Raman spectroscopic study of high-pressure behavior of Ag₃[Co(CN)₆]

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In situ Raman spectroscopic studies have been carried out on $Ag_3[Co(CN)_6]$ at high pressures up to 16 GPa. From the pressure dependence of the Raman frequencies, the mode Grüneisen parameters in the trigonal and the monoclinic phases are obtained. Besides the reported trigonal-to-monoclinic transition at 0.2 GPa, it is observed that the compound shows pressure-induced amorphization above 13 GPa. The recovered sample shows features characteristic of amorphous carbon nitride, indicating the decomposition of the parent compound in the pressure-reducing cycle. Temperature dependence of the mode frequencies over the range 80–290 K is also investigated, from which the modes that are more anharmonic than other modes are identified.

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I. INTRODUCTION

Following the report of isotropic negative thermal expansion (NTE) in cubic ZrW_2O_8 over a large temperature range,¹ and subsequently in many other tungstates and molybdates,² there have been numerous experimental³ and computational investigations⁴ toward understanding the thermal expansion and phase transition behavior of compounds that have flexible framework structures. Many dicyanides, such as Zn(CN)2 and Cd(CN)₂,⁵ are also reported to exhibit NTE wherein the coefficient of thermal expansion (CTE) was found to be about twice as much as that reported in ZrW_2O_8 . The underconstrained nature of the Zn(CN)₂-type structure, which has extra degrees of freedom imparted by the cyanide anions compared to those of the same structures linked by monatomic anions, supports a large number of low energy rigid unit modes with a negative Grüneisen parameter. This is considered to be the primary factor for the observed NTE in dicyanides.^{5,6} On the other hand, experimental investigation on $Zn(CN)_2$ revealed that vibrational modes of \sim 350 cm⁻¹ (\sim 44 meV), because of the C \equiv N librational and translational modes, also have negative Grüneisen parameters,7 thus contributing to the NTE. Colossal thermal expansion was reported in the compound $Ag_3[Co(CN)_6]$, the CTE being nearly an order of magnitude greater than that observed in other crystalline materials.⁸ The compound exhibits positive thermal expansion (PTE) along the *a*-axis and comparable NTE along the *c*-axis over a temperature range of 16-500 K, its decomposition temperature,⁸ the net volume thermal expansion being positive. Anisotropic thermal expansion behavior has also been reported in $Ni(CN)_2$;⁹ however, the disordered crystal structure¹⁰ makes a direct comparison of the phonon behavior in this system with other related compounds difficult. Besides a large CTE, the compound $Ag_3[Co(CN)_6]$ is found to exhibit anisotropic negative linear compression (NLC); while the *a*-axis contracts with pressure, the *c*-axis expands significantly and the magnitude of NLC is found to be much larger than that known in other materials.¹¹

At ambient conditions, crystal structure of $Ag_3[Co(CN)_6]$ is trigonal (phase PI) consisting of three interpenetrating distorted cubic networks, each with CoC_6 octahedra at the cube apices and the edges formed by nearly linear Co-CN-Ag-NC-Co linkages⁸ parallel to the crystallographic [101] axis. This linkage is in a manner that the PTE in one direction results in a NTE in the perpendicular direction by way of the flexing of the framework structure.⁸ Such a mechanism also qualitatively explains the observed NLC behavior.¹¹ Many related cyanide-based compounds crystallizing in cubic structure, the Prussian blue analogs, are reported to show nearly zero or very low (isotropic) thermal expansion behavior.^{12,13} Few experimental investigations are available to understand the microscopic origin of the colossal thermal expansion $Ag_3[Co(CN)_6]$. The isostructural compound $D_3Co(CN)_6$ is found to exhibit a much reduced CTE.⁸ The flexibility of the framework structure in $Ag_3[Co(CN)_6]$, along with weak Ag...Ag interactions (termed argentophillic interactions), are believed to be responsible for its unusually large thermal expansion.^{14,15} Systematic investigation of several dicyanometallate compounds revealed that compounds with strong metallophilic interactions indeed have smaller values of CTE, such as in the case of Au-based compounds.¹⁶ DFT calculations suggested that the energy required for the flexing of the structure is very small and that the observed thermal expansion may be achieved even with a moderate thermal Grüneisen constant.¹⁷ Reverse Monte Carlo analysis of the neutron scattering data on $Ag_3[Co(CN)_6]$ revealed that the expansion of individual bonds is also considerable; all bond lengths showed PTE.¹⁴ High-pressure Raman spectroscopic studies on ZrW₂O₈¹⁸ and Zn(CN)₂⁷ have identified phonon modes with negative Grüneisen parameters that directly contribute to the NTE. There are no experimental reports on the mode Grüneisen parameters of $Ag_3[Co(CN)_6]$.

