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Neutron and X-ray Diffuse Scattering of Calcium-Stabilized Zirconia at Temperatures up to 1500 K

TH. PROFFEN,[a] M. KEILHOLZ,[a] R. B. NEDER,[a] F. FREY[a] AND D. A. KEEN[b]

[a]*Institut für Kristallographie und Mineralogie, LMU München, Theresienstrasse 41, D-80333 München, Germany, and* [b]*ISIS Science Division, RAL, Didcot OX11 0QX, England*

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Abstract

The temperature dependence of disorder diffuse scattering of calcium-stabilized zirconia was measured with neutron and X-ray scattering methods up to 1500 K. A quantitative interpretation of the diffuse scattering is given in terms of a correlated distribution of two types of microdomains. A pronounced decrease of the integrated intensity of the diffuse maxima was found in the temperature range 1250–1300 K in both neutron and X-ray cases. However, the half-width of the diffuse maxima and the corresponding correlation length shows a different temperature behaviour. The neutron data indicate an almost constant correlation length as a function of temperature, whereas the X-ray data show a maximum at 1170 K. A tentative interpretation is given.

1. Introduction

Cubic stabilized zirconia doped with CaO, Y_2O_3 or MgO is of outstanding interest in material science due to its excellent mechanical and electrical properties, which strongly depend, amongst others, on the specific defect and disorder structures. The disorder may be influenced by the dopant oxide, *i.e.* type of dopant and dopant concentration, temperature–time treatment, actual temperature, applied electric field and other factors. In this paper we will concentrate on the temperature dependence of the diffuse scattering of calcium-stabilized zirconia. At ambient pressure pure ZrO_2 has tnree polymorphs of monoclinic, tetragonal and cubic symmetry with transformation temperatures $T_{m-t} \sim 1443$ and $T_{t-c} \sim 2643$ K. The high-temperature cubic phase can be retained at room temperature by doping with oxides of bi- or trivalent metals. The average structure of cubic zirconia is the fluorite-type structure, space group $Fm3m$, with Zr on (0,0,0) and O on $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$.

The defect structure of calcium-stabilized zirconia (7 and 15 mol% CaO) can be described by a correlated distribution of two types of microdomains based on single and paired oxygen vacancies within the cubic matrix of the crystal (Neder, Frey & Schulz, 1990*a*,*b*; Proffen, Neder, Frey & Assmus, 1993; Proffen, Neder & Frey, 1996). In a previous study of the temperature dependence of elastic neutron diffuse scattering of calcium-stabilized zirconia doped with 15 and 10 mol% CaO we reported a pronounced decrease in the intensity of the diffuse maxima within the temperature range 1150–1350 K (Proffen, Neder, Frey, Keen & Zeyen, 1993). This decrease occurs in the temperature region where a deviation from Arrhenius behaviour of the ionic conductivity was reported by Strickler & Carlson (1964). No significant change of the half-width and shape of the diffuse maxima was observed, from which we concluded that the amount of correlated microdomains decreases, whereas the correlation length remains almost constant (Proffen, Neder, Frey, Keen & Zeyen, 1993). In a recent paper Kahlert, Frey, Boysen & Lassak (1995) reported diffuse scattering from zirconia as a function of temperature and an applied electric field. They confirmed the temperