

# The Disordered Crystal Structures of $\text{Zn}(\text{CN})_2$ and $\text{Ga}(\text{CN})_3$

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The structure of  $\text{Zn}(\text{CN})_2$  has been reexamined using neutron time-of-flight diffraction and has been determined to have symmetry  $Pn\bar{3}m$ ,  $a=5.9227(1)$  Å at 14 K and  $5.8917(1)$  Å at 305 K (negative thermal “expansion”). The CN groups are disordered in contrast to the ordered arrangement with symmetry  $P\bar{4}3m$  assumed in earlier X-ray diffraction experiments. Zn is tetrahedrally surrounded with average  $\text{Zn}-(\text{C}, \text{N})=1.9697(3)$  and  $\text{C}-\text{N}=1.1897(1)$  Å.  $\text{Ga}(\text{CN})_3$  has been examined for the first time. X-ray powder diffraction shows it to have a cubic Prussian blue framework structure, symmetry  $Pm\bar{3}m$ ,  $a=5.295(2)$  Å, also with CN disorder. Ga is octahedrally surrounded with average  $\text{Ga}-(\text{C}, \text{N})$  distance  $=2.072(2)$  Å and  $\text{C}-\text{N}=1.148(1)$  Å © 1997

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## INTRODUCTION

Many fascinating structures have frameworks composed of the cyanides of Zn and especially Cd. Simple examples are the compounds  $\text{N}(\text{CH}_3)_4 \cdot M\text{Zn}(\text{CN})_4$  with  $M = \text{Cu}$  (1) or Li (2) in which the tetramethyl ammonium ions is in the cavities of a diamond-like framework of  $M$  and Zn linked by  $-\text{CN}-$  groups. In  $\text{Zn}(\text{CN})_2$  itself (1), two independent such frameworks are interlaced.  $\text{LiGa}(\text{CN})_4$  and  $\text{CuGa}(\text{CN})_4$  have recently be shown to have the same arrangement (3). Other examples are provided by Brousseau *et al.* (3) and by Hoskins and Robson (1) who examined the structures of  $\text{Zn}(\text{CN})_2$  and  $\text{Cd}(\text{CN})_2$  by X-ray single-crystal diffraction and concluded that they were isostructural. In the structures originally proposed (4, 5) the CN groups were ordered, so that half the Zn or Cd atoms were bonded to four C atoms and the other half were bonded to four N atoms. Hoskins and Robson apparently confirmed the ordering, but we remained skeptical for several reasons, one being that the reported metal-carbon bond lengths were shorter than the metal-nitrogen bond lengths, and it was expected (6) that for equal bond valence (strength) Zn-C bonds should be ca. 0.06 Å longer than Zn-N bond lengths. It is in fact very difficult to distinguish C and N by X-ray diffraction and Hoskins and Robson (1) remarked that if they interchanged the C and N atoms in their structure and kept them constrained in the new positions there were no significant

differences between the  $R$  values for the two refinements. In fact, the C, N disorder was also deduced (7) in  $\text{Cd}(\text{CN})_2$  from solid-state  $^{113}\text{Cd}$  NMR studies.

