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Disorder, superlattice canting and chiral domains in zirconia–niobia ceramic alloys

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Dedicated to Professor A. F. Moodie on the occasion of his 75th birthday

Abstract

The structures of the zirconia-based ceramic oxide superlattice alloy phases $Nb_2Zr_{x-2}O_{2x+1}$ ($x \approx 7$–12) are reviewed. It is noted that recent investigations into the alloys' structure suggest they are not strictly crystalline, with consequences for their diffraction properties. It is suggested that several aspects of their behaviour may be interpreted as proper to a frustrated two-dimensional *XY* model, where the distinctive planes of oxygen atoms in the alloys form a lattice of planar *XY* 'spins'. Evidence is presented for the existence of frustration, which produces superlattice canting in the model including electron-microscope evidence for the existence of domains of staggered Ising-type chirality in the alloys, as predicted for the frustrated two-dimensional *XY* model by Villain [*J. Phys. C* (1977), **10**, 1717–1734].

1. Introduction

As an engineering ceramic, zirconia is usually stabilized in a room-temperature phase which is (on average) of cubic structure by the addition of oxides of metals of valency lower than four. Though these anion-deficient alloys are currently still an active field of ceramics research, considerable interest has also recently been expressed (see *e.g.* Thompson *et al.*, 1990) in the consequences of 'stabilizing' zirconia to comparable doping levels with oxides of metals with valency greater than four (*e.g.* Nb_2O_5, Ta_2O_5), in particular because of their wide solid-solution range, their seemingly anomalous behaviour, and for the light they may shed on the operation of the engineering alloys.

The alloys are structurally complex, so some explanation of the current incomplete state of our understanding of them is in order. The description of the structures of these anion-excess alloys has in fact undergone considerable change with time in the last 25 years or so. Early diffraction experiments showed that the results of such anion-excess doping were alloys with structures very different from the familiar cubic zirconias mentioned above. The main consequence of doping with niobia (Nb_2O_5) appeared to be the production of orthorhombic long-period superlattices with very sharp electron diffraction spots and an apparently continuous distribution of dopant-dependent superlattice wavevectors within the composition limits $5{:}1 \leq ZrO_2{:}Nb_2O_5 \leq 8{:}1$, *i.e.* a continuous series of alloys with formula $Nb_2Zr_{x-2}O_{2x+1}$ ($x \approx 7$–12) such that each phase with non-integral x was a single superlattice structure rather than an intergrowth of two adjacent phases each with integer values for x (Roth *et al.*, 1972). The average metal subcell is still roughly cubic but the early single-crystal X-ray studies of two 'integral x' phases with simple stoichiometries, $Nb_2Zr_6O_{17}$ (Galy & Roth, 1973) and $Ta_2Zr_8O_{21}$ (J. Galy, unpublished), determined using conventional three-dimensional space-group analysis, resulted in apparent eightfold and tenfold superlattices in the [100] direction. In 1974, a radical new interpretation appeared that furnished an efficient description of the mechanism by which this alloy series could accommodate continuous non-stoichiometry. According to Hyde *et al.* (1974), the ortho-

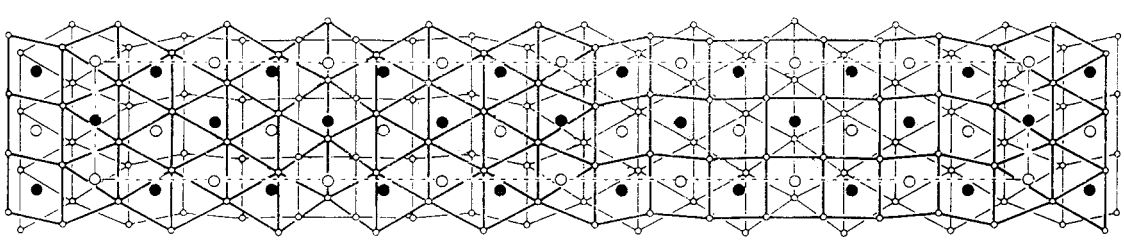

Fig. 1. [010] projection of $Nb_2Zr_6O_{17}$ after Hyde *et al.* (1974). The dashed rectangle is a projection of the unit cell: long axis (parallel to [100] direction) approximately 41 Å, short axis (parallel to [001] direction) approximately 5 Å. Following Fütterer *et al.* (1995), large empty circles are disordered cations of height approximately zero in the [010] direction, large dark circles are disordered cations of height approximately 0.5. Small empty circles are oxygen atoms. Lower net approximately 0.25, upper net approximately 0.75.