Furthermore, *in situ* high-pressure neutron diffraction studies on Ag₃[Co(CN)₆] revealed that under the application of pressure, it exhibits a structural transition at 0.19 GPa¹¹ to a monoclinic phase (PII), which is found to be stable up to at least 7.65 GPa. The volume change across the PI-PII transition is found to be ~16%, a rather large change compared to the typical volume changes reported in other compounds; e.g., the volume change across the cubic–orthorhombic transition reported in ZrW₂O₈¹⁹ ~0.2 GPa is about 5%. From the qualitative understanding of the NTE and NLC behavior, we would expect that the transition may also be induced by temperature variation. However, x-ray and neutron diffraction experiments down to 16 K did not show any evidence for structural transition.^{8,14} What drives this transition is not clear at present. Interestingly, phase PII also has both NLC and NTE behavior, the magnitude of NTE being less in phase PII.¹¹ In the present work, *in situ* high-pressure Raman spectroscopic studies are carried out on Ag₃[Co(CN)₆] to investigate the spectral changes across the reported trigonal–monoclinic transition, obtain the mode Grüneisen parameters in both phases, and further investigate the stability of the monoclinic phase at higher pressure. Behavior of the compound at low temperatures down to 80 K is also investigated to understand the anharmonicity of different vibrations.

II. EXPERIMENTAL DETAILS

The compound $Ag_3[Co(CN)_6]$ was prepared by precipitation from the aqueous solution of $K_3Co(CN)_6$ and AgNO₃ in a procedure similar to that reported by Goodwin *et al.*⁸ and was characterized by a powder x-ray diffraction pattern. The refined unit cell parameters a = 7.025(1) and c = 7.102(1) Å (space group $P\bar{3}lm$) match well with the reported data.²⁰ Raman measurements at high pressure were carried out from inside a diamond anvil cell (DAC) (model B-05, Diacell Products, Leicester, U.K.). A 4:1 methanol-ethanol mixture was used as the pressure transmitting medium. Raman spectrum of polycrystalline sample from inside the DAC was excited using a 532-nm line of power of \sim 15 mW. Pressure inside the cell was measured using the standard ruby fluorescence technique.²¹ Scattered light was analyzed using a home-built 0.9-m single monochromator, coupled with a supernotch filter and detected by a cooled charge coupled device (Andor Technology). The entrance slit was kept at 50 μ m, which gives a spectral band pass of 3 cm⁻¹, and Raman spectra could be reproduced with an accuracy of ± 0.2 cm⁻¹. Raman measurements at low temperatures up to 80 K were carried out using the temperature stage Linkam THMS 600.

III. RESULTS AND DISCUSSION

The compound Ag₃[Co(CN)₆] belongs to centrosymmetric space group $P\bar{3}Im$ (D_{3d}^{-1}) , with Z = 1 at ambient conditions.²⁰ The Raman- and infrared-active modes are mutually exclusive. In the absence of single crystals, Raman-active modes are identified comparing the spectrum with that of H₃Co(CN)₆²² which is isostructural to the title compound,²³ and of related hexacyano compounds,²⁴ such as $K_3Co(CN)_6^{25}$ and $K_3Fe(CN)_6^{25,26}$ Figure 1 shows the Raman spectrum of $Ag_3[Co(CN)_6]$ at ambient conditions. The lowest frequency mode that could be followed in the present studies, appears at 87 cm^{-1} . Librations corresponding to Co-(CN)₆ and Ag-related modes appear at frequencies of less than 200 cm⁻¹. The region 300-600 cm⁻¹ consists of Co-CN bending and Co-C stretching vibrations.^{25,26} Raman bands in the region 2000–2300 cm⁻¹ corresponds to the C=N stretching vibrations.^{22,24–26} The mode at 139 cm⁻¹ and those in the C \equiv N stretching vibrations appear as the strongest bands in phase PI.

Upon increasing the pressure, the strong modes of the ambient phase lose intensity rapidly, and above 0.2 GPa, a



FIG. 1. Raman spectrum of $Ag_3[Co(CN)_6]$ at various pressures. (a) The asterisks indicate the weak modes of phase PII. (b) The arrow indicates the broad C=N stretching mode in phase PII, which has a negative pressure dependence.

new set of modes appear, consistent with large changes in the framework structure reported across the trigonal to the monoclinic transition of ~0.19 GPa.¹¹ A new set of broad bands appear in the spectral region of 230 and 320 cm^{-1} in the high-pressure phase. In some high-pressure runs, relatively sharp Raman bands of $\sim 200, 450, \text{ and } 475 \text{ cm}^{-1}$ were also noted in phase PII. Figure 1 shows the Raman spectrum of the title compound at high pressure from such runs, wherein relatively sharp modes were also observed in phase PII. Coexistence of both phase PI and phase PII were noted over a small range of pressure, and typically at pressures above 1 GPa, no Raman bands characteristic of phase PI could be observed. Experiments were also carried out without any pressure transmitting medium. Figure 2 shows the evolution of Raman spectrum when no pressure transmitting medium is used. The weak, sharp bands at 450, 475 cm^{-1} above 1 GPa in Fig. 1 are identical to those observed in Fig. 2. Furthermore, sharper Raman bands are observed in the spectral region 140-400 cm⁻¹, which match with the sharp features of hydrostatic runs. In the context of understanding the structural relationship of phases PI and PII and the mechanism of transformation, Goodwin et al.¹¹ proposed shearing of the unit cell perpendicular to the c-axis in phase PI. It is well known that shear-induced transitions are favored under nonhydrostatic conditions.²⁷ More complete transformation to phase PII observed in the present work, under nonhydrostatic conditions, may be interpreted as the shear component of the uniaxial stress facilitating the transformation.

Figure 3 shows the pressure dependence of Raman modes in phases PI and PII. Two of the modes, at 325 and 335 cm⁻¹ in phase PI, show negative pressure dependence, which is more clearly seen in the nonhydrostatic experiment. One of the new modes in the C \equiv N stretching region has negative pressure



FIG. 2. (a) and (b) Evolution of the Raman spectrum of $Ag_3[Co(CN)_6]$ at high pressures when no pressure transmitting medium is used.



dependence in phase PII, up to about 1 GPa; thereafter, it is positive. With further pressurization, the broad peak occurring $\sim 230 \text{ cm}^{-1}$ dominates the Raman spectra in the low frequency region [Fig. 1(a)] accompanied by another broad peak [indicated by the arrow in Fig. 1(b)] appears toward the low frequency side of the $C \equiv N$ stretching mode, which is noted as the dominant feature in the spectrum above 6 GPa. The broad feature in the C \equiv N stretching region has two components; both of them exhibit negative pressure dependence in phase PII. Broadening of the Raman bands may be because of disorder (a wider distribution in bond lengths and bond angles in the system) or because of disorder-induced breakdown of Raman selection rules, resulting in phonons other than zone center phonons contributing to Raman intensity. Pressure dependence of all mode frequencies is found to be decreased in phase PII. Above 10 GPa, the sample turned black and only broad features dominated the Raman spectrum. Even in the experiments where no pressure transmitting medium is used, the sharp Raman bands rapidly lose intensity with the appearance of broad features in the Raman spectrum, clearly indicating that the high-pressure behavior of the compound is same under hydrostatic or nonhydrostatic conditions.

The Raman spectrum of the pressure-released sample showed broad modes occurring ~1370 and 1570 cm⁻¹, which are typical of amorphous carbon nitride, *a*-CN^{28,29} along with weak intensities corresponding to partially recovered phases PI and PII of Ag₃[Co(CN)₆]. In addition, broad modes are observed occurring ~500 and 700 cm⁻¹. Figure 4 shows the Raman spectra recorded from different regions of pressure cycled (p-cycled) Ag₃[Co(CN)₆]. The typical spectrum of the p-cycled sample is shown in curve (c) of Fig. 4. From



FIG. 3. Pressure dependence of Raman mode frequencies of $Ag_3[Co(CN)_6]$. The arrow indicates the trigonal-to-monoclinic transition pressure. Open and filled symbols are from experimental runs with and without pressure transmitting medium, respectively.

FIG. 4. Raman spectra of $Ag_3[Co(CN)_6]$ (a) at ambient conditions and (b) and (c) at different regions of the sample recovered from 14 GPa. Positions (in reciprocal centimeters) marked in curve (b) are found to match the set of Raman modes expected for crystalline Co_3O_4 (Ref. 30).

Frequency	PI			PII	
ω (cm ⁻¹)	$d\omega/dP (\mathrm{cm}^{-1}/\mathrm{GPa})$	γi	$d\omega/dT \times 10^2 \text{ (cm}^{-1}/\text{K)}$	$d\omega/dP$ (cm ⁻¹ /GPa)	γi
87	10(1)	0.75	-1.0(2)		
139	20(2)	0.94	-0.9(1)		
165	11(2)	0.43	-0.9(1)		
167 ^{c,d}				5.2(8)	0.37
194 ^{c,d}				5.8(6)	0.35
246 ^c				2.4(3)	0.12
310 ^{c,d}				-3.0(3)	-0.11
323 ^{c,d}				-1.6(3)	-0.06
325 ^d	-9(2)	-0.18			
332 ^{c,d}				-0.4(3)	-0.01
335 ^d	-4.7(8)	-0.09	-0.03(1)		
457°				2.3(6)	0.06
474	3.5(8)	0.05	-0.2(1)		
475°				4.2(4)	0.1
521	25(3)	0.31	-3.4(2)		
2110 ^c				-5.3(6)	-0.03
2141 ^c				-3(1)	-0.02
2141 ^c				2.9(4)	0.02
2146 ^c				4.0(4)	0.02
2153°				4.9(3)	0.03
2184	6(1)	0.02	-5.1(3)		
2204	10(1)	0.03	-5.7(3)		

TABLE I. Pressure coefficients of all observed Raman modes in Ag₃[Co(CN)₆] in both phase PI and phase PII are given.^{a,b}

^aGrüneisen parameters (γ_i) are calculated using values of bulk modulus $B_0 = 6.5$ and 11.8 GPa for the two phases PI and PII, respectively. ^bPressure and temperature dependence were obtained by linear fit to the experimental data. Numbers in the parentheses denote error in the last significant digit.

^cFrequency of the new Raman modes appearing in phase PII extrapolated to ambient pressure.

^dData obtained from nonhydrostatic experiments.

a few spots of the recovered sample, a sharp set of modes characteristic of crystalline compound, different from both the trigonal and the monoclinic phase of $Ag_3[Co(CN)_6]$, is observed in addition to the amorphous feature. The representative spectrum is shown in curve (b) of Fig. 4. This set of modes is identified to result from crystalline, Co_3O_4 ,³⁰ clearly showing evidence for partial decomposition of $Ag_3[Co(CN)_6]$ in the pressure-reducing cycle. This further suggests that the broad features occurring \sim 500 and 700 cm⁻¹ in curve (c) may be because of poorly crystallized Co_3O_4 . The Raman spectrum of the p-cycled sample obtained in the present studies appears to be similar to that reported in $FeCo(CN)_6$. Pressure-induced amorphization was reported in the Prussian blue analog²⁹ FeCo(CN)₆, wherein the Raman spectrum of the pressure-cycled sample showed features of amorphous CN_x . In addition, evidence for the Co atom being expelled from the lattice is clearly observed in the present work.