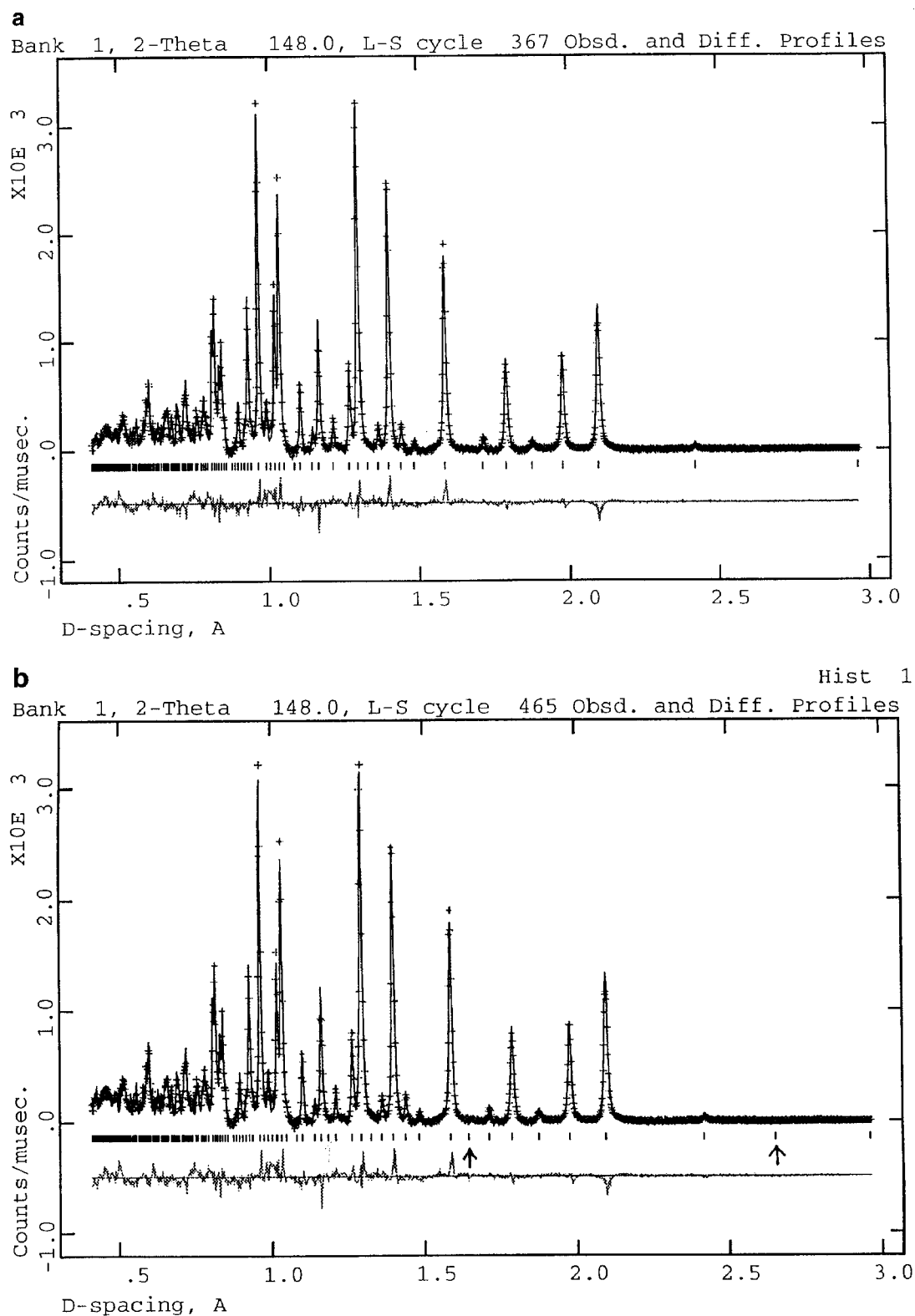
The difficulty of distinguishing C and N by X-ray diffraction does not extend to neutron diffraction, as the bound coherent scattering lengths for C and N (averaged for natural abundance of isotopes) are 6.46 and 9.36 fm respectively (8). Unfortunately the  $(n, \gamma)$  resonance at thermal neutron energies of  $^{113}\text{Cd}$  renders Cd with normal isotopic composition (12%  $^{113}\text{Cd}$ ) unsuitable for neutron diffraction experiments so we have studied only  $\text{Zn}(\text{CN})_2$  by neutron diffraction.

We (3) subsequently succeeded in preparing crystalline  $\text{Ga}(\text{CN})_3$  for the first time and X-ray powder diffraction leads to a related structure with C, N disorder which we also report here.

