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Optical, synchrotron X-ray and neutron diffraction investigations of structural changes in the layered compound $K_2Na[Ag(CN)_2]_3$

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Abstract

We report a study of single-crystal Raman scattering, powder synchrotron X-ray and neutron diffraction as well as specific heat for the layered compound $K_2Na[Ag(CN)_2]_3$ in the temperature range 2–300 K. Analysis of the Raman scattering data provides evidence for structural changes at approximately 210 K. Synchrotron X-ray and neutron powder diffraction results indicate essential, gradual changes with temperature in the range from 1.5 to 300 K and in particular small, but significant deviations from trigonal symmetry of the pseudo-hexagonal lattice parameters $a = a_{\mathrm{ortho}}/\sqrt{3}, b$ below approximately 210 K. The c-lattice parameter increases anomalously with decreasing temperature. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: C. Crystal structure and symmetry; C. X-ray scattering; D. Optical properties; E. Inelastic light scattering; E. Neutron scattering

1. Introduction

Single crystals of $K_2Na[Ag(CN)_2]_3$ have recently been studied by our research groups. We have found that they display luminescence thermochromism, an optical phenomenon in which different emission bands are observed at different temperatures [1,2]. The photoluminescence spectra of $K_2Na[Ag(CN)_2]_3$ show two emission bands: a lower energy (LE) blue emission with a maximum around 410 nm and a higher energy (HE) ultraviolet emission with a maximum near 315 nm [3]. We observe luminescence thermochromism upon increasing the temperature from 10 K to room temperature. The HE band dominates at 10 K, but upon increasing temperature, the LE band increases in intensity to become the dominant emission at 80 K. As the temperature is further increased, the HE band reappears and becomes the dominant emission at near ambient temperatures. One possible explanation for this behavior is that the system undergoes a structural change near 80 K, which leads to a change in the distribution of the clusters responsible for the luminescence bands.

The structure of the title compound has previously been determined at room temperature by means of single crystal X-ray diffraction, corresponding to space group $P\bar{3}1m$ [4]. However, since the luminescence data suggest structural variations, variable temperature Raman scattering, specific heat, synchrotron X-ray and neutron powder diffraction studies have been conducted to further investigate the chemical structure of the title compound in the temperature range from 1.5 to 300 K. Results from these investigations, which will be reported herein, indicate essential structural changes as a function of temperature.

Phase transitions in other dicyanoargentates (I) have previously been investigated through pressure dependent Raman scattering studies. For example, the vibrational spectra of $KAg(CN)_2$ are well-documented in the literature [5–7], as are the pressure dependent spectra [8,9]. To the best of our knowledge, this is the first temperature dependent Raman scattering study of structural changes in a dicyanoargentate.

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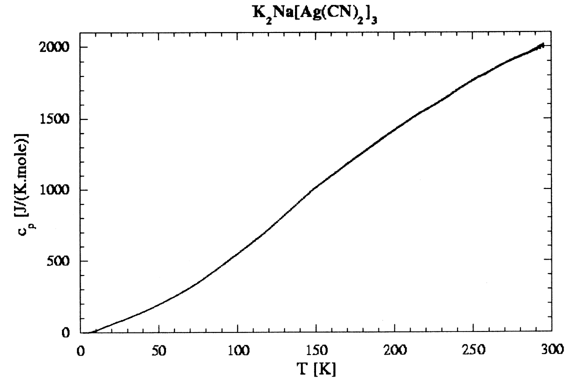

Fig. 1. Temperature dependence of the specific heat of $K_2Na[Ag(CN)_2]_3$.

2. Experimental

Single crystals of $K_2Na[Ag(CN)_2]_3$ were grown as described in the literature [4]. The Raman scattering experiments were carried out using the 514.5 nm line of an Innova 90-2A argon ion laser as the excitation source. A Ramanor 2000M holographic double monochromator equipped with a Pelletier water-cooled quantum photometer, Princeton Applied Research Model 1140, was used to collect and record the data. The sample was mounted on a copper holder and placed within a Model Lt-3-110 Heli-Tran cryogenic liquid transfer system from Air Products equipped with a temperature controller. Liquid nitrogen was used as the coolant for most of the low-temperature experiments. Liquid helium was used for measurements made below 80 K. The same single crystal was used for all Raman measurements.