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rhombic niobia–zirconia alloys could best be described as having periodic approximately face-centred cubic metal positions with periodic two-dimensional nets of oxygen atoms alternating smoothly between 3^6 locally hexagonal nets and 4^4 locally tetragonal nets in the superlattice direction and arrayed in antiphase in the [010] direction of the orthorhombic superlattice structures. These need only small rotations of the oxygen nets in order to change gradually between the two net types, *i.e.* the nets alternate smoothly in the [100] superlattice direction and are stacked in antiphase in the [010] direction (Hyde *et al.*, 1974). The hexagonal (more correctly pseudohexagonal) segments of the nets are denser than the tetragonal segments so that essentially any niobia–zirconia 'nonstoichiometric' composition in the orthorhombic range can be accommodated by suitable rotation of the nets and subsequent shifts of [001] rows of oxygen atoms in the [100] direction. This description is somewhat idealized however, owing in part to its deduction from the conventional three-dimensional refinements of the alloys as commensurate superstructures (Galy & Roth, 1973) and to the disorder recently found to exist in both the metal and oxygen sublattices (Fütterer *et al.*, 1995). See Fig. 1 for a representation of the rotation of the nets. For a detailed description of the $x = 8$ niobia–zirconia structure (Galy & Roth, 1973) and of the $x = 10$ tantala–zirconia structure (Galy, 1980), see Makovicky & Hyde (1981) and Hyde & Andersson (1989). For the zirconia-rich end of the niobia–zirconia phase diagram, see Thompson *et al.* (1990).

A notable consequence of this 'vernier' model for niobia–zirconia alloys is that such small topological changes in the nets can lead to a continuous variation in oxygen coordination polyhedra of the metal atoms along the superlattice direction corresponding approximately to planar regions of well known structure types. In particular, in the description due to Hyde *et al.* (1974) above, the hexagonal oxygen net segments are longer than the tetragonal segments in the [100] direction and are considered to overlap in the [010] direction to produce periodic planar regions of local structure type approximating that of α-PbO_2. The α-PbO_2 regions extend throughout the entire crystal and are clearly visible as antiphase boundaries (a.p.b.'s) when viewed in the [001] projection (see Fig. 2). The rotation of the tetragonal segments of the oxygen nets is sharpest in the regions adjacent to the a.p.b.'s, which we shall call 'gradient regions'. The more niobium dopant the zirconia dissolves, the closer together along the [100] axis orthorhombic superlattice direction the α-PbO_2-type antiphase boundaries become. The structurally similar $Y(O, F)_{2+\delta}$ compounds (Bevan & Mann, 1975) are considered to differ structurally from the niobia–zirconia alloys chiefly in not possessing such antiphase regions (but see Papiernik & Frit, 1986). The (pseudo-) hexagonal and tetragonal nets in the $Y(O, F)_{2+\delta}$ compounds are thus not considered to alternate by

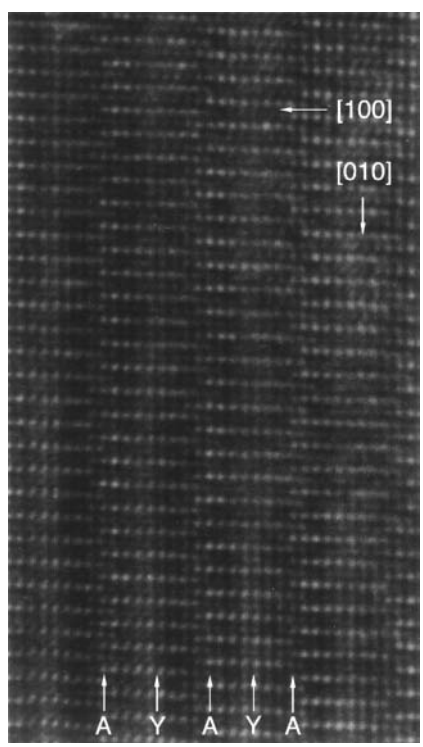

Fig. 2. [001] projection of $Nb_2Zr_{x-2}O_{2x+1}$ near $x = 10$. This is a view along the 'infinite' strips of smoothly transforming hexagonal and tetragonal nets, continuous in the [100] direction. Note the two-dimensional character of this projection. The hexagonal and tetragonal nets are alternating in the [010] direction. A representation of the overlap of the denser hexagonal net segments is evident at the a.p.b.'s. (The distance between *Y* arrowheads is approximately 25 Å.)

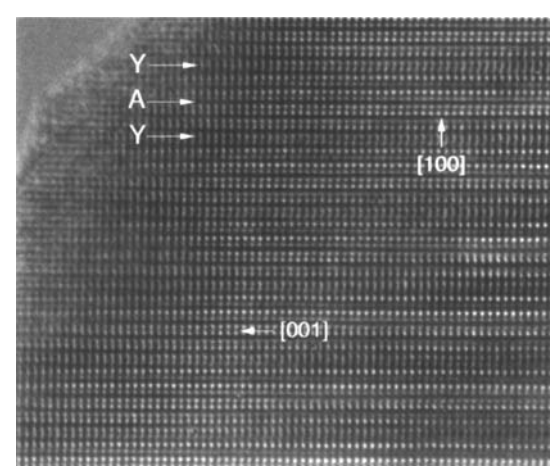

Fig. 3. [010] projection of $Nb_2Zr_{x-2}O_{2x+1}$ near $x = 10$. This projection looks down on the smoothly transforming tetragonal and hexagonal layers. Note the position of the α-PbO_2 (*A*) and YF_3 (*Y*) structural elements. (The distance between *Y* arrowheads is approximately 25 Å).

rotation smoothly between hexagonal and tetragonal segments in the superlattice direction, having instead their 'two-dimensionally infinite' oxygen planes stacked alternately hexagonal and tetragonal in the [100] direction. The orthorhombic niobia–zirconia superlattices, by contrast, are 'infinite' only in their [001] direction.

Midway between successive a.p.b.'s in the niobia–zirconia structures stand mirror planes, the structure around which closely approximates the YF_3 structure type. Between the YF_3-type regions and the α-PbO_2-type regions, Hyde *et al.* (1974) pointed out that a structure resembling baddeleyite (monoclinic zirconia, space group $P2_1/c$) could be described. Figs. 2 and 3 display electron micrographs of the orthorhombic alloy structure in the [001] and [010] projections. The approximate positions of the α-PbO_2 (A) and YF_3 (Y) structure-type regions are shown. Although the electron micrographs were recorded in the multiple-scattering regime of n-beam dynamical diffraction, the alternant symmetry of the a.p.b.'s is clearly in evidence.

More recently, investigations have been undertaken into the orthorhombic alloys employing four-dimensional space-group methods (Janssen *et al.*, 1992). Thompson *et al.* (1990) suggested that the alloys are more appropriately described as incommensurate compositely modulated structures (a metal substructure and an oxygen substructure), with a continuously variable composition-dependent primary modulation vector. Their description by a $[3+1]$-dimensional composite modulated structure is strictly valid only when the irrational component of the primary modulation wavevector points along the $a^*_{M'}$ direction of the metal substructure. This, however, is not generally the case, as Thompson *et al.* (1990) point out. The observed noncollinearity of the satellite reflections with the subcell reflections implies that the oxygen array is canted away from the subcell [100] direction, so that it is now generally incommensurate with the metal array in all three subcell directions. The alloys, then, are strictly speaking triclinic. Examples of the observed superlattice canting are exhibited in Fig. 4. These diffraction patterns were produced by rapid furnace cooling of the specimens from 1870 K, resulting in canting larger than that usually found in water-quenched or slowly furnace cooled specimens.

Thompson *et al.* (1990) used mixed oxide powders heated for relatively short times (days) at 1620 K to avoid niobia loss in the experiments referred to above. This procedure resulted in values for x between 7.1 and 10.3. In a subsequent single-crystal refinement employing synchrotron radiation, moreover, Fütterer *et al.* (1995) extended the upper limit in the value of x to 12 ($Nb_2Zr_{10}O_{25}$) using a lower-temperature flux method. Several other important results emerged from this refinement as well, creating considerable conceptual difficulties for both the incommensurate composite modulation model and the earlier vernier superstructure approach of Hyde *et al.* (1974). Using X-ray absorption-edge experiments, Fütterer *et al.* (1995) found no

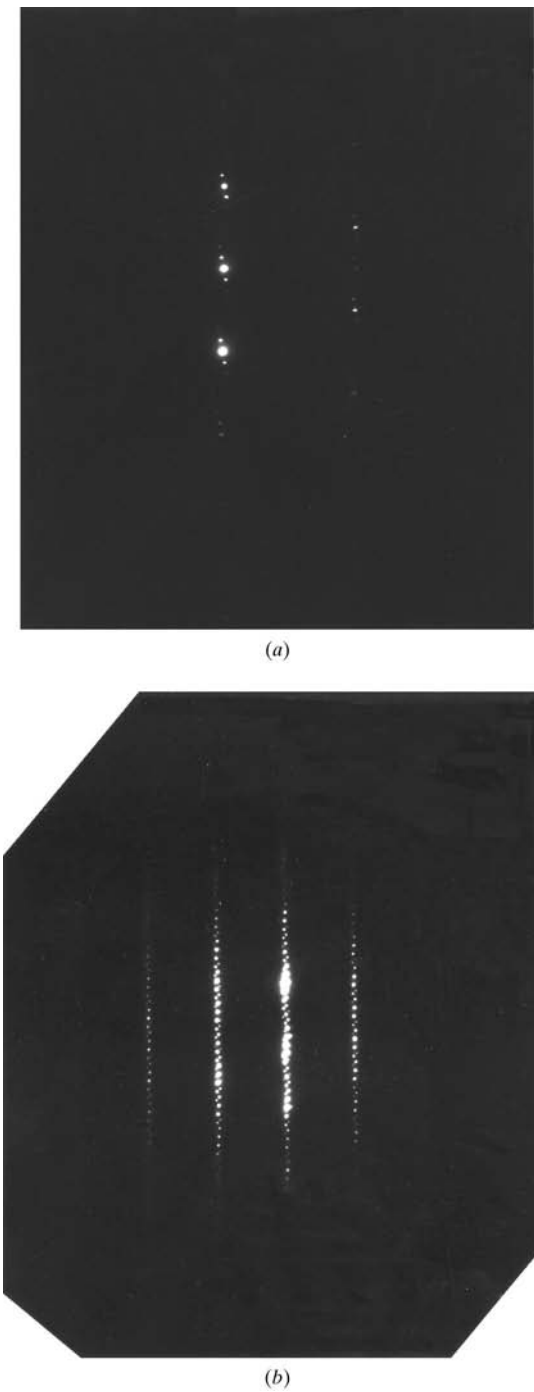

Fig. 4. (*a*) Large-angle canting of the superlatttice observed after rapid cooling from 1870 K. Prepared with initial Nb_2O_5:6ZrO_2 powder stoichiometry. Projection near $[0\bar{3}1]$. (*b*) Large-angle canting observed after rapid cooling from 1870 K. Prepared with initial Nb_2O_5:5ZrO_2 powder stoichiometry. Projection near $[0\bar{2}1]$.

chemical ordering evident in the cation distribution, so that the niobium atoms do not appear to cluster at the a.p.b.'s as had been suspected on valency grounds. Similarly, the anisotropic thermal parameters of the oxygen array were measured to be an order of magnitude larger than those of the metal atoms on average. A discrepancy also arose between the R values of the main reflections and the first-order satellite reflections indicating a considerable departure from the expected fit to a modulated structure. Although the parent metal substructure X-ray reflections are sharp, the oxygen substructure reflections appeared 'broad and ill-defined' and were interpreted as symptomatic of severe displacive disorder among the oxygen atoms, with displacements as large as $\sim$0.5 Å from their average positions compared with $\sim$0.1 Å for the metal-atom array. Both three- and four-dimensional X-ray structure determinations depend on long-range order (LRO) for their validity however, so that details of structural descriptions of the now 'pseudo-orthorhombic' or 'pseudo-triclinic' alloys determined using modulated structure methods or the vernier approach may be subject to considerable uncertainty due to disorder among the oxygen atoms.

Assuming that the crystallochemical insights afforded by the detailed determinations described above are still substantially valid in some average sense despite the recent discovery of extensive disorder, in the present paper we propose to use their results supported by further electron optical observations to identify a common origin both for the oxygen lattice disorder and the superlattice canting.

2. Experimental

The preparation of all electron-microscope specimens presented in this work was carried out using Nb_2O_5 and ZrO_2 powders mixed, pressed, fired, reground, pressed again and annealed at various temperatures in small sealed platinum tubes or in the open air supported on a setter of the same stoichiometry. For a discussion of specimen-preparation procedures, see Thompson *et al.* (1990). All imaging and diffraction experiments were carried out in a JEOL 200 CX electron microscope operating at 200 kV and using a double-tilt top-entry specimen stage with $\pm 10^\circ$ of tilt. The alloy specimens were ground in air or under liquid nitrogen in a mortar and pestle, then dispersed in water and collected on holey carbon grids.

