20.4-01   SURSTRUCTURES ET INCOMMENSURABILITE DANS LA
THIOUREE. By A. Moudden, F. Denoyer, M. Lambert, Univer-
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Nous discuterons le diagramme de phase P.T de la thiou-
rée $SC(ND_2)_2$, nous montrerons que la phase modulée se
subdivise en plusieurs surstructures commensurables sim-
ples 3, 7, 9 ...

Nous présenterons qualitativement le mécanisme des ac-
crochages de la période de surstructure aux multiples
impairs de la période du réseau moyen. A partir des
règles de sélection des reflexions satellites nous dis-
cuterons la valeur du déphasage entre sous-réseaux et
déduire le super groupe d'espace possible lorsque la
période de modulation est incommensurable et voir sa
compatibilité avec le groupe d'espace tridimensionnel
habituel lorsque la période est commensurable. Nous ana-
lyserons, ensuite, les variations de l'amplitude de
l'onde de modulation et de ses harmoniques ; nous dé-
duirons des facteurs Debye-Waller dits anormaux la con-
tribution des défauts locaux de la période que nous com-
parerons à la théorie des fluctuations de phase des
structures modulées.

with a splitting parallel to the b-axis and corresponding
to about 100Å in real space. Another doublet at [010]
had splitting in the cubic [101] direction. A third
series of incommensurate reflections occurred in the
cubic [110] direction with splittings both in the direc-
tion of $[110]_c$ and $[010]_c$. The incommensurate reflec-
tions and lattice images indicate a modulation of the
structure interpretable as antiphase domains. Structure
models will be proposed.

20.4-02 $Er_{1.2}Mo_6S_8$--STRUCTURE WITH THREE INCOMMENSU-
RATE SUPERSTRUCTURES AND DISORDER. H. Brigitte Krause,
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A series of $(Sn_xEr_{1-x})_{1.2}Mo_6S_8$ compounds was examined
with selected area electron diffraction and high reso-
lution electron microscopy. In addition to the expected
rhombohedral (approximately cubic) Chevrel phase, sev-
eral different superlattices and sublattices were ob-
served. Furthermore, for $Er_{1.2}Mo_6S_8$ a new monoclinic,
or nearly monoclinic, structure type was discovered.
The b-direction of the monoclinic unit cell coincided
with the b-direction of the pseudocubic Chevrel phase,
and the lattice constant $b_c=b_M$ 6.37Å is identical for
both phases. The monoclinic a-axis is a_M=12.10Å, the c-
axis is c_M=8.17Å, and the angle β_M=96.5°. The monoclinic
axes are rotated with respect to the pseudocubic axes
such that $[101]_M$ is in the direction of $[001]_c$ and $[10\bar{1}]_M$
approximatley in the direction of $[100]_c$.

In spite of the similarities between the cubic and mono-
clinic geometry, there are distinct differences: the
volume ratio of $\frac{V_M}{V_c}$ =2.4 does not allow a simple interpre-
tation in terms of an Mo_6S_8 cube arrangement as in the
Chevrel phase. In addition to regular monoclinic reflec-
tions, incommensurate reflections and diffuse scattering
were observed. The diffuse scattering occurred in recip-
rocal lattice sheets perpendicular to the b-direction.
One of the incommensurate doublets occurred at $[110]_M$

20.4-03   THE MODULATED STRUCTURE OF CUBIC PHASE
Cu_9BiS_6.   By K. Tomeoka and M. Ohmasa*, Dept. of
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Ibaraki, Japan.

Quenched single crystals synthesized at about 550°C
for compositions near Cu_9BiS_6 were found to reveal non-
integral type satellite reflections in the X-ray dif-
fraction patterns. The crystals reveal fundamental re-
flections corresponding to cubic α-chalcocite, which has
a=5.54-5.57Å cell edge and a face-centered cubic cell.
Around the fundamental reflections, many non-integral
type extra reflections occur in clusters. These are
described as follows: (I) The period of the satellite
reflections corresponds to a non-integral multiple of
the subcell and changes in the range of 6.0 to 6.75a.
(II) The satellites appear three-dimensionally and make
a body-centered cubic reciprocal lattice in the same
manner as the main reflections. (III) Generally, in-
tensities of the satellites are very strong, and some
of them are much stronger than the main ones. (IV)
Compared with the mains, the satellites are slightly
diffuse. The degree of diffuseness differs in each
sample. (V) Asymmetry of intensities between pairs of
satellites is very remarkable. Generally, intensities
of lower angle satellites are stronger than those of
higher angle ones. This cubic phase has a solid so-
lution range of some extent. The positions and the
diffuseness of the satellites are correlated with the
change of composition of the crystal.
The superstructure was investigated by using X-ray
diffraction intensity data, measured on a crystal having
a 6.5 multiple of the subcell, because the period can
be made integral (13 multiple) simply by doubling 6.5.
Since the satellites form a body-centered cubic lattice

and satisfy m3m point symmetry, the superstructure was assumed to have the highest space group Fm3m for convenience of crystallographic calculations. The actual structure was examined as a superstructure having a face-centered cubic lattice with a lattice constant of $\underline{a}'=13\underline{a}=72.32\text{Å}$.