Complementary high-resolution synchrotron X-ray and high-resolution neutron diffraction investigations of well crystalline powder samples of the title compound were performed at SNBL/ESRF and on diffractometer D1A at the high flux reactor of ILL, Grenoble, respectively, in the temperature range from 1.5 to 300 K. For the diffraction experiments crystallites of $K_2Na[Ag(CN)_2]_3$ were powdered and enclosed under a He gas atmosphere into thin quartz capillaries or into a container of 15 mm diameter and approximately 5 cm height in case of X-rays and neutrons, respectively.

Using the PPMS system of the laboratory for neutron scattering of ETHZ & PSI, the specific heat of $K_2Na[Ag(CN)_2]_3$ was measured in the temperature range from 1.5 to 300 K. In particular at higher temperatures, corrections for contributions due to the low-temperature grease were found to be important. The results are shown in Fig. 1.

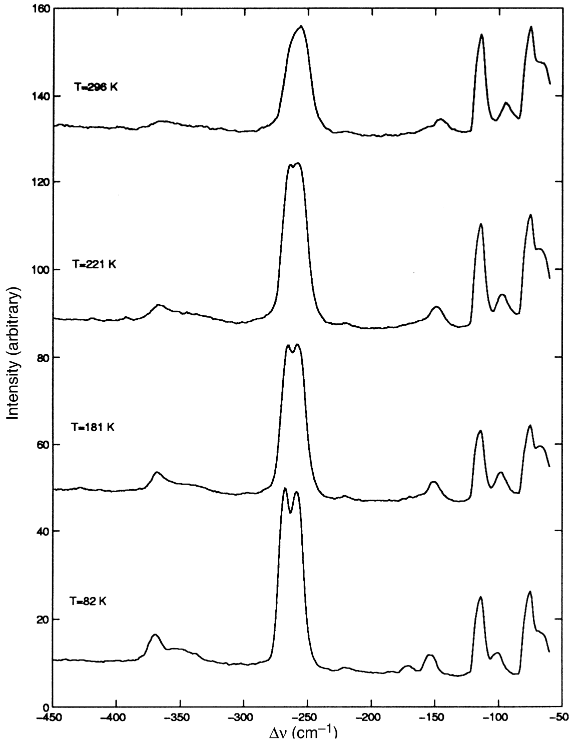

Fig. 2. Raman shift vs. intensity for $T = 82$, 181, 221 and 296 K. The plots are offset by 40 units each for clarity.

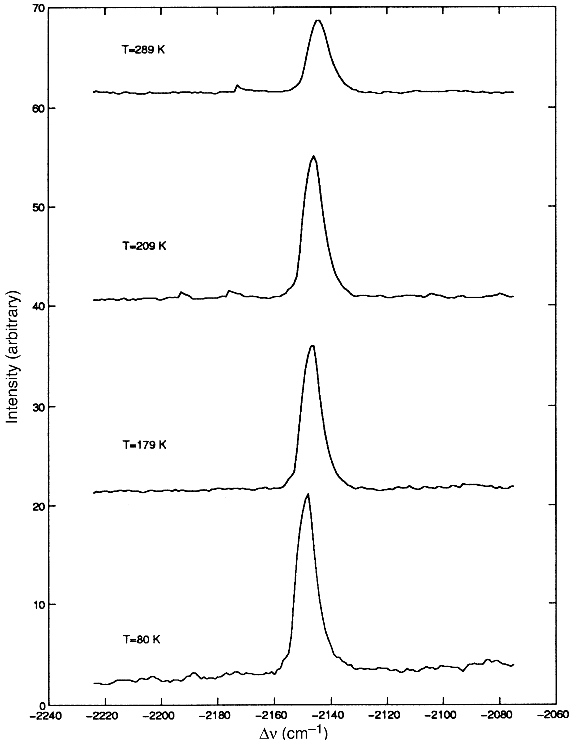

Fig. 3. Raman shift vs. intensity for $T = 80$, 179, 209 and 289 K. Plots are offset by 20 units each for clarity.