3. Theoretical background

3.1. *A two-dimensional XY model*

In this section, we introduce a possible new structural viewpoint on the behaviour of these alloys. A long-range-ordered strictly crystalline interpretation for the structure of the alloys, for example, would rule out any independent rotation of the oxygen atom nets. However, although crystalline solids (having periodically broken translational symmetry) are invariant with respect to both translation and rotation, low-energy rotational distortions are fully determined by the translational distortions, so that there are no separate rotational elastic variables (see *e.g.* Chaikin & Lubensky, 1995). Fütterer *et al.* (1995), however, suggested that in the light of the apparent disorder discovered especially in the oxygen atom array during their synchrotron experiments, the oxygen substructure might usefully be described as similar to a paracrystal (Hosemann & Bagchi, 1962) with a disordered lattice topologically equivalent to a crystalline one but with a random distribution of bond lengths, bond angles and cell volumes. [Despite their reported disorder, the pseudo-tetragonal and pseudohexagonal nets of Hyde *et al.* (1974) and their smooth transformation back and forth appear however to survive as structural elements in the synchrotron X-ray analysis.] To interpret all the experimental data reported in previous sections and to describe the new results presented in this paper, we, on the other hand, propose that the alloy structure is indeed composite, but that the oxygen lattice is approximated by a stack of two-dimensional layers of atoms, each layer capable of continuous small-angle rotation in the [010] plane (at least near the gradient regions) and represented by a two-dimensional vector as its order par-

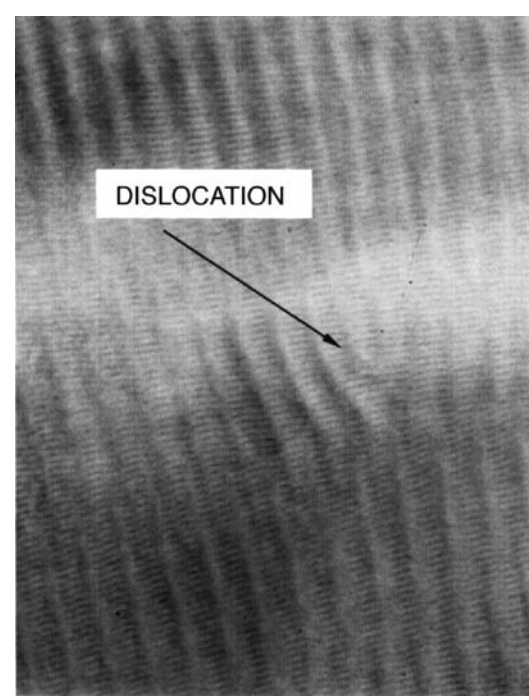

Fig. 5. Superlattice dislocation observed in the [001] projection of zirconia–niobia: specimen quenched from 1770 K.

ameter. Such a description means the alloys are now no longer strictly crystalline. The rotatable oxygen layers are coupled elastically and are separated by an essentially stationary approximately cubic array of metal atoms, which serves to maintain average charge neutrality and to define an approximately periodic lattice. The two-dimensional vectors corresponding to small rotations of the oxygen planes, then, are our fundamental analytical focus. Such a two-dimensional vector model is already well developed in the theory of magnetism (the *XY* model of planar spins). The elastic analogy with the *XY* model under construction in the present paper may be considered valid near phase transformations, since the universality of critical phenomena posits that only the dimensionality of the order parameter ($n = 2$) and that of the space in which it operates ($d = 2$) are relevant near the transition rather than detailed interactions. We shall henceforth employ appropriate analogies with established results expressed in the magnetic language to support assertions and deductions we make regarding the niobia–zirconia alloys, viewed as elastic systems. We consider, then, that the two-dimensional vectors corresponding to small rotations in the gradient regions of the oxygen planes are analogous to ferromagnetically coupled *XY* spins on a lattice with a two-dimensional order parameter. We further assume that near criticality the correlation length of the density fluctuations will be large enough to ensure that our stacked composite structure can be approximated by a planar *XY* model.

3.2. *Evidence in support of XY model*

The disorder reported by Fütterer *et al.* (1995) can be immediately deduced from the assumptions above. *XY* symmetry implies that, as an essentially two-dimensional system, the oxygen atom nets can never achieve long-range order (LRO) except at $T = 0$ K, since as their single rotational degree of freedom can be considered continuous, a 'continuous symmetry' results that cannot be broken at finite temperatures (Mermin & Wagner, 1966). That is, disorder is invariably to be found in any system analogous to a two-dimensional *XY* system.