## EXPERIMENTAL

### $\text{Zn}(\text{CN})_2$

$\text{Zn}(\text{CN})_2$  of claimed 99.9% purity was checked by X-ray diffraction and found to be well crystallized, with no observable second phase, so it was used as received from Aldrich Chemical Company. Neutron powder diffraction data were collected at 14 and 305 K on the General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. The data were collected using the  $\pm 148^\circ$ ,  $\pm 90^\circ$ , and  $\pm 60^\circ$  detector banks, which were symmetrically summed following the collection, and covered a  $d$ -spacing range from 0.4 to 5.7 Å. Data for the three sets refined comparably and the results reported below are for the three sets (a total of 11,111 points). The structure was refined using the General Structure Analysis System (GSAS), a Rietveld profile analysis code developed by Larson and Von Dreele (9). The structural models were refined for lattice parameters, atomic positions, and isotropic thermal parameters. Background coefficients, scale factor, anisotropic strain terms in the profile function, and sample absorption were also refined.



**FIG. 1.** (a) TOF neutron diffraction profile fit to  $148^\circ$  bank for  $\text{Zn}(\text{CN})_2$ . The data are shown as + and the tick marks are at the Bragg positions. The solid line is the calculated profile for the disordered model and the difference curve is shown at the bottom on the same scale. (b) The same as (a) but now the solid line is the calculated profile for the ordered model. Arrows indicate the  $P43m$  superstructure peaks 210 at  $d = 2.65 \text{ \AA}$  and 320 at  $1.64 \text{ \AA}$ .

*Ga(CN)<sub>3</sub>*

Crystalline  $\text{Ga}(\text{CN})_3$  was prepared (3) by the reaction of  $\text{Me}_3\text{SiCN}$  with  $\text{GaCl}_3$  which proceeds quantitatively to  $\text{Ga}(\text{CN})_3$  and (volatile)  $\text{Me}_3\text{SiCl}$ . Samples for X-ray powder diffraction were loaded into an environmental cell with a kapton window (10) and data were collected with a Rigaku D/max IIB diffractometer using  $\text{CuK}\alpha$  radiation. A preliminary run showed that the material gave rather broad diffraction peaks, all of which could be indexed using a primitive cubic cell with  $a \approx 5.3 \text{ \AA}$  and no systematic absences (although the near extinction of 111 is informative, see below).

The data refined consisted of two sets, each being a sum of 10 step scans, one of  $0.02^\circ$  steps at a rate of  $3.0^\circ/\text{min}$  for the  $2\theta = 5^\circ$  to  $90^\circ$  set, and the other of  $0.04^\circ$  steps at a rate of  $3.0^\circ/\text{min}$  for the  $2\theta = 80^\circ$  to  $140^\circ$  set. The refinement using GSAS (9), fitted 5498 data points for 35 reflections. The C and N atoms were constrained to have occupancy of 1/2 and identical isotropic displacement parameters,  $U$ . Ga was also assigned an isotropic displacement parameter. Background coefficients, scale factor, anisotropic strain terms in the profile function, and sample absorption were also refined.

## RESULTS

*Zn(CN)<sub>2</sub>*

In the disordered model the symmetry is  $Pn\bar{3}m$ . With the origin at a center of symmetry, Zn atoms are in 2  $a$ :  $\pm(1/4, 1/4, 1/4)$  and C and N each have half occupancy in 8  $e$ :  $\pm(x, x, x, \text{etc.})$ . Using this model with isotropic displacement parameters (constrained equal for N and C), the refinement of the 14 K data converged smoothly to  $a = 5.9227(1) \text{ \AA}$ ,  $x = 0.44200(3)$ . The displacement parameters (in  $\text{\AA}^2$ ) are  $U_{\text{Zn}} = 0.0060(3)$ ,  $U_{\text{C,N}} = 0.0089(1)$ . For the final refinement  $\chi^2 = 5.6$ ,  $R_p = 3.3\%$ ,  $R_{wp} = 4.5\%$  for a total of 57 parameters. Figure 1a shows observed and calculated histograms for bank 1 which covers most of the  $d$ -spacing range.

