Modifikation gefunden wurde (Dittmar & Schäfer, 1975). Die Schichten bestehen aus GeSe$_4$-Zweiereinfachketten (Liebau, 1962), die über kantenverknüpfte Doppeltetraeder zweidimensional vernetzt sind. In Tabelle 3 sind die Abstände und Winkel zusammengestellt. Sie entsprechen weitgehend denen des isotypen Sulfids. Die gefundenen Ge–Se-Abstände von im Mittel 2,356 Å stimmen mit der Summe der Tetraederradien nach Pauling für diese Elemente (2,36 Å) überein.

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On the room-temperature structure of Cs$_2$LiCr(CN)$_6$.

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Neutron powder diffraction data rules out the space group $P4_22_12$ for the room-temperature structure of Cs$_2$LiCr(CN)$_6$, suggested by Ryan & Swanson [*Inorg. Chem.* (1974), **13**, 1681–1684]. Successful refinement of the structure has been achieved in a different space group, namely $P4/mnc$.

Since Wolberg (1969) synthesized cobalt dicaesium lithium hexacyanide, Cs$_2$LiCo(CN)$_6$, and reported that the compound crystallizes in the highly symmetric cubic space group $Fm3m$, considerable interest has been focused on the structure of the series Cs$_2$LiM(CN)$_6$ (M = Cr, Mn, Fe, Co). One of the objectives of these structural investigations has been the accurate determination of the M–C and C–N bond lengths in an isostructural series, which could then be used to formulate M^{III}–CN bonding theories (see, for example, Swanson & Ryan, 1973; Ryan & Swanson, 1974). On the basis of an X-ray single-crystal study, Swanson & Ryan (1973) reported that at room temperature the Mn and the Fe compounds are isostructural with Wolberg's structure, in which the transition metal and the lithium atoms occupy octahedral sites while the Cs atoms occupy tetrahedral sites; the Cr compound, on the other hand, was found to have a tetragonal structure at room temperature. From the observed systematic absences they suggested the space group $P4_22_12$ for the structure. In a later publication (Ryan & Swanson, 1974) the authors reported confirmation of the tetragonal cell [$a = 7\cdot600$ (3) and $c = 10\cdot778$ (3) Å; $Z = 2$] and the space group. But they did not succeed in refining the structure in their chosen space group $P4_22_12$. The compound is known to undergo a phase transition at ~350 K becoming isostructural with the room-temperature phase of Mn, Fe and Co compounds. In this note we report that neutron powder diffraction data, collected on the PANDA diffractometer at AERE Harwell, completely rule out the possibility of the space group $P4_22_12$ for the room-temperature structure of the Cr compound. Detailed analysis of the neutron powder data will

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be reported in another paper (Chowdhury, Wedgwood, Chadwick & Wilde, 1977), where we show that the room-temperature tetragonal structure is related to the high-temperature cubic phase by rotations of the Cr(CN)$_6$ octahedra about the tetragonal c axis.

The systematic absences consistent with the space group $P4_22_12$ are $00l$: $l = 2n + 1$ and $h00$: $h = 2n + 1$. Our neutron powder profile does not exhibit any of the reflexions of these forbidden groups; in addition, no positive evidence of reflexions of the type $0kl$: $k + l = 2n + 1$ and hhl: $l = 2n + 1$ can be found in the observed profile. It should, however, be pointed out that one cannot be absolutely certain about the systematic absences in a powder profile because of the occurrence of overlapping peaks – especially at high angles.

It can reasonably be expected that the atomic arrangements in the room-temperature phase would be closely related to the corresponding ones in the high-temperature cubic phase. One is thus led to opt for the following setting for the positional coordinates with $P4_22_12$ as the space group (*International Tables for X-ray Crystallography*, 1952):

Cr	$0,0,0$;	Li	$0,0,\frac{1}{2}$;	Cs	$0,\frac{1}{2},z$	
C(1)	$0,0,z$;	C(2)	$x,x,0$;	C(3)	$x,-x,0$	
N(1)	$0,0,z$;	N(2)	$x,x,0$;	N(3)	$x,-x,0$.	

One can immediately see that in this setting the Cr(CN)$_6$ octahedron is allowed to distort only along the three octahedral axes (*i.e.* along [001], [110] and [$\bar{1}$10], which in terms of the high-temperature cubic cell correspond to [001], [100] and [010] respectively); it does not permit any rotation or tilt of the octahedron with respect to its cubic phase position.

