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CuCN: An orientational glass

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Rhombohedral crystal phase of CuCN forms irreversibly on heating a mixture of its orthorhombic and monoclinic phases to 593 K. In its space group, $R3m$ ($a=b=0.6026$ nm, $c=0.4823$ nm, $\alpha=\beta=90°$, $\gamma=120°$, $Z=3$, $V_0=0.1516$ nm^3, and $D_x=2.94$ g/cm^3), positions of C and N atoms are disordered, and therefore orientations of the CN group in the (N-Cu-C) chain structure are random. Its heat capacity increases in the manner of a sigmoid shape over the 350–380 K range, analogous to that observed on kinetic unfreezing of a canonical glass, as does that of a mixture of crystal phases obtained by flocculation process. The CuCN phase appears as the simplest orientational glass whose state is trapped in a deep minimum with a corrugated bottom, and each corrugation corresponding to one configurational excitation.

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I. INTRODUCTION

Configurational excitations in simple crystals of the nonspherical rigid groups confined to lattice sites, are seen as useful for understanding the manner in which slowing of molecular diffusion vitrifies a liquid. In the 1980s, mixed KCN-KBr crystal was seen as an ‘‘orientational glass’’ and an archetype of canonically disordered solids such as SiO_2. This was mainly because freezing-in of the configurational excitations associated with their ellipsoid-shaped CN group produced unusual features in their electrical, mechanical, and vibrational properties.[1] At that time, it had seemed that only mixed crystals could be used for this study, even though three entities in such crystals, two anions and one cation, had complicated interpretations of their data. As part of our studies of even simpler ‘‘orientational glasses,’’ we have investigated a variety of pure cyanides and found that CuCN undergoes a phase transformation on heating to a phase that does not transform back on cooling. Instead, it undergoes a gradual configurational freezing. This feature and the structure of the CuCN orientational glass is described here. Its study is of further interest because in the structure of its low-temperature phase infinitely long linear chains of —NC—Cu—CN— units resemble a polymer chain, analogous to those in the structure of AuCN in which alternating Au-C and Au-N are arranged in the chains and Au atoms form a sheet.[2]

II. EXPERIMENTAL METHOD

CuCN (99.99% purity) was purchased from Aldrich Chemicals. The as-received sample was of off-white color and density 2.92 g/cm^3. It had been prepared by flocculation of CuCN precipitate from an aqueous solution.[3] The particle size of the as-received CuCN was 1–5 μm, which became air borne easily. On heating to 593 K in an Argon atmosphere, its color changed from white to beige, and remained so on cooling back to 298 K. Its particles appeared to repel each other when attempts were made to grind it in an agate mortar and pestle. The powder was mounted on a glass plate, and x-ray diffraction spectra obtained at 298 K using three instruments. (i) Nicolet diffractometer, which used the Cu K_α radiation to obtain the diffraction in the range $10°<2\theta<50°$ in steps of 0.04°, (ii) Guinier camera, which used only the Cu $K_{\alpha 1}$ line, and (iii) Brucker D8 Advance diffractometer, which also used the Cu K_α radiation to obtain the diffraction in the range $20°<2\theta<130°$ in steps of 0.03°. A differential scanning calorimeter (Perkin-Elmer Corp. model DSC 4) was used for calorimetric studies. The instrument was calibrated with indium for both the temperature and the heat effects. Open and sealed aluminum and copper pans were used to contain the sample and argon was used as the purge gas. The base line was determined for the empty pans prior to the experiment, and this base line was subtracted from the measured DSC signal. The temperature was corrected for the thermal lag. The accuracy of the heat of transformation is 2%.

III. RESULTS AND DISCUSSIONS

Powder x-ray diffraction of the as-received CuCN measured at 298 K and of that heated to 533 K and thereafter cooled to 298 K showed no change in the diffraction peaks. The spectra of the latter CuCN sample is shown in Fig. 1(a). Standard powder x-ray diffraction data in the literature provide two structures of CuCN; (i) monoclinic (JCPDS 1-492) without unit cell parameters[4] and (ii) orthorhombic (JCPDS 9-152) in a unit cell with $a=1.279$ nm, $b=18.14$ nm, $c=7.82$ nm, $Z=36$, $D_x=2.951$ g/cm^3, and $D_m=2.97$ g/cm^3 but no atomic positions.[5] The peaks observed in Fig. 1(a) are attributable to the suggested monoclinic (JCPDS-ICCD 1-492) (Ref. 4) and orthorhombic structures (JCPDS-ICCD 9-152),[5] whose lines are shown in Figs. 1(b) and 1(c), respectively. Due to the lack of information about these structures, it is not possible to determine the relative amounts of the two phases in the as-received CuCN.