In the ordered model of  $\text{Zn}(\text{CN})_2$  the symmetry is  $P\bar{4}3m$ . Zn(1) is at 0, 0, 0 and Zn(2) is at  $1/2, 1/2, 1/2$ . N atoms in 4  $e$  at  $x_N, x_N, x_N$  form a tetrahedron about Zn(1) and C atoms in 4  $e$  at  $x_C, x_C, x_C$  form a tetrahedron about Zn(2). If the parameters were the same as in the disordered model  $x_N = x - 1/4 = 0.192$  and  $x_C = 3/4 - x = 0.308$ . We found  $x_N = 0.1937(2)$ ,  $x_C = 0.3098(2)$  but now very different atomic displacement factors for C and N; explicitly:  $U_C = 0.0013(4)$  and  $U_N = 0.0152(4) \text{ \AA}^2$ . For the final refinement  $\chi^2 = 5.9$ ,  $R_p = 3.4\%$ ,  $R_{wp} = 4.6\%$  essentially the same as for the disordered model. An examination of observed and calculated histograms in Fig. 1b shows the same agreement as for the ordered model.

In the disordered ( $Pn\bar{3}m$ ) model, reflections  $hkl$  with  $h + k$  odd have zero intensity. In our powder experiments

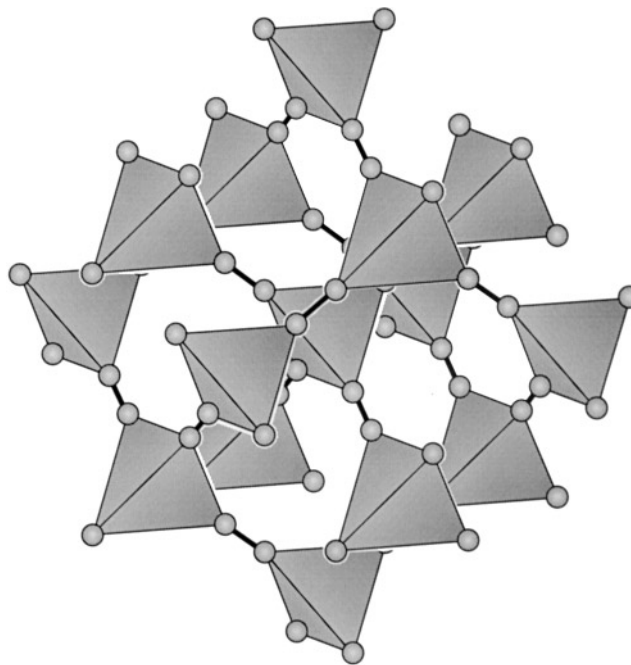
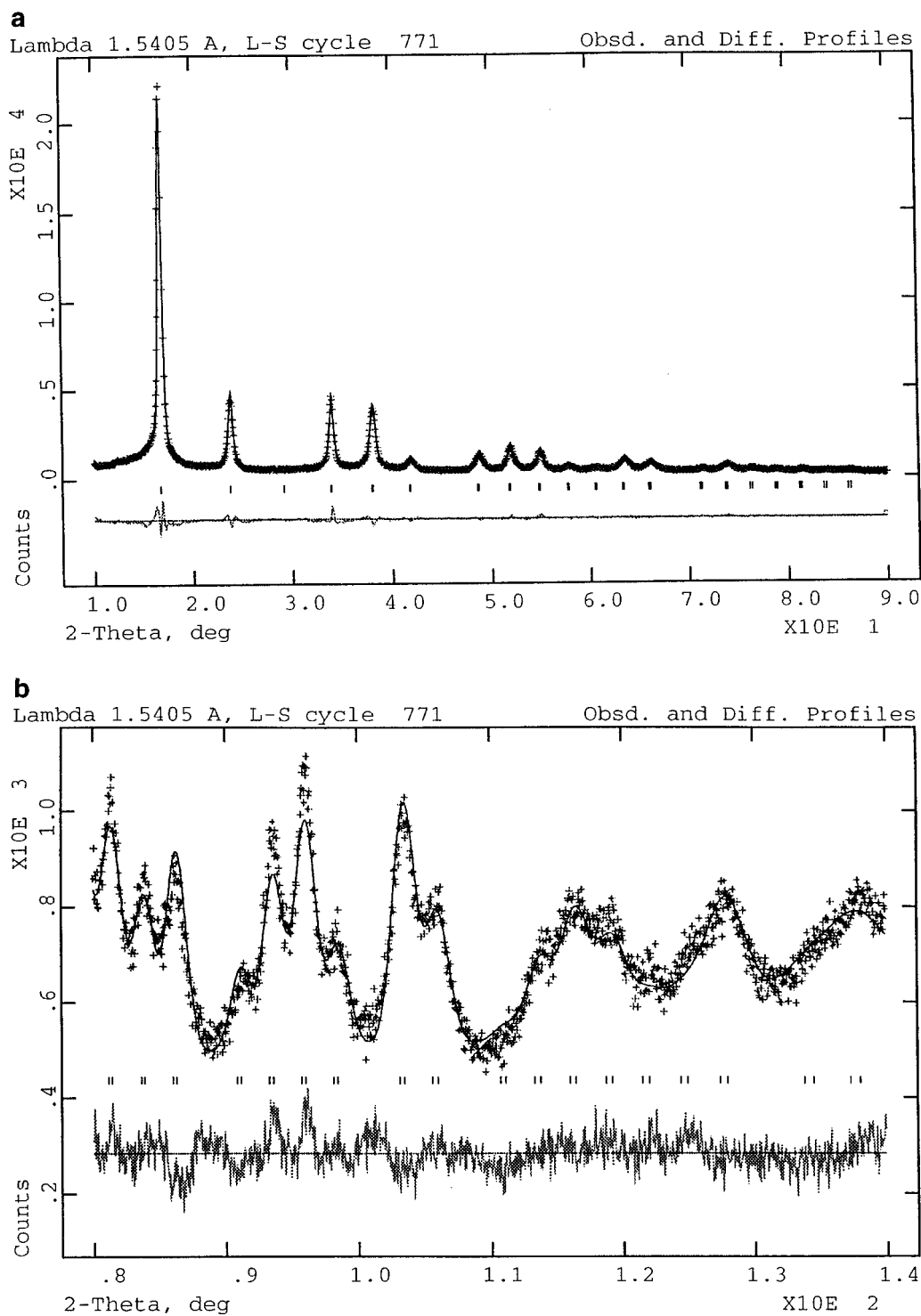


