22.3—5   THREEDIMENSIONAL ANALYSIS OF
VITREOUS SILICA BY THE PARACRYSTAL CONCEPT.
By R. Hosemann, M.P. Hentschel, A. Lange,
U. Schmeißer, Gruppe Parakristallforschung,
c/o BAM, and R. Brückner, Institut für Nicht-
metallische Werkstoffe der TU, Berlin, FRG.

The combined interpretation of the X-ray in-
tensity distribution of vitreous silica, its
autocorrelation function and a rotatory distor-
ted model of the high cristobalite symmetry
Fd3m for the first time yields a threedimen-
sional solution of this paracrystalline struc-
ture. A 17°-twist of adjacent SiO_2-motives
clock- and counterclockwise around one cell
axis bends the tetraedric angles by $+17^\circ$ and
-3° and Si-O-Si-angles by 35°. The calculated
convolution product of this arrangement leads
to a radial density function, which is in good
agreement with the reduced radial density func-
tion, derived from the intensity plot of R.L.
Mozzi and B.E. Warren (J. Appl. Cryst. (1969),
2, 164). The stressed chemical bonds cause the
bearing (111)-netplanes to perform a standard
deviation $g \cong 10$ % of their mean distance
$d_{111} = 4,15$ Å, as determined by the unfolded
prominent reflection. The known hexahedral rings
of Si-atoms combine to form a spatial network
within paracrystals of octahedral shape con-
sisting of $N+1 = 4$ (111)-netplanes. These de-
fine their boundary surfaces with a roughness
$\alpha^* = \sqrt{N} \cdot g = 0,17$. The calculated structure
factor and the atomic scattering factors com-
bine well in order to fit the measured inten-
sity of the X-ray diffraction.

22.3—6   A QUASI-CRYSTALLINE SIMULATION OF
"$Pb_2M_t^{II}M_t^{III}F_9$" FLUORIDE GLASSES STRUCTURE. by A. Le Bail,
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Interference functions (neutrons, X-ray) and RDF of a
serie of isomorphous substituted glasses "$Pb_2M_t^{II}M_t^{III}F_9$"
($M_t^{II} = Mn^{2+}, Zn^{2+}$; $M_t^{III} = Fe^{3+}, V^{3+}, Ga^{3+}$) have been
simulated using a new "quasi-crystalline" method. The
procedure is based on the well known equations used in
X-ray line profile analysis of imperfect crystals (B.E.
WARREN, X-ray Diffraction, Addison-Wesley Pub., 1969)
where of course only the broadening due to strain is
considered (and not small coherent domains). The choice
of a Gaussian strain distribution and of a deformation
increasing as the square of the distance leads to a
gaussian peak-shape varying in halfwidth for each re-
flexion hkl of a simulated powder pattern. Good results
are obtained with structural models like $BaFeF_5$ or
Ba_2CoFeF_9-type which confirm previous interpretations in
terms of corner-sharing M_tF_6 octahedra and close packing
of large ions F^- and Pb^{2+} for the glasses. The number of
parameters needed for a simulation is the same as for a
crystalline structure with only two additional one's
relative to strain, so that it is believed that this me-
thod could be used as a basis for structural refinement
of the model in cases where several interference func-
tions with large variations are known (isotope and iso-
morph substitution experiments). Tests are actually made
on our data in this direction.

22.3—7   LARGE-ANGLE X-RAY SCATTERING STUDY OF
AMORPHOUS METALLIC COMPLEXES OF DITHIOOXAMIDE

by A. Mosset, M. Abboudi and J. Galy

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Dithiooxamide (rubeanic acid) is known to give
metallic complexes with remarkable electric, magnetic
and catalytic properties. Spectroscopic studies, es-
pecially on nickel and copper complexes, raised up
conflicting hypothesis about the ligand coordination
scheme.
     In order to correlate the physical properties
with the structural order, we have prepared and
studied, by the LAXS method, two amorphous complexes :
$CuL(H_2O)$ and $Ni_4L_5(H_2O)_{0.25}$ (L = dithiooxamide).

The two compounds have essentially the same local
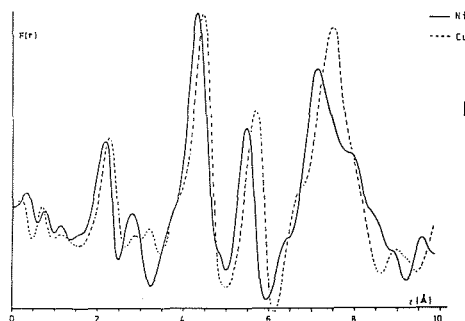structure as it can be seen on the radial distribution
functions F(r) (Fig. 1).

— Ni
···· Cu

Fig. 1

     The shift on the peak positions (= 0.2 Å)
is due to the variation of coordination bond lenghts.
The difference in peak intensities are correlated to
the chain lenght. So a structural model has only been
designed for the Ni complex.
     This model corresponds to the theoretical RDF in
figure 2 and can be described by the following
features :
     - the ligand is in trans conformation and planar.
     - The coordination is ensured by the four donor
atoms (S,N) and the Ni environment is square planar.
     - The ribbons, thus formed, stack perpendicularly
to the ligand plane with an interval equal to 3.6. Å.
     - This very high symmetry of the model must be
attenuated by a kind of variability in the local
structure (small variations in bond lenghts and angles
-small deviations to the ligand planeity and to the
stacking interval-...) to explain the amorphous nature
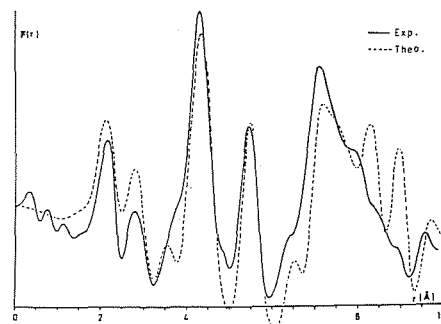of the studied materials.

— Exp.
···· Theo.

Fig. 2