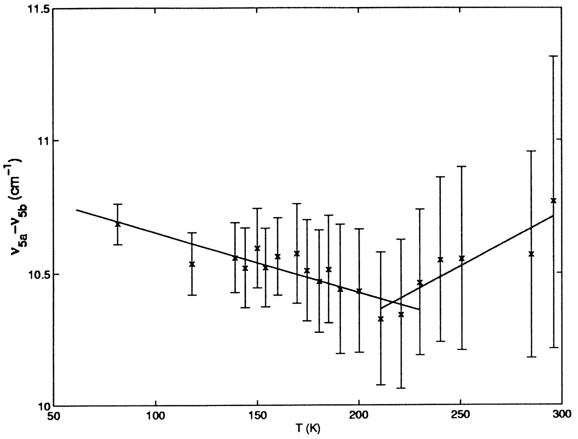

Fig. 4. Relative energy of split peaks in C–N bending mode as a function of temperature.

Table 1
Assignment of frequencies in Raman spectrum of $K_2Na[Ag(CN)_2]_3$

ν(RT, cm^{-1})	ν(80 K, cm^{-1})	Assignment	Representation
75	75	Phonons	
96	101		
114	114		
146	154	ν_{7a}	Π_u
147	171	ν_{7b}	Π_u
255	258	ν_{5a}	Π_g
265	268	ν_{5b}	Π_g
365	365	ν_2	Σ_g^+
2144	2148	ν_1	Σ_g^+

3. Results and discussion

Representative Raman spectra at selected temperatures are shown in Figs. 2 and 3. The $Ag(CN)_2^-$ ions are virtually linear in the crystal, with the C–Ag–C angle reported as 180° and the N–C–Ag angle as 176.65° [4]. Approximating this as a linear ion, we assign it to the space group $D_{\infty h}$. The vibrational modes of a linear A–B–C–B–A type molecule have been worked out previously [5] and the notation from this reference will be followed here. Frequency assignments are given in Table 1.

Examining the low frequency region of the spectrum, we note the splitting of the C–N bending mode (ν_5, ~265 cm^{-1}) at low temperatures. To further investigate this splitting, a nonlinear least squares fitting routine was applied to fit the data to a sum of two Gaussian functions on a quadratic background, yielding frequencies for each of the two peaks. Fig. 4 shows a plot of the relative frequency, $\nu_{5a} - \nu_{5b}$, as a function of temperature. We note that the peaks grow closer together until approximately 210 K at which point they begin to grow steadily further apart. The error associated with each point increases significantly at higher temperatures due to the overlapping of the peaks. Since the change is so slight and the error is so great, we expect there to be a fair amount of uncertainty in the point of interest 210 K, which is where we expect to see structural changes.

Fig. 5 shows the position as a function of temperature of the five lowest energy bands resolved, three of which we have assigned as phonon bands. These three phonon bands all experience small, continuous increases in energy with

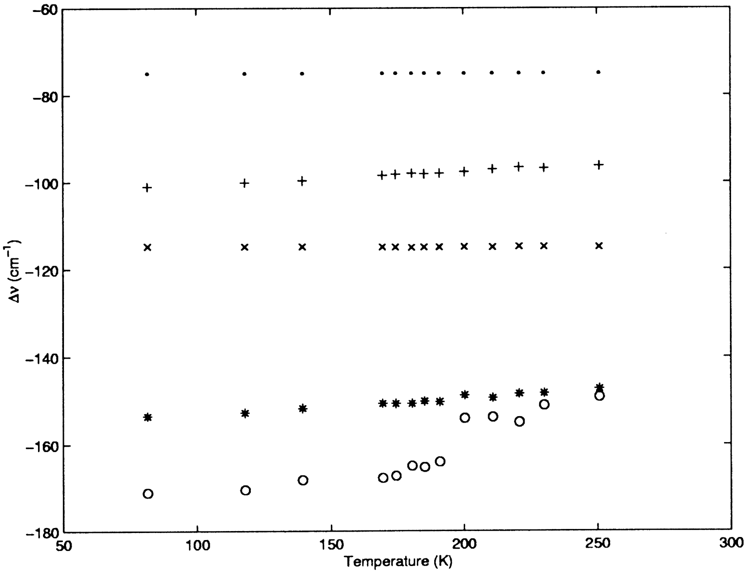

Fig. 5. Frequencies of five low energy bands as a function of temperature.