FIG. 2. The structure of  $\text{Zn}(\text{CN})_2$ . The tetrahedra of four (C, N) atoms (spheres) are shown connected by heavy lines representing C–N bonds.

$hkl = 100$  ( $d = 5.92 \text{ \AA}$ ) is outside the range of the spectrometer, 300 is coincident with 221, and 410 is coincident with 322. This leaves only two  $hk0$  reflections with  $h + k$  odd and with  $d > 1.2 \text{ \AA}$ . These are 210 ( $d = 2.65 \text{ \AA}$ ) and 320 ( $d = 1.64 \text{ \AA}$ ); they are indicated in Fig. 1b, and it may be seen that there is no observable intensity in these reflections. It might be noted that the evidence obtained in the X-ray diffraction experiment (1) for observed intensity in reflections  $hkl$  with  $h + k$  odd is less than compelling (B. F. Hoskins, private communication).

Despite the similarity in agreement indices, and the relative paucity of direct observation of absences, we are confident that the disordered model can be identified as correct. This is because the C–N triple bond is very strong (and hence stiff) compared to the other bonds in the structure, so we would expect the atomic displacement parameters ( $U$ ) for C and N to be virtually the same, rather than differing by more than a factor of 10 in the ordered model. The apparent large  $U_N$  obtained for this model must surely arise because too much scattering power is placed at the putative N site and similarly the small  $U_C$  arises because too little scattering power is placed at the C site (cf. the scattering lengths quoted in the introduction).