Powder x-ray diffraction of the CuCN solid, which had been obtained by heating the as-received sample to 593 K in argon atmosphere, is shown at 298 K in Fig. 1(d). The peak positions and intensities from the Guinier diffraction measured in the range of $10°<2\theta<90°$ were fitted by Gaussian function, and 11 peaks were identified. The data were input into CRYSFIRE program, which integrates eight different programs for indexing the powder-diffraction data. The several

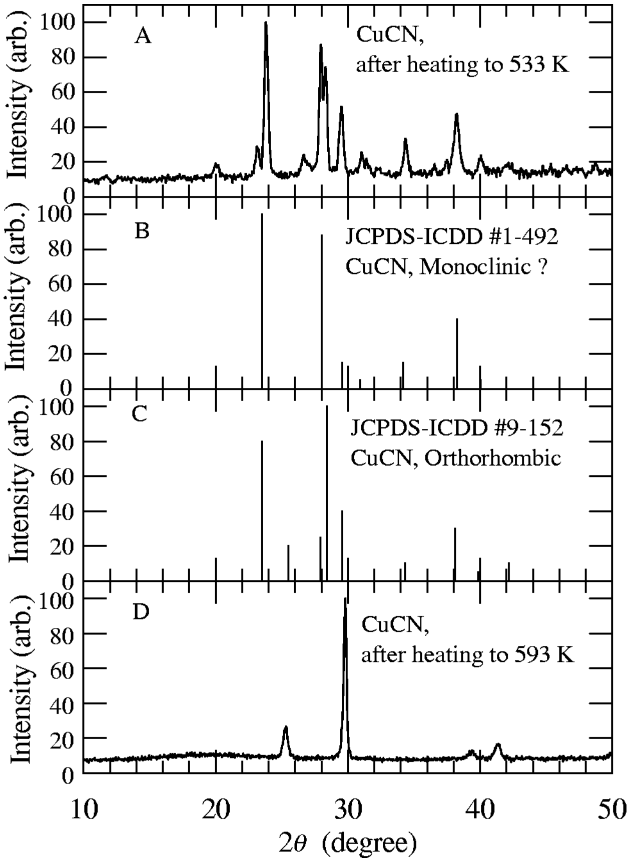

FIG. 1. The powder x-ray diffraction patterns of, (a) the as-received CuCN measured at ~298 K, (b) the lines and their relative intensities for the reported monoclinic structure from JCPDS 1-492, (c) the lines and their relative intensities for the orthorhombic structure from JCPDS 9-152, and (d) the phase of CuCN obtained after heating to 593 K in an argon environment and thereafter cooling to 298 K.

solutions obtained from TRIOR90 program for possible unit cells were input to another program CHECKCELL and were compared against the entire Guinier diffraction pattern. Systematic absences suggested that the space group should be among the $R3$, $R\overline{3}$, $R3m$, $R\overline{3}m$, and $R32$ set. For $Z=3$, i.e., three molecules in the unit cell, this set of rhombohedral unit cells predicts a theoretical density D_x of 2.94 g/cm^3. The $R3m$ space group was found to fit well and for that group Rietveld refinement of the data obtained from D8 diffractometer was done by using FULLPROF program. This refinement gave satisfactory results.

The Rietveld refinement was then done by choosing C and N positions. The best fit for one set of positions for C and N atoms was found to be $a=b=0.6028$ nm, $c=0.4823$ nm, $\alpha=\beta=90°$, and $\gamma=120°$. Further refinement gave two different, but equally probable, positions of C and N atoms. The final fitting parameters are $a=b=0.6035$ nm, $c=0.4829$ nm, with residual $R=5.91\%$ and $\chi^2=3.25\%$. This refinement is compared against the measured diffraction spectra of the CuCN phase in Fig. 2, and the atomic positions and occupancies in the unit cell are shown in the inset of Fig. 2. The final values are $x=0$, $y=0$, $z=0$, and occupancy 1.0 for Cu. The respective values for other atoms are 0, 0, 0.400, and 0.5 for C(1); 0, 0, 0.648, and 0.5 for N(1); 0, 0, 0.627, and 0.5, for C(2); and: 0, 0, 0.390, and 0.5, for N(2). Inclusion of the anisotropic effect did not lead to further refinement. Thus the CuCN phase has chains of $(\text{N—Cu—C})_n$ in the crystal, which appear to be confined to one dimension with a distortion caused by interchain interactions.

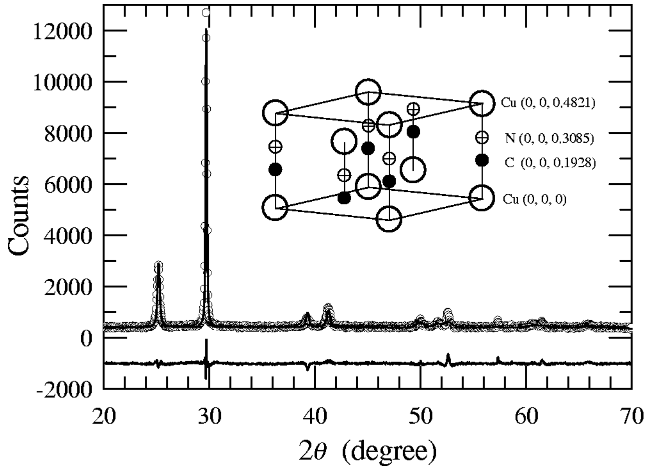

FIG. 2. The results of the Rietveld analysis of the powder x-ray diffraction of CuCN after heating to 593 K in an argon environment and thereafter cooling to 298 K. Inset shows the unit cell of CuCN structure, with the positions of Cu indicated by large circles, those of C by small filled circles and those of N by small empty circles.

The rate of heat release, which is equivalent to the specific heat, C_p, measured on heating the as-received CuCN at 30 K/min is shown by curve (1) in Fig. 3(a). It shows a broad sigmoid shape rise in the 330–360 K range and a large endothermic peak due to the phase transformation in the 550–580 K range. The total heat evolved is 850 J/mol. With the transition temperature 563 K, this corresponds to an entropy increase, ΔS, by 1.5 J/(mol K) on structural transformation of CuCN. According to the Born–von Karman relation, $\Delta S = R \ln(\nu_2/\nu_1)$, the increase in entropy indicates that the new phase has 20% higher phonon frequencies than the original mixed crystals made from flocculation process.

This phase was cooled to 77 K and reheated. Its thermogram provided in Fig. 3(a) shows no endothermic peak in the 550–580 K range, thus showing the irreversibility of the structural transformation. But it still shows the sigmoid-shape increase in C_p which has shifted to a higher-temperature range of 350–380 K. These are clearly seen by comparison of curves (1) and (2) on an enlarged scale in Fig. 3(b). The samples were annealed at $T<330$ K and the annealed sample showed an enhanced sigmoid-shape C_p curve with shaper features. This confirmed that the C_p change was due to the kinetic unfreezing of the orientational disorder. Unfortunately, the dc conductivity of CuCN crystals was too high to allow us to determine the dielectric relaxation time with sufficient accuracy. It seems that the as-received flocculation produced mixed crystals also contained an orientationaly disordered CuCN phase, as discussed below.