The *XY* model also possesses a remarkable 'two-dimensional melting' transition between different disordered phases known as a Kosterlitz–Thouless (KT) transformation (Kosterlitz & Thouless, 1973). The high-temperature symmetry is not strictly speaking broken but is considered to undergo a topological phase transition. For a recent discussion, see Glaser & Clark (1993). Though the topological defect whose proliferation is believed to mediate the transformation – a superlattice dislocation in the niobia–zirconia alloy case – has been detected sporadically in the present series of electron optical experiments (see Fig. 5), no claim is made in the present paper regarding such observations as definite confirmation of the KT transformation. The lower-temperature KT phase, nonetheless, exhibits characteristic diffraction properties offering a plausible explanation for the distribution in reciprocal space of the diffuse scatter that must invariably occur in diffraction from disordered or partly ordered matter. The low-temperature phase below the Kosterlitz–Thouless transition temperature (T_{KT}) is considered to be in a critical state exhibiting quasi-long-range order (QLRO), with a power-law decay of order-parameter correlation. For some temperature range, then, the alloys can be considered to be continually on the verge of a phase transition.

In such a state, the corresponding susceptibility is high for a temperature range below T_{KT} and can be expected to display the effects of low-energy long-wavelength perturbations in its diffraction pattern. The slow-decaying long-tail correlations found in QLRO afford another means of distinguishing the two-dimensional *XY* model from the other possible alternatives. At low temperatures, a notionally 'perfect' crystal, possessing essentially perfect translational and rotational invariance, would scatter into ideally sharp δ-function-like diffraction spots. By contrast, the apparent reciprocal-space profile of diffraction spots owing to scatter from a critical phase, where fluctuations occur on all length scales, results in power-law correlation decay and

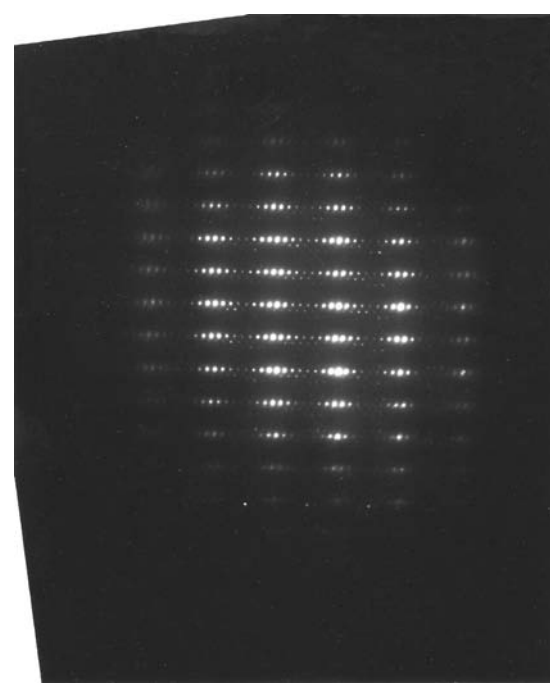

Fig. 6. [001] projection diffraction pattern displaying extra spots from another modulation of the lattice, different from the original [100] superlattice. The long-wavelength density correlations may be evidence for a critical temperature interval near 1770 K. Note the sharpness of the extra spots: $x \approx 8$. Specimen annealed for one month at 1770 K then quenched.

consequent sharp spots without any definite average width. The apparent width of the spots in the *XY* case will thus depend to some extent on the brightness and coherence of the probe and the strength of the scatter, which may help explain the sharp satellite reflections in the electron diffraction patterns of the alloys as displayed in Fig. 6 and their broadening in the synchrotron experiments conducted on $Nb_2Zr_{10}O_{25}$ reported by Fütterer *et al.* (1995). The set of very fine spots in Fig. 6 diffracted from planes possibly at large angles from the oxygen nets may also be evidence for other long-wavelength density correlations to be expected near criticality. Our suggested lattice *XY* model thus appears plausibly consistent with the criteria arising from established theories of the phase stability of vector models and with the experiments discussed here so far.

3.3. *Superlattice canting and the possibility of frustration*

So far, no explanation has been offered for the appearance of oxygen superlattice canting in the alloys. In this section, we suggest that the canting is the result of frustration on our system of *XY* 'spins'.