To further check on the validity of the disordered model, we refined that model with anisotropic  $U$ 's for the C, N site. The site symmetry is  $3m$  with the threefold axis along  $[111]$  so  $U_{11} = U_{22} = U_{33}$  and  $U_{12} = U_{13} = U_{23}$ . The refinement produced no significant changes in the structural



**FIG. 3.** X-ray diffraction profile fit for  $\text{Ga}(\text{CN})_3$ . The data are shown as + and the tick marks are the Bragg positions. The solid line is the calculated profile and the difference curve is shown at the bottom on the same scale.

parameters and resulted in  $U_{11} = 0.0056$ ,  $U_{12} = 0.0046 \text{ \AA}^2$ . The “thermal” ellipsoid corresponding to these parameters has its major axis along the line  $\text{Zn}-\text{X}-\text{X}-\text{Zn}$  (here X refers to C, N) reflecting the fact that  $\text{Zn}-\text{C}$  and  $\text{Zn}-\text{N}$  bonds will be

of different length and X will be at slightly different positions along the  $\text{Zn}-\text{Zn}$  vector according to whether X is C or N.

A sketch of the structure is shown in Fig. 2. The interatomic distances are  $\text{Zn}-(\text{C}, \text{N}) = 1.9697(3)$  and  $\text{C}-\text{N} = 1.1897(1) \text{ \AA}$ .

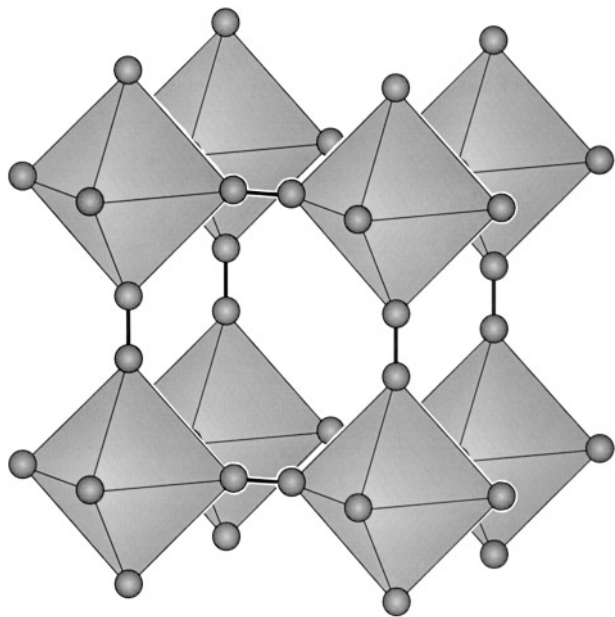


FIG. 4. The structure of  $\text{Ga}(\text{CN})_3$ . The octahedra of six (C, N) atoms (spheres) are shown connected by heavy lines representing C–N bonds.

Refinement of the 305 K data was carried out using the same profile coefficients as for the low-temperature data. This was done as we wanted to compare lattice parameters at the two temperatures, and in refinement of neutron time-of-flight data the lattice parameter shows some interaction with anisotropic profile coefficients. The refinement converged smoothly to  $a = 5.8917(1) \text{ \AA}$ ,  $x = 0.4423(1)$ . The displacement parameters (in  $\text{\AA}^2$ ) are now  $U_{\text{Zn}} = 0.0250(7)$ ,  $U_{\text{C,N}} = 0.0333(3)$ . For the final refinement  $\chi^2 = 2.9$ ,  $R_p = 4.3\%$ ,  $R_{\text{wp}} = 5.7\%$ .

### $\text{Ga}(\text{CN})_3$

The only plausible possibility for structure of cubic  $\text{Ga}(\text{CN})_3$  with the small primitive cell is a disordered one with Ga at the cell corners and octahedrally coordinated by (C, N) and joined by C–N bonds aligned along the cell edges as in the well-known iron cyanides of the Prussian blue family (11). Specifically in space group  $Pm\bar{3}m$ , Ga is in  $1 a: 0, 0, 0$  and (C, N) disordered in  $6 e: x, 0, 0$ , etc. At this point, a good approximation to the structure can be obtained by noticing the fortuitous near-extinction of the 111 reflection at  $2\theta = 29.2^\circ$  (Fig. 3). For extinction of 111, it is easy to show that  $x \approx 1/2 - (1/2\pi) \sin^{-1} [f_{\text{Ga}}/3(f_{\text{C}} + f_{\text{N}})] \approx 0.4$ ; here the  $f$ 's are the atomic scattering factors. This approximation gave reasonable interatomic distances and led us to attempt a Rietveld refinement of the data which was successful despite the broad and overlapping peaks. The particle size, estimated using the Scherrer for-

mula (12) applied to the width of the first four peaks is  $\approx 300 \text{ \AA}$ .