Through analysis of the partial Patterson function, the superstructure was found to be basically defined by clusters of Bi and of Cu. These two kinds of metal clusters occur alternately and are arranged in a face-centered cubic lattice mode. Such local clustering of the atoms is interpreted to be a combination of two different kinds of modulation factors: the periodic substitution between Bi and Cu and the periodic positional displacement of the atoms. Structure factor calculations, based on the clustering structure, gave substantial agreement with observed intensities.

The problems of the clustering structure can be attributed to the process of cooling from high temperature. This cubic phase and $Cu_3Bi_5S_9$, which also has a non-integral type superstructure(Ohmasa, Tomeoka & Sadanaga, 1979, AIP Conf. Proc., 53, 355), are stable only at temperature higher than 400°C and metastable at room temperature. In their stable high temperature phases, the crystals exist with random replacement between Bi and Cu and have structures approximating the substructures as defined in our studies (Ohmasa, 1973, Neues Jahrb. Miner. Monatsh., 227; Tomeoka, Ohmasa & Sadanaga, 1980, Mineralogical Journ., 10, 57.) During quenching, however, the metal atoms segregate into two kinds of clusters. The long-range repeat distances are directly influenced by these metal clusters and seem to be independent of the period of the subcell.

departure from stoichiometry. We also establish that at very low deviations from stoichiometry, dissociation of CS planes into anion vacancies may be possible due to the closeness in energy of the point defect mode of reduction with the extended defect mode. From our simulations we have thus been able to rationalise the apparently complex relationship between structure and composition in these nonstoichiometric oxides.

20.4-04   THE ENERGETICS OF FORMATION AND ORDERING OF CRYSTALLOGRAPHIC SHEAR PLANES IN ReO₃ STRUCTURED OXIDES. By A.N. Cormack, C.R.A. Catlow, University College London, and P.W. Tasker, AERE, Harwell.

We present the results of a detailed atomistic computer simulation study of extended defect formation in ReO₃ (DO₉) structured nonstoichiometric oxides. The phenomenon of crystallographic shear (CS) planes, as extended defects, in such compounds as WO_{3-x} and MoO_{3-x} has been extensively studied by both X-ray diffraction and high resolution electron microscopy. This combination of Reciprocal Space and Real Space crystallography has shed considerable light on the geometrical structure of these defects which may be considered as perturbations of a periodic, modulated structure (Proc. Int. Conf. on 'Modulated Structures', Hawaii 1979. American Institute of Physics conf. proc. No. 53, Plenum Press, New York.). At the same time, however, several fundamental problems have been raised concerning the preferred orientation for the formation of isolated CS planes, and their long range ordering into regular, or nearly regular, arrays at greater concentrations in the crystal. Our model correctly establishes that (102) CS planes are the most energetically favoured isolated CS planes in ReO₃ type structures and we also show that lattice relaxations play an essential part in stabilising this orientation over others such as (001) and (103). However, the energies of these defects are sufficiently close, so that the difference between them in the isolated case becomes outweighed by terms arising from their interaction at larger concentrations with increasing

20.4-05   IMPLICATIONS OF PSEUDO SYSTEMATIC ABSENCES IN APPARENT TETRAGONAL 4/MMM DIFFRACTION SYMMETRY. By A.D. Rae, School of Chemistry, University of New South Wales, Kensington, 2033, N.S.W. Australia.

The absences $F(hh\ell) = 0$, $h + \ell = 2n + 1$ and $F(hh\ell) = 0$, $h = 2n + 1$ do not correspond to symmetry elements of any primitive space group of 4/mmm Laue symmetry. When either systematic absence occurs in data of apparent 4/mmm diffraction symmetry, it may imply that the true crystal structure is not 4/mmm Laue symmetry but is of either mmm or 4/m Laue symmetry. Diffraction data with $\{hk\ell\}$ strong only for $h + k = 2n$ may be described as arising from a disordered structure in a subcell of axial lengths $a/\sqrt{2}$. $a/\sqrt{2}$, c which may indeed be of 4/mmm Laue symmetry. Systematic absences of $F(0k'\ell') = 0$ for $k' + \ell' = 2n + 1$ or $F(0k'\ell')$ for $k' = 2n + 1$ correspond to an allowed symmetry element for this disordered subcell structure. Twinning must be a condition for $\{hk\ell\}$ data with $h + k = 2n + 1$ to also have 4/mmm diffraction symmetry, should a satisfactory disordered structure consistent with the systematic absences of the subcell be obtained. Two structures based upon spacegroup $P4_2/mmm$ have been refined, one of true spacegroup $P4_2/n$, the other of true spacegroup Pbam. Both showed $|F(hk\ell)| = |F(kh\ell)|$ for all data. Constrained refinement is essential when twinning occurs. Fourier analysis methods identify which combinations of parameters are poorly defined.