Briefly, frustration is the inability of a system of spins to satisfy all its energy-minimizing interactions simultaneously (Toulouse, 1977). The classical example is that of a planar triangular array of antiferromagnetically

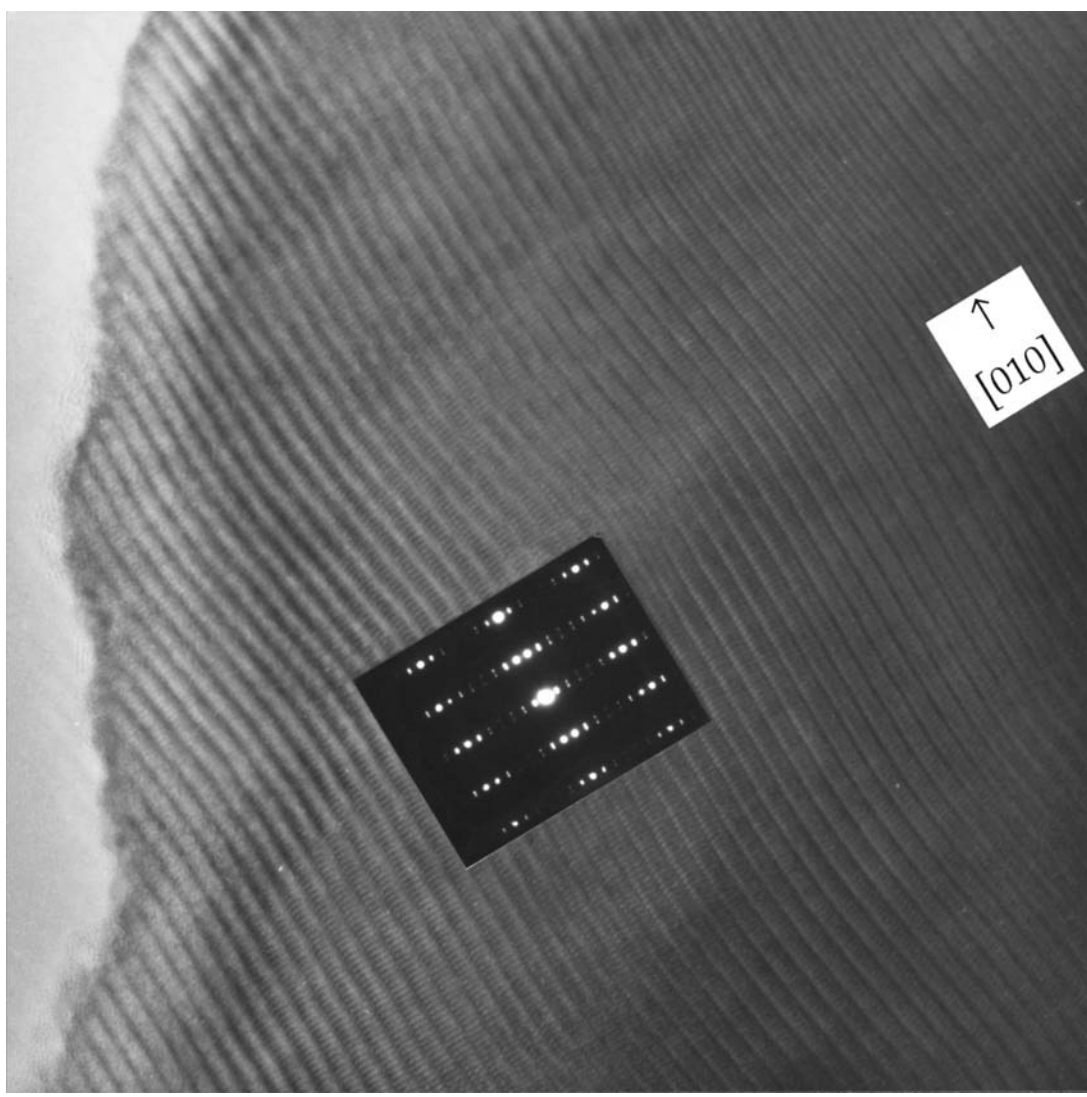

Fig. 7. [001] projection of $Nb_2Zr_{x-2}O_{2x+1}$ with x near 7.1 prepared in equilibrium with $Nb_{24}ZrO_{62}$. Initial powder stoichiometry Nb_2O_5:4ZrO_2. Specimen cooled from 1870 to 1670 K over two days, followed by one week's annealing at 1670 K, then one month at 1570 K: finally quenched to room temperature. Chiral domains may be detected by viewing at a glancing angle along [010] direction (marked).

coupled Ising spins (Wannier, 1950). It is known to be dependent on lattice geometry and involves competing interactions on the lattice. An example of a possible elastic analogy to be found in niobia–zirconia alloys is the following. The continuously variable sequence of coordination polyhedra corresponding to (*e.g.*) rutile, YF_3 and baddeleyite as described in the *Introduction* can be represented by an elasticity tensor whose major axes rotate continuously. As an example, Hyde *et al.* (1972) have demonstrated a simple transformation pathway involving small topological changes, which would rotate the principal axis of the local stress tensor through a right angle in moving from a region of (locally) rutile-type structure to one of baddeleyite, each of which has a unique axis (Hyde *et al.*, 1972). Because elastic forces are long range, it seems likely that this non-uniform (but approximately periodic) distribution of noncollinear tensors, held in place by the strain wave of the excess oxygen ions, will be frustrated. At this point, the existence of frustration is only a suggestion. When combined with the two-dimensional *XY* character of the nets, however, it provides a reasonably clear explanation for the appearance of canting in the oxygen superlattice and for a further highly distinctive experimental result, by analogy with several results in well known magnetic systems (see below). For a current review of frustration in magnetic systems with competing interactions, see Plumer *et al.* (1994).

