P}_2\text{O}_7$: Insights and implications for the interpretation of negative thermal expansion, *Matter* **8**, 102149 (2025).
- [21] B. E. Robertson and C. Calvo, The crystal structure and phase transformation of $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$, *Acta Crystallogr.* **22**, 665 (1967).
- [22] B. E. Robertson and C. Calvo, Crystal structure of $\beta\text{-Cu}_2\text{P}_2\text{O}_7$, *Can. J. Chem.* **46**, 605 (1968).
- [23] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/t6fk-c61v> for figures showing the fitting of the RMC to the experimental data for each temperature, the figures showing the fitting of the Rietveld refinement to the neutron powder diffraction for each bank of detectors, the tables presenting the refined crystal structure of each temperature, and a discussion of why the strains are expected to be proportional to the square of the order parameter.

- [24] D. C. Palmer, Visualization and analysis of crystal structures using crystalmaker software, *Zeitschrift für Kristallographie-Crystalline Materials* **230**, 559 (2015).
- [25] R. Bianchi, T. Pilati, V. Diella, C. M. Gamaccioli, and G. Mannucci, A re-examination of thortveitite, *Am. Mineral.* **73**, 601 (1988).
- [26] W. W. Schmahl, I. P. Swainson, M. T. Dove, and A. Graeme-Barber, Landau free energy and order parameter behaviour of the α/β phase transition in cristobalite, *Zeitschrift für Kristallographie* **201**, 125 (1992).
- [27] M. G. Tucker, M. P. Squires, M. T. Dove, and D. A. Keen, Dynamic structural disorder in cristobalite: Neutron total scattering measurement and reverse Monte Carlo modelling, *J. Phys.: Condens. Matter* **13**, 403 (2001).
- [28] H. Effenberger, Structural refinement of low-temperature copper(II) pyrophosphate, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **46**, 691 (1990).
- [29] R. Cowley, Structural phase transitions I. Landau theory, *Adv. Phys.* **29**, 1 (1980).
- [30] E. Salje, Application of Landau theory for the analysis of phase transitions in minerals, *Phys. Rep.* **215**, 49 (1992).
- [31] M. T. Dove, Theory of displacive phase transitions in minerals, *Am. Mineral.* **82**, 213 (1997).
- [32] M. A. Carpenter, E. K. Salje, and A. Graeme-Barber, Spontaneous strain as a determinant of thermodynamic properties for phase transitions in minerals, *Eur. J. Mineral.* **10**, 621 (1998).
- [33] B. Sheng, J. Xie, Q. Shao, K. Zhao, S. Zhao, J. Guo, E. Liang, Y. Qiao, B. Wei, and Q. Gao, Structure and abnormal thermal expansion in $\text{Cu}_{2-x}\text{Mg}_x\text{P}_2\text{O}_7$, *Phys. Lett. A* **525**, 129843 (2024).
- [34] Y. Liang, G. Zeng, X. Hao, J. Guo, X. Liu, Q. Gao, Y. Jia, and E. Liang, Distinct Jahn-Teller-induced negative thermal expansion behaviors in $\text{Cr}_2\text{P}_2\text{O}_7$, *Phys. Rev. B* **112**, 104307 (2025).
- [35] M. Khalid, Y. Liang, C. Wang, X. Hao, J. Guo, X. Ren, Q. Gao, Y. Jia, and E. Liang, Giant negative thermal expansion in $\text{Zn}_2\text{P}_2\text{O}_7$ driven by pseudo Jahn-Teller effect, *Phys. Rev. B* **113**, 094309 (2026).
- [36] M. G. Tucker, D. A. Keen, M. T. Dove, A. L. Goodwin, and Q. Hui, RMCProfile: Reverse Monte Carlo for polycrystalline materials, *J. Phys.: Condens. Matter* **19**, 335218 (2007).
- [37] W. A. Sławiński, C. J. Kerr, Y. Zhang, H. Y. Playford, M. T. Dove, A. E. Phillips, and M. G. Tucker, RMCProfile7: Reverse Monte Carlo for multiphase systems, *J. Appl. Crystallogr.* **57**, 1251 (2024).
- [38] M. G. Tucker, A. L. Goodwin, M. T. Dove, D. A. Keen, S. A. Wells, and J. S. O. Evans, Negative thermal expansion in ZrW_2O_8 : Mechanisms, rigid unit modes, and neutron total scattering, *Phys. Rev. Lett.* **95**, 255501 (2005).
- [39] A. L. Goodwin, S. A. T. Redfern, M. T. Dove, D. A. Keen, and M. G. Tucker, Ferroelectric nanoscale domains and the 905 K phase transition in SrSnO_3 : A neutron total-scattering study, *Phys. Rev. B* **76**, 174114 (2007).
- [40] J. Du, A. E. Phillips, D. C. Arnold, D. A. Keen, M. G. Tucker, and M. T. Dove, Structural study of bismuth ferrite BiFeO_3 by neutron total scattering and the reverse Monte Carlo method, *Phys. Rev. B* **100**, 104111 (2019).