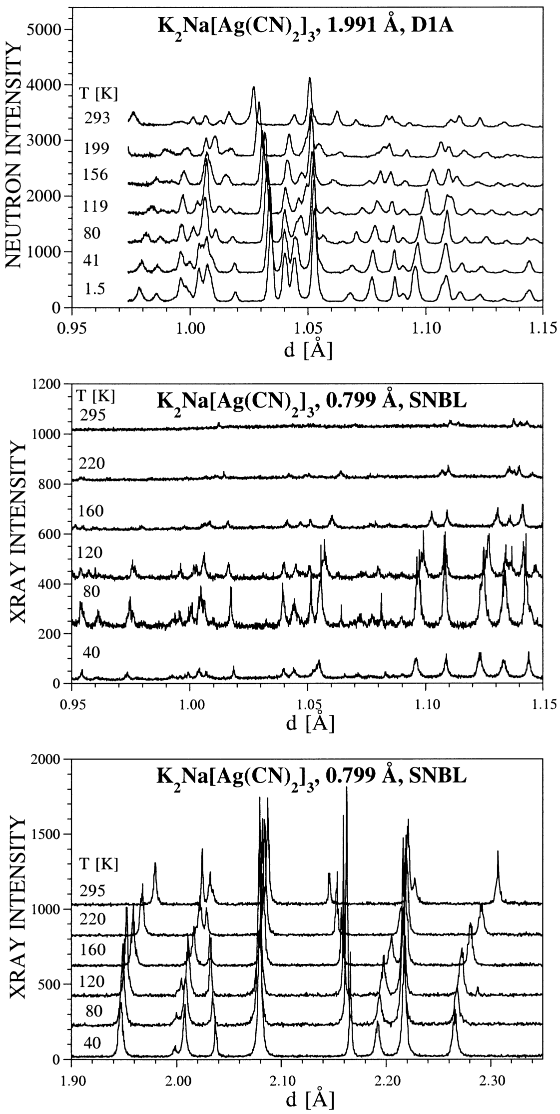

Fig. 6. Comparison of neutron and SNBL X-ray diffraction data of $K_2Na[Ag(CN)_2]_3$ versus lattice spacing *d*, as a function of temperature.

decreasing temperatures. However, the highest energy band in this group exhibits a discontinuous jump of 10 cm^{-1} at ~200 K, with a total shift of ~24 cm^{-1} in going from 80 K to room temperature. This behavior has led us to assign this highest energy pair to the typically Raman-inactive C–Ag–C bending mode (ν_7, Π_u). This assignment is in agreement with that of Loehr [7] and Bottger [6] from their studies of the similar compound $KAg(CN)_2$.

The C–N stretching mode (ν_1, ~2150 cm^{-1}), however, does not exhibit any splitting over the entire temperature range studied. It does undergo a small, apparently continuous increase in energy as the temperature decreases, with a total shift of ~5 cm^{-1}.

The very weak Ag–C stretching mode (ν_2, ~360 cm^{-1}) appears to split at low temperatures. Analysis of this splitting reveals three closely spaced peaks. Preliminary examination of the frequency shifts of these three peaks reveals that the highest energy peak (~365 cm^{-1}) exhibits behavior similar to that of the C–N stretching mode, shifting a total of approximately 5 cm^{-1} between 80 and 296 K. However, the other two peaks, which are vanishingly weak at higher temperatures, behave in a manner similar to that of the bending modes, with a discontinuity at approximately 200–210 K. This suggests that this is not one mode split into three peaks, but perhaps two separate modes. Following the findings of Loehr [7], we tentatively assign the two LE peaks in this group to the typically Raman-inactive asymmetric bending mode, ν_6, Π_u and the highest energy peak to the previously mentioned stretching mode ν_2, Σ_g^+.

The discontinuous behavior in the bending modes around 200–215 K indicates structural variations in this temperature range. We suspect that the different patterns of behavior in the stretching and bending modes (continuous as opposed to discontinuous variations) is related to the changes in the lattice parameters as a function of temperature.