In brief, Teitel & Jayaprakash (1983) demonstrated that a two-dimensional periodic array of coupled Josephson junctions frustrated by a uniform magnetic field normal to the plane of the junctions is well described by a fully frustrated two-dimensional *XY* model and that the periodicity of the flux superlattice is governed by the degree of frustration. Choi & Doniach (1985) also calculated the expected Brillouin zones corresponding to the flux superlattices arising from varying degrees of frustration and found it to influence not only the magnitude of the average wavevector but also its direction. Hence, frustration of a sufficient strength in a two-dimensional *XY* system can cause canting of a superlattice. In a similar way, we claim (appealing to universality) that a corresponding elastic frustration due to a non-uniform stress tensor may be the source of canting of the oxygen nets. In the next section, we report striking experimental evidence for our claim that niobia–zirconia alloys may be adequately described by a frustrated *XY* model.

4. Further evidence for a frustrated *XY* model: coexisting *XY* and Ising symmetries: chiral domains

Probably the most remarkable property predicted in Villain's (1977) analysis of a frustrated *XY* model on a square two-dimensional lattice ('spin glass with nonrandom interactions') was a ground-state degeneracy of two coexisting with Kosterlitz–Thouless-type phases. This degeneracy corresponds to a chiral degree of freedom with Ising (*i.e.* up/down, plus/minus) symmetry. Fig. 7 displays what we believe to be the elastic analogue of these chiral degrees of freedom. The micrograph is a [001] projection of the alloy with composition near the solid-solubility limit for 1570 K. The effects of possible niobium loss during firing are avoided by preparing the alloy with an initial Zr:Nb ratio of 2:1 corresponding to the two-phase region containing the alloys and the line phase $Nb_{24}ZrO_{62}$. In this way, it is possible to prepare the alloy specimens with concentration at the niobia solid-solubility limit for the final quench temperature, in this case 1570 K, yielding grains with $x \approx 7.1$ in equilibrium with grains of $Nb_{24}ZrO_{62}$. In Fig. 7, the superlattice fringes are parallel to the [010] direction and are approximately 18 Å apart. If viewed at a glancing angle along [010], the 'twinned' character of the image becomes clear, with the direction of the superlattice fringes changing direction every 400 Å or so. These 'domains' correspond to an Ising-like symmetry with alternating chirality (*i.e.* handedness with respect to the local two-dimensional phase variables) in consecutive domains. Their appearance and disappearance between 1570 and 1670 K is reversible.

5. Conclusions

With both the paracrystalline disorder and the rotating oxygen nets in mind, it has been proposed that the oxygen nets be modelled by a lattice of two-dimensional (planar) *XY*-type vector spins. The essentially stationary metal atoms serve to define the lattice geometry and to balance the overall valency requirements. The effective periodic frustration in the model is afforded by the rotating elastic tensor axes and embodied in the structure types defined by the metal atoms and the average oxygen atom positions as described in the *Introduction*. Superlattice canting and low-temperature disorder follow immediately from this model. The alloy structures are no longer able to be considered completely crystalline and the frustration (if it occurs) will be able to affect the superlattice to the extent that the oxygen nets are able to rotate continuously and independently as planar *XY* 'spins'. The elastic analogues of the Ising-like chiral domains predicted by Villain (1977) have been detected, which are specifically related to frustrated two-dimensional planar *XY* models.

It is known (Papiernik & Frit, 1986) that the presence of a.p.b.'s in vernier-type compounds is not a guarantee that a given material has two types of cation and one type of anion but that ordering of the anions may take a role in determining whether a.p.b.'s occur. Similarly, superlattice canting never seems to appear in $Y(O, F)_{2+\delta}$ compounds. This may be because, although these a.p.b.-less structures also possess part of the sequence of lattice types which we claim leads to frustration, they tend to be anion-ordered, which may reduce the driving force for

frustration or, since they possess no gradient regions, disqualify them as *XY* models altogether.

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