- [41] M. T. Dove, J. Du, Z. Wei, D. A. Keen, M. G. Tucker, and A. E. Phillips, Quantitative understanding of negative thermal expansion in scandium trifluoride from neutron total scattering measurements, *Phys. Rev. B* **102**, 094105 (2020).
- [42] J. Xu, L. Mei, W. Yin, X. Wang, W. Cai, Z. Li, T. Bo, H. Chen, B. Wang, and Y. Chen, Physical design of multipurpose physics neutron diffractometer for the CSNS, *Nucl. Instrum. Methods Phys. Res., Sect. A* **927**, 161 (2019).
- [43] J. Xu, Y. Xia, Z. Li, H. Chen, X. Wang, Z. Sun, and W. Yin, Multi-physics instrument: Total scattering neutron time-of-flight diffractometer at China Spallation Neutron Source, *Nucl. Instrum. Methods Phys. Res., Sect. A* **1013**, 165642 (2021).
- [44] D. A. Keen, A comparison of various commonly used correlation functions for describing total scattering, *J. Appl. Crystallogr.* **34**, 172 (2001).
- [45] M. T. Dove and G. Li, Review: Pair distribution functions from neutron total scattering for the study of local structure in disordered materials, *Nuclear Analysis* **1**, 100037 (2022).
- [46] S. Wang, M. Gao, Y. Qin, S. Zhang, L. Tan, and M. T. Dove, Accounting for instrument resolution in the pair distribution functions obtained from total scattering data using Hermite functions, *J. Appl. Crystallogr.* **58**, 1269 (2025).
- [47] B. H. Toby and R. B. Von Dreele, GSAS-II: The genesis of a modern open-source all purpose crystallography software package, *J. Appl. Crystallogr.* **46**, 544 (2013).
- [48] M. T. Dove and G. Rigg, RMCgui: a new interface for the workflow associated with running Reverse Monte Carlo simulations, *J. Phys.: Condens. Matter* **25**, 454222 (2013).
- [49] M. T. Dove, Complete set of data for the RMC simulations, generation of the PDFs from the total scattering data, and the Rietveld refinements using GSAS II, Zenodo, 2026, <https://doi.org/10.5281/zenodo.20263257>.
- [50] M. G. Tucker, M. T. Dove, and D. A. Keen, Direct measurement of the thermal expansion of the Si-O bond by neutron total scattering, *J. Phys.: Condens. Matter* **12**, L425 (2000).
- [51] <https://cstr.cn/31113.02.CSNS>.
- [52] <https://cstr.cn/31113.02.CSNS.MPI>.
- [53] X. Xing, J. Deng, J. Chen, and G. Liu, Novel thermal expansion of lead titanate, *Rare Metals* **22**, 294 (2003).
- [54] J. Chen, X. R. Xing, R. B. Yu, and G. R. Liu, Structure and enhancement of negative thermal expansion in the $\text{PbTiO}_3\text{-CdTiO}_3$ system, *Appl. Phys. Lett.* **87**, 231915 (2005).
- [55] J. Chen, X. R. Xing, G. R. Liu, J. H. Li, and Y. T. Liu, Structure and negative thermal expansion in the $\text{PbTiO}_3\text{-BiFeO}_3$ system, *Appl. Phys. Lett.* **89**, 101914 (2006).
- [56] P. Lloveras, E. Stern-Taulats, M. Barrio, J. Tamarit, S. Crossley, W. Li, V. Pomjakushin, A. Planes, L. Mañosa, N. D. Mathur, and X. Moya, Giant barocaloric effects at low pressure in ferroelectric ammonium sulphate, *Nat. Commun.* **6**, 8801 (2015).
- [57] G. Cai, J. Liu, H. Y. Playford, H. C. Walker, A. E. Phillips, and M. T. Dove, Hydrogen bonding order, librational entropy, and negative thermal expansion in the barocaloric material ammonium sulfate (unpublished).
- [58] F. Qin, L. Hu, Y. Zhu, Y. Sakai, S. Kawaguchi, A. Machida, T. Watanuki, Y.-W. Fang, J. Sun, X. Ding, and M. Azuma, Integrating abnormal thermal expansion and ultralow thermal conductivity into $(\text{Cd,Ni})_2\text{Re}_2\text{O}_7$ via synergy of local structure

- distortion and soft acoustic phonons, [Acta Mater.](#) **264**, 119544 (2024).
- [59] M. T. Dove, Comment on “integrating abnormal thermal expansion and ultralow thermal conductivity into $(\text{Cd, Ni})_2\text{Re}_2\text{O}_7$ via synergy of local structure distortion and soft acoustic phonons”, [Scripta Materialia](#) **282**, 117395 (2026).
- [60] T. Claeys, B. Fahs, G. Lambert, and C. Webb, How much can the eigenvalues of a random Hermitian matrix fluctuate? [Duke Math. J.](#) **170**, 2085 (2021).
- [61] P. Li, P. Yao, G. Cai, T. Li, A. E. Phillips, and M. T. Dove, Dynamic structural disorder and negative thermal expansion (unpublished).