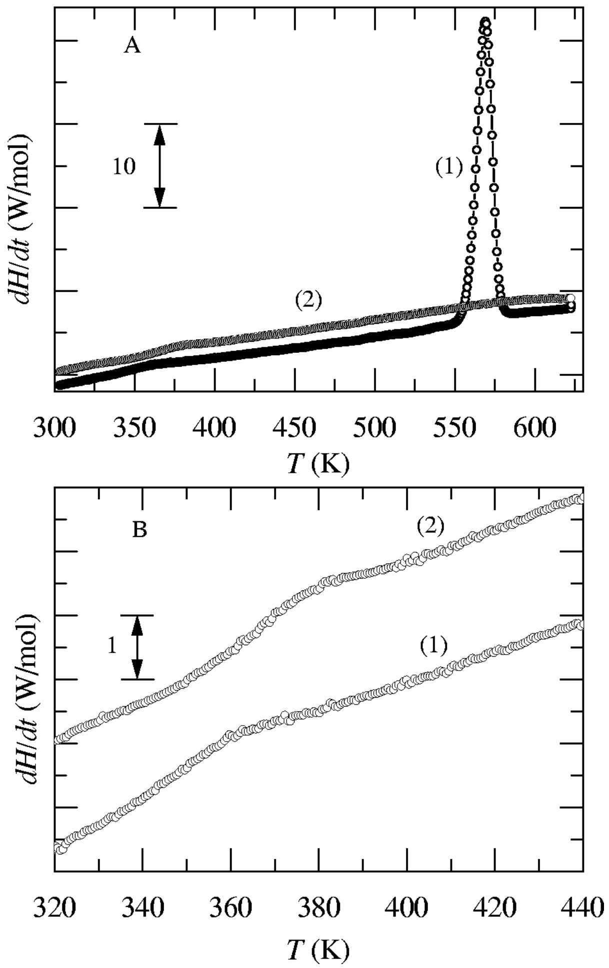

FIG. 3. (a) The differential scanning calorimetry thermogram of CuCN obtained by heating at 30 K/min heating rate is shown by curve (1), and that of the structurally transformed sample which had been cooled to 77 K and then heated is shown by curve (2). (b) The enlarged parts of curves (1) and (2) in Fig. 1(a) show the sigmoid shape C_p increase for the original CuCN and of its phase. Curve (1) is offset with respect to curve (2) in both panels.

The sigmoid shape increase in C_p is a characteristic feature of the onset of molecular diffusion in the glass-softening range in canonical glasses, of the configurational excitation onset in orientational glasses, e.g., KCN-KBr crystals, and of the onset of rotational diffusion on all lattice sites in orientationally disordered crystals. Accordingly, one or both of the low-energy forms of CuCN crystals in the as-received CuCN (prepared by flocculation process) and the metastable rhombohedral form are orientational glasses at 298 K. But their configurational excitation onset occurs at different temperatures, 338 K for the as-received and 350 K for the present form. It is also possible that the C_p increase in the 340–375 K range in all the three forms of CuCN is due to the increase of anharmonic force contributions in the librational motions of CN on their lattice sites. In this theory, which has been justified for another orientational glass $TlNO_2$,[6] a vacancy defect randomly diffuses to the neighboring site of the CN group. The proximity of the vacancy and CN group distorts, asymmetrically, the shape of the potential-energy well and thus increases the anharmonic force contribution from the librations of the CN group. Therefore the C_p increases on orientational unfreezing. This increase is small and spreads over a broader range due to the low activation energy for vacancy diffusion. Inasmuch as the vacancy diffusion leads to a change in the configuration of a crystal, this C_p increase may be seen also as configurational, but its contribution to C_p is much less. According to this mechnism, slowing of the vacancy diffusion rate and decrease in the vacancy population would cause the loss of configurational excitations on cooling and the formation of an orientational glass. Conversely, increase in the vacancy diffusion rate and population on heating would cause gain of configurational excitations and thus a rise in C_p, as has been observed for $TlNO_2$.[6]

IV. CONCLUSION

The observations on the CuCN crystals enable us to examine the behavior of configurational excitations in orientational glasses more simply than has been possible from a study of KCN-KBr and related mixed crystals, where quadrupole interactions appear to dominate.[1] Although their excess entropy over an ordered crystal phase cannot be determined, the study of CuCN crystals would provide a simpler approach to understand the merit of configurational and vibrational contributions to C_p and the entropy of canonical glasses. The thermodynamic and kinetic behaviors of these glasses are currently being computer simulated in terms of the potential-energy landscape or inherent structure models of a condensed phase, but within the precepts of statistical mechanics and harmonic approximation.[7] In one such approach, the structure of the CuCN crystal as an orientational glass can be seen to belong to a deep configurational minimum from which escape to a neighboring minimum of a lower-energy, ordered crystal structure is thermally improbable, i.e., the high-temperature form is metastable with respect to the low-temperature form. This deep minimum for the crystal may be seen to have a corrugated bottom rather than a round one, with corrugations of different depths representing configurations of lower energy. These configurations are achievable by the diffusion of vacancies but still in the disordered arrangement of the high-temperature crystal phase. Asymmetry of the potential energy corresponding to each corrugation represents the anharmonic forces, which change when the vacancy appears next to a nonspherical CN group. In this case, the C_p rise on configurational excitation onset is a reflection of the accessibility of the local minima envisaged as corrugations in a deep potential minimum. Since there is no escape from one overall configuration of a deep minimum to another deep minimum, the α-relaxation process, which involves co-operation motions, does not emerge from the Johari-Goldstein relaxation,[8] as it also did not emerge for $TlNO_2$ (Ref. 6) and in other solid such as ice clathrates.[9] We propose that as in several other crystals,[6,9] the α-relaxation process does not evolve in CuCN crystal.

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