Pressure dependence of the mode frequencies was analyzed to obtain the mode Grüneisen parameter of Ag₃[Co(CN)₆] in phases PI and PII, and the results are shown in Table I. The Raman modes at 139 and 521 cm⁻¹ are found to have very large values of pressure dependence of 20 and 25 cm⁻¹/GPa, respectively, in PI, whereas the mode at 474 cm⁻¹ shows weak pressure dependence. Pressure dependence of CN bending modes and stretching modes in Ag₃[Co(CN)₆] are comparable to that reported in Zn(CN)₂.⁷ From Table I, only two of the nine observed Raman modes exhibit softening in the trigonal phase in Ag₃[Co(CN)₆]. Both of these modes are cobalt-related bending modes. However, because the mode Grüneisen parameter (γ_i) of these modes is small, their contribution is outweighed by that of modes with large γ_i . Phonon calculations in $Ag_3[Co(CN)_6]^{14}$ estimated the mode Grüneisen parameters γ_i to be widely varying from -3 to +3; the observed values of γ_i in $Ag_3[Co(CN)_6]$ are however lesser, ranging from -0.12 to 0.94.



FIG. 5. (a) Raman spectra of $Ag_3[Co(CN)_6]$ in the temperature range 80–290 K, and (b) the temperature dependence of mode frequencies.

Frequencies at ambient conditions (cm^{-1})	Mode description	ω_p at 0.19 GPa (cm ⁻¹)	ω_T at 80 K (cm ⁻¹)
87		88.9(2)	89.1(4)
139	C-Co-C deformation ²⁵	142.8(4)	140.9(2)
165	N-Ag-N bending ¹³	167.1(4)	166.9(2)
335	Co-CN bending ²⁵	334.1(2)	335.06(2)
474	Ag-N stretching ¹³	474.8(1)	474.4(2)
521	Co-C stretching ²⁵	525.8(6)	528.1(4)
2184	$C \equiv N$ stretching	2185.1(2)	2194.7(6)
2204	C≡N stretching	2205.9(2)	2216(1)

TABLE II. Frequencies of all Raman modes in $Ag_3[Co(CN)_6]$ in phase PI at ambient conditions, at pressure 0.19 GPa in phase PI, and at 80 K.

To have further insight to the phonon behavior of this compound, Raman spectroscopic studies of $Ag_3[Co(CN)_6]$ in the temperature range 80–290 K were carried out. Figure 5(a) shows the Raman spectrum of $Ag_3[Co(CN)_6]$ at different temperatures. All Raman frequencies are found to increase with decrease in temperature; furthermore, the changes in the line width are gradual. No discontinuous changes are noted in the Raman spectrum down to 80 K, the lowest temperature reached in the present work. Absence of any phase transition agrees well with those of the structural and differential scanning calorimetric studies.⁸ Temperature-driven phase transition in a few other cyanide compounds such as $K_3Co(CN)_6^{31}$ and $K_3Fe(CN)_6^{32}$ is known; however, these are soft-mode-driven second-order displacive transitions, unlike in $Ag_3[Co(CN)_6]$.

Temperature dependence of mode frequencies is shown in Fig. 5(b). Temperature dependence of the phonon frequencies, which reflects the anharmonicity of the vibration, may be resolved into two components, i.e., the implicit (arising because of change in volume) and explicit (true anharmonicity) contributions.³³ Implicit contribution is estimated from the reported P-V relation of the compound and the observed pressure dependence of the phonon frequencies, thus enabling us to infer the truly anharmonic contributions of different vibrations. In the case of Ag₃[Co(CN)₆], from the available structural data at high pressures,¹¹ we see that the reported volume V^{34} at 0.19 GPa (295.8 Å³) is very close to the volume reported on cooling down to 80 K. Table II shows the frequency of Raman modes in phase PI observed at comparable volumes achieved by pressurization and cooling down to 80 K. The frequency shift of four of the Raman modes at the volume V by way of compression is nearly the same as that achieved by lattice contraction upon cooling, implying that the temperature dependence of the mode frequencies is predominantly from implicit contribution. The differences in the phonon frequencies are significant for the modes at 139, 521, 2184, and 2204 cm^{-1} , indicating the highly anharmonic nature of these modes. In the context of understanding the trigonal-monoclinic transition, Goodwin *et al.*¹¹ conjectured that the transition may be because of Ag-Ag interactions that are highly anharmonic, which do not allow the system to accommodate further reduction in volume at room temperature. Present results, which indicate many modes are indeed highly anharmonic, support this view, though they do not give specific information about the Ag-related modes. Interestingly, we find that the cobalt-related modes and the C=N stretching modes are more anharmonic than the other modes. The ambient pressure trigonal phase being a centrosymmetric structure, there may be more vibrations that are highly anharmonic but not identified in the present work because they may not be Raman active.