Since it is known that the structure is tetragonal (Ryan &

Swanson, 1974; Chowdhury *et al.*, 1977) it can reasonably be expected that the Cr–C and C–N bond lengths along [110] and [$\bar{1}$10] (*i.e.* on the tetragonal basal plane) would be the same, allowing the corresponding bond lengths along [001] to be different. This entails putting constraints on the positional parameters of C(2), C(3) and N(2), N(3) such that x[C(2)] = x[C(3)] and x[N(2)] = x[N(3)]. With such a constrained situation contributions from C and N atoms to reflexions of the type hkl: $h+k+l=2n+1$ are nil. As no other atom contributes to reflexions of the type $hk0$: $h+k=2n+1$, reflexions of this type should be systematically absent from the diffraction pattern. But our neutron powder pattern does contain diffraction peaks corresponding to these reflexions; for example, the 120 reflexion can be observed as a well-resolved and very intense peak. One is, therefore, led to rule out the possibility of the structure conforming to the above physical picture. Further confirmation of inconsistency with the above model is provided by the presence of intense non-body-centred peaks (*i.e.* reflexions for which $h+k+l=2n+1$) in the neutron data. Contributions to these reflexions can only come from deviations of the Cs atom z coordinate from $z=0.25$, the position it occupies in the cubic phase. The strong peaks corresponding to the reflexions 122, 124, 232 *etc.* observed in the neutron diffraction pattern cannot be accounted for by any small deviation of the Cs atom z coordinate.

We tried to refine our room-temperature neutron data without imposing any constraint on the positional parameters using the now well established profile refinement technique (Rietveld, 1967). The program used in this refinement was a modified version of the original Rietveld program (Hewat, 1973). The starting parameters for the least-squares refinement were either the same or very similar to those reported by Ryan & Swanson (1974) for the high-temperature cubic structure (*Fm3m*). All our efforts to refine the structure in $P4_22_12$ failed: for no amount of distortion of the Cr(CN)$_6$ octahedron would the calculated profile reasonably agree with the observed profile. Thus, although the observed systematic absences do not

rule out the possibility of the space group $P4_22_12$, the analysis of the neutron diffraction profile completely rules out the space group for the room-temperature structure of the compound. It is now not difficult to see why Ryan & Swanson (1974) did not succeed in refining their single-crystal X-ray data in this space group.

As mentioned earlier, we have, however, succeeded in refining our neutron diffraction profile, but in a different space group (*P4/mnc*). The refinement reveals that the tetragonal distortion of the high-temperature cubic structure consists primarily of a rotation of the Cr(CN)$_6$ octahedron about the *c* axis and an elongation of the octahedron along the same axis. Detailed analysis of the structure will be published in a separate paper (Chowdhury *et al.*, 1977). The success of the neutron diffraction technique over the X-ray method in this particular case lies in the fact that scattering from C and N is much more sensitive for neutrons than for X-rays – the neutron scattering cross-sections of both C and N being large but different from each other.

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Triethylenediamine. III. The II⟵⟶I phase transition. By J. K. Nimmo and B. W. Lucas, *Department of Physics, University of Queensland, St. Lucia, Brisbane, Queensland, Australia*

The II ⟷ I structural phase transition (at 351 K) of triethylenediamine is discussed with reference to h.c.p. ⟷ f.c.c. transitions. A close relation is shown to exist between the molecular orientations in the two phases. Comparison is also made with a recent theoretical structure prediction [Reynolds, *Mol. Phys.* (1974), 28, 633–652].

Triethylenediamine (TEDA), N(CH$_2$CH$_2$)$_3$N, is a globular molecule with a structural phase transition at 351 K for atmospheric pressure (Trowbridge & Westrum, 1963). The structures of both phases have been determined by Nimmo & Lucas (1976*a,b*), and are illustrated in Fig. 1 together with the relation between their respective unit cells. Phase II may be regarded as having an approximately h.c.p. structure with $a=6.14$ (2), $c=9.46$ (2) Å at 298 K, space group $P6_3/m$, $Z=2$ ($c/a=1.54$ and the molecular shape

approximates to a spheroid), while phase I is f.c.c. with $a=8.860$ (5) Å at 354 K, effective space group *Fm3m*, $Z=4$. The II ⟷ I transition may therefore be considered in terms of h.c.p. ⟷ f.c.c. transitions.

The structural changes occurring on transition can be thought to be produced as follows: by translating appropriate layers of molecules parallel to the a_{hex} b_{hex} plane, the transformation from a h.c.p. to a f.c.c. arrangement is made in the usual way (the packing sequence perpendicular