Characteristic results of the neutron and X-ray diffraction experiments are illustrated in Fig. 6. Because of rather large preferred orientation effects in the D1A measurements with stationary sample we first performed both for neutrons and X-rays profile matching fits with program FullProf [10] to obtain the temperature dependencies of the lattice parameters. Although the crystallinity of the powder sample of $K_2Na[Ag(CN)_2]_3$ proved to be very good in the synchrotron

Table 2
Interatomic Ag···Ag distances as a function of temperature for the *C*2/*m* structural model

T (K)	Ag(1)···Ag(2) (Å)	Ag(2)···Ag(2′) (Å)	
40	3.46192(3)	3.45805(3)	Ag(1)···Ag(2)> Ag(2)···Ag(2′)
80	3.46641(3)	3.46222(4)	Ag(1)···Ag(2)> Ag(2)···Ag(2′)
120	3.47247(4)	3.46870(5)	Ag(1)···Ag(2)> Ag(2)···Ag(2′)
160	3.48502(3)	3.48146(4)	Ag(1)···Ag(2)> Ag(2)···Ag(2′)
220	3.49818(3)	3.50208(3)	Ag(1)···Ag(2)< Ag(2)···Ag(2′)
295	3.52232(4)	3.52535(5)	Ag(1)···Ag(2)< Ag(2)···Ag(2′)

Table 3
Unit cell dimensions as a function of temperature for the *C*2/*m* structural model, as determined from the synchrotron X-ray data

T (K)	a_m (Å)	b_m (Å)	c_m (Å)	β(°)
40	6.91610(6)	11.99690(11)	8.66420(6)	90.026(2)
80	6.92445(9)	12.01281(15)	8.65184(8)	90.039(2)
120	6.93740(9)	12.03333(16)	8.63869(8)	90.036(2)
160	6.96292(8)	12.07656(14)	8.63117(8)	89.978(2)
220	7.00415(6)	12.11355(11)	8.61212(7)	89.969(2)
295	7.05070(10)	12.19818(18)	8.58368(9)	90.035(2)

X-ray measurements, the small deviations from trigonal symmetry are only reflected in slightly larger peak widths of trigonal Bragg reflections such as (*hk0*) compared to (001), as space group $P\bar{3}1m$ does not impose extinction rules. This is presumably the reason why automatic peak indexing of the first 20 lines by programs such as DICVOL91 of e.g. the 40 K X-ray data was less conclusive, also suggesting the trigonal lattice as a possible solution. We therefore also considered the possibility of anisotropic peak broadening. However, in view of the optical results showing evidence for a structural phase transition around 210 K, we abandoned this idea and think that the true symmetry of $K_2Na[Ag(CN)_2]_3$ is monoclinic at least at temperatures below 210 K, but the synchrotron X-ray data point to at least orthorhombic symmetry at room temperature.

The high-resolution neutron diffraction and synchrotron X-ray powder data measured at sample temperatures from 1.5 to 300 K were analyzed using the profile constrained structural refinement computer program ZOMBIE based on the Rietveld refinement method [11,12]. The $Ag(CN)_2^-$ ions were constrained to be linear with interatomic distances Ag–C and C–N kept constant at essentially those distances found in the previously reported single crystal X-ray diffraction study at room temperature [4]. It was found that although the previously reported structure with space group $P\bar{3}1m$ [4] gave good agreement with the observed profile data, significantly better agreement could be obtained for a monoclinic structure with space group *C*2/*m*.

The interatomic distances between the neighbouring Ag-atoms, and unit cell dimensions for the C2/m structural model, are shown in Tables 2 and 3, respectively, for sample temperatures between 40 and 295 K. Coordinates of equivalent (silver) positions are:

$$(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},0)$$

$$+\ \mathrm{Ag}(1):\ 0,\tfrac{1}{2},0;(2/m) \rightarrow 2\ \text{atoms/unit cell}$$

$$\mathrm{Ag}(2):\ \tfrac{1}{4},\tfrac{1}{4},0;\ \tfrac{1}{4},\tfrac{3}{4},0;\ (\bar{1}) \rightarrow 4\ \text{atoms/unit cell.}$$

The relationship between the monoclinic unit cell (*C*2/*m*) and the pseudo-hexagonal unit cell is given by:

$$a_h = a_m,\ \ b_h = \frac{1}{2}\sqrt{(a_m^2 + b_m^2)},\ \ c_h = c_m,$$

$$\alpha_h = 90°,\ \ \beta_h \approx 90°,\ \ \gamma_h = 90° + \tan^{-1}\left(\frac{a_m}{b_m}\right)$$

It is noted that the pseudo-hexagonal (trigonal) structure would become actual hexagonal (trigonal) with space group $P\bar{3}1m$, if the following relationships are satisfied:

$$a_h = a_m = b_h = \left(\frac{1}{\sqrt{3}}\right)b_m,\ \ c_h = c_m,$$

$$\alpha_h = \alpha_m = 90°,\ \ \beta_h = \beta_m = 90°,$$

$$\gamma_h = 90° + \tan^{-1}\left(\frac{a_m}{b_m}\right) = 120°$$

The two site symmetries for *C*2/*m* would both become (2/*m*)