IV. CONCLUSION

High-pressure behavior of Ag₃[Co(CN)₆] is investigated up to 16 GPa using Raman spectroscopy. Mode Grüneisen parameters in the trigonal and monoclinic phases are evaluated. Three of the Raman modes below 165 cm^{-1} show large positive values of Grüneisen parameters in the trigonal phase; in addition, the mode at 521 cm^{-1} is found to have a comparable mode Grüneisen parameter. Two Raman modes are found to have negative Grüneisen parameters in phase PI. The compound has been found to undergo irreversible amorphization above 13 GPa. The pressure-released spectrum of the compound indicates decomposition of the compound into amorphous carbon nitride. In addition, the p-released spectrum was noted to be due to crystalline Co_3O_4 , confirming decomposition of the compound in the p-reducing cycle. Temperature dependence of the phonon frequencies in the trigonal phase at ambient pressure is obtained, and the modes that are more anharmonic compared to the other modes are identified.

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¹J. S. O. Evans, T. A. Mary, T. Vogt, M. A. Subramanian, and A. W. Sleight, Science **272**, 90 (1996).

²J. S. O. Evans, T. A. Mary, and A. W. Sleight, J. Solid State Chem. **133**, 580 (1997) and references therein.

- ³C. A. Perottoni and J. A. H. da Jornada, Science **280**, 886 (1998); W. I. F. David, J. S. O. Evans, and A. W. Sleight, Euro. Phys. Lett. **46**, 661 (1999); J. D. Jorgensen, Z. Hu, S. Teslic, D. N. Argyriou, S. Short, J. S. O. Evans, and A. W. Sleight, Phys. Rev. B **59**, 215 (1999); T. R. Ravindran, A. K. Arora, and T. A. Mary, Phys. Rev. Lett. **84**, 3879 (2000); D. Cao, F. Bridges, G. R. Kowach, and A. P. Ramirez, Phys. Rev. B **68**, 014303 (2003); C. A. Kennedy and M. A. White, Solid State Commun. **134**, 271 (2005); M. G. Tucker, A. L. Goodwin, M. T. Dove, D. A. Keen, S. A. Wells, and J. S. O. Evans, Phys. Rev. Lett. **95**, 255501 (2005); C. Pantea, A. Migliori, P. B. Littlewood, Y. Zhao, H. Ledbetter, J. C. Lashley, T. Kimura,
- J. VanDuijn, and G. R. Kowach, Phys. Rev. B 73, 214118 (2006).
 ⁴A. K. A. Pryde, K. D. Hammonds, M. T. Dove, V. Heine, J. D. Gale, and M. C. Warren, J. Phys. Condens. Matter 8, 10973 (1996);
- R. Mittal and S. L. Chaplot, Phys. Rev. B **60**, 7234 (1999). ⁵A. L. Goodwin and C. J. Kepert, Phys. Rev. B **71**, 140301(R) (2005).
- ⁶J. W. Zwanziger, Phys. Rev. B **76**, 052102 (2007).
- ⁷T. R. Ravindran, A. K. Arora, S. Chandra, M. C. Valsakumar, and N. V. Chandra Shekar, Phys. Rev. B **76**, 054302 (2007).
- ⁸A. L. Goodwin, M. Calleja, M. J. Conterio, M. T. Dove, J. S. O. Evans, D. A. Keen, L. Peters, and M. G. Tucker, Science **319**, 794 (2008).
- ⁹S. J. Hibble, A. M. Chippindale, A. H. Pohl, and A. C. Hannon, Angew. Chem. Int. Ed. **46**, 7116 (2007).
- ¹⁰A. L. Goodwin, M. T. Dove, A. M. Chippindale, S. J. Hibble, A. H. Pohl, and A. C. Hannon, Phys. Rev. B **80**, 054101 (2009).
- ¹¹A. L. Goodwin, D. A. Keen, and M. G. Tucker, Proc. Natl. Acad. Sci. USA **105**, 18708 (2008).
- ¹²S. Margadonna, K. Prassides, and A. N. Fitch, J. Am. Chem. Soc. **126**, 15390 (2004).
- ¹³K. W. Chapman, P. J. Chupas, and C. J. Kepert, J. Am. Chem. Soc. 128, 7009 (2006).
- ¹⁴M. J. Conterio, A. L. Goodwin, M. G. Tucker, D. A. Keen, M. T. Dove, L. Peters, and J. S. O. Evans, J. Phys. Condens. Matter 20, 255225 (2008).
- ¹⁵A. L. Goodwin, D. A. Keen, M. G. Tucker, M. T. Dove, L. Peters, and J. S. O. Evans, J. Am. Chem. Soc. **130**, 9660 (2008).