We note that C, N ordering would require a large unit cell, the simplest case being a  $Fm\bar{3}m$  cell with  $a$  twice that of the present primitive cell as reported for  $\text{CdPd}(\text{CN})_6$  (13). We do not observe any superstructure peaks but, because of the similarity in X-ray scattering power of C and N, such peaks would be very weak. However, in this case we have independent NMR data (7) indicating C, N disorder.

For the final refinement  $a = 5.295(2) \text{ \AA}$ ,  $x = 0.3913(6)$ ,  $U_{\text{Ga}} = 0.030(1) \text{ \AA}^2$ ,  $U_{\text{C,N}} = 0.046(1) \text{ \AA}^2$ . The agreement indices are  $\chi^2 = 2.0$ ,  $R_p = 5.9\%$ ,  $R_{\text{wp}} = 7.4\%$  for a total of 23 parameters. Observed and calculated diffraction profiles are shown in Fig. 3; notice the good fit for the high-angle data, for which  $R_{\text{wp}} = 4.8\%$ . A sketch of the structure is shown in Fig. 4. Interatomic distances are  $\text{Ga}-(\text{C, N}) = 2.072(2) \text{ \AA}$  and  $\text{C}-\text{N} = 1.148(1) \text{ \AA}$ .

## DISCUSSION

The conclusion that  $\text{Zn}(\text{CN})_2$  and  $\text{Ga}(\text{CN})_3$  have disordered structures should not come as a surprise. Of all the cyanides  $M(\text{CN})_n$  (here  $M$  is any metallic element) listed in the Inorganic Crystal Structure Database (14), only  $\text{Zn}(\text{CN})_2$ ,  $\text{Cd}(\text{CN})_2$ ,  $\text{Hg}(\text{CN})_2$ , and  $\text{As}(\text{CN})_3$  are reported to have ordered structures. The first two we now believe to be disordered, and the second two are molecular crystals with  $M$  bonded to C only. The example of  $\text{RbCN}$ , which is found (15) to be disordered even at 4 K is typical, although we note that an approximate ordered structure was given long ago (16) for  $\text{LiCN}$ . In the case of  $\text{Cd}(\text{CN})_2$ , which appears to be isostructural with  $\text{Zn}(\text{CN})_2$  (1)  $^{113}\text{Cd}$  NMR (7) provides strong evidence for C, N disorder.

Our analysis of the C, N thermal displacement parameters in  $\text{Zn}(\text{CN})_2$  at low temperature shows that they are fairly small and elongated along the direction of the  $\text{Zn}-(\text{C, N})$  bond vector. This suggests strongly that the disorder is static in what has been termed an orientational glass (7). It is expected that the dominating local configuration is one in which each Zn is bonded to two C and two N atoms, certainly this would be expected to be preferred to one in which  $\text{ZnC}_4$  and  $\text{ZnN}_4$  tetrahedra alternate. In the same way local configurations in  $\text{Ga}(\text{CN})_3$  in which each Ga is bonded to three C and three N should be preferred to alternating  $\text{GaC}_6$  and  $\text{GaN}_6$  octahedra.

Attention is drawn to the large decrease in lattice parameter of  $\text{Zn}(\text{CN})_2$  in going from 14 to 305 K, the value of  $\delta a/a = -0.0053$  is approximately twice as large as recently reported (17) for  $\text{ZrW}_2\text{O}_8$ . The same behavior might be expected (18) for other materials, such as cyanides, in which polyhedral groups are joined by linear  $M-\text{C}-\text{N}-M$  links, and we plan to investigate the phenomenon further.

## ACKNOWLEDGMENTS

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