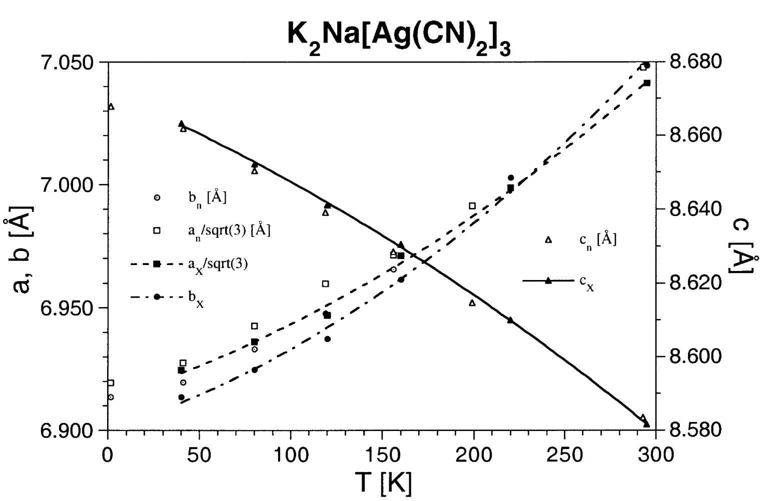

Fig. 7. Temperature variations of pseudo-hexagonal lattice parameters of $K_2Na[Ag(CN)_2]_3$, as determined by profile matching.

and

$$\mathrm{Ag(1)}\cdots\mathrm{Ag(2)} = \mathrm{Ag(2)}\cdots\mathrm{Ag(2')} = \frac{1}{2}a_\mathrm{h} = \frac{1}{2}b_\mathrm{h}.$$

From Tables 2 and 3, this closely occurs when $T = 200$ K and the Ag-atom environments become essentially identical. Coordinates of equivalent Ag-atom positions are:

$$\mathrm{Ag(1)} \equiv \mathrm{Ag(2)};\ \tfrac{1}{2}, 0, 0; 0, \tfrac{1}{2}, 0;\ (2/m) \longrightarrow 3\ \text{atoms/unit cell.}$$

Both Fig. 6 and the corresponding lattice parameters, which are shown in Table 3 and Fig. 7, indicate essential, continuous changes of the chemical structure as a function of temperature in the range from 1.5 to 300 K. However, the *c*-lattice parameter increases anomalously with decreasing temperature.

Apart from a possible slight change in slope around 150 K, the specific heat data of $K_2Na[Ag(CN)_2]_3$ shown in Fig. 1, do not indicate a structural phase transition.

4. Conclusions

Raman, synchrotron X-ray and neutron diffraction as well as specific heat data have been presented which provide evidence for essential, gradual structural changes as a function of temperature in the layered compound $K_2Na[Ag(CN)_2]_3$ in the temperature range from 1.5 to 300 K, indicating monoclinic symmetry.

The results in this study do not indicate the presence of any phase transitions in the vicinity of 80 K, the temperature at which we see a reversal in the trend of the intensity ratio of the two luminescence bands. It is therefore concluded that the changes in the luminescence behavior above and below 80 K are not due to phase transitions near that temperature. Instead, they are most likely due to changes in the kinetics of the photophysical processes following light absorption. The details of these photophysical processes will be published elsewhere.

From the neutron and X-ray powder diffraction data analysis, we conclude that the structural changes detected differ significantly from what may be described as a “conventional” phase transition. In such transitions major changes normally occur in the atomic structure when the transition takes place, usually accompanied by relatively large energy changes in the crystalline system (e.g. the specific heat measured as a function of temperature shows a sharp peak at the transition temperature). For the structural changes observed here, no such peak in the specific heat curve occurs, the atomic structural change with temperature change seems to be one of gradual and continuous change with relationships that cause the positions to coincide with what would be the hexagonal (trigonal) $P\bar{3}1m$ structure from the monoclinic $C2/m$ atomic structure at the sample temperature of approximately 200 K. In this regard, the present investigation may be considered to show the possibility of a novel type of phase change with temperature.

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