- ¹⁶L. Korčok, M. J. Katz, and D. B. Leznoff, J. Am. Chem. Soc. **131**, 4866 (2009).
- ¹⁷M. Calleja, A. L. Goodwin, and M. T. Dove, J. Phys. Condens. Matter **20**, 255226 (2008).
- ¹⁸T. R. Ravindran, A. K. Arora, and T. A. Mary, Phys. Rev. B **67**, 064301 (2003).
- ¹⁹J. D. Jorgensen, Z. Hu, S. Teslic, D. N. Argyriou, S. Short, J. S. O. Evans, and A. W. Sleight, Phys. Rev. B **59**, 215 (1999).
- ²⁰V. A. Ludi and H. U. Gudel, Helv. Chim. Acta **51**, 1762 (1968).
- ²¹G. J. Piermarini and S. Block, Rev. Sci. Instrum. **46**, 973 (1975).
- ²²R. Haser, B. Bonnet, and J. Rozere, J. Mol. Struct. **40**, 177 (1977).
- ²³L. Pauling and P. Pauling, Proc. Natl. Acad. Sci. USA **60**, 363 (1968).
- ²⁴W. P. Griffith and G. T. Turner, J. Chem. Soc. A 858 (1970).
- ²⁵I. Nakagawa, Bull. Chem. Soc. Japan **46**, 3690 (1973).
- ²⁶Z. Iqbal, J. Phys. C Solid State Phys. **10**, 3533 (1977).
- ²⁷H. Giefers and F. Porsch, Physica B **400**, 53 (2007).
- ²⁸A. C. Ferrari, S. E. Rodil, and J. Robertson, Phys. Rev. B 67, 155306 (2003); R. Rao, T. Sakuntala, S. K. Deb, and R. Mukhopadhyay, J. Phys. Condens. Matter 17, 2633 (2005).
- ²⁹J. Catafesta, J. Haines, J. E. Zorzi, A. S. Pereira, and C. A. Perottoni, Phys. Rev. B **77**, 064104 (2008).
- ³⁰V. G. Hadjiev, M. N. Iliev, and I. V. Vergilov, J. Phys. C 21, L199 (1988).
- ³¹Y. Morioka and I. Nakagawa, J. Phys. Soc. Japan 52, 23 (1983).
- ³²A. Saito, Y. Morioka, and I. Nakagawa, J. Phys. Chem. **88**, 480 (1984).
- ³³B. A. Weinstein and R. Zallen, in *Light Scattering in Solids IV*, edited by M. Cardona and G. Guntherodt (Springer-Verlag, Berlin, 1984) p. 463.
- ³⁴Taking the lattice parameters a = 7.0255 Å and c = 7.1251 Å at ambient conditions (Ref. 14), volume V_P of Ag₃[Co(CN)₆] at 0.19 GPa, calculated using bulk modulus $B_0 = 6.5$ GPa (Ref. 11), turns out to be 295.8 Å³. Reported lattice parameters at 80 K, taken from Fig. 3 of Ref. 8, of a = 6.82 Å and c = 7.33 Å give a volume of 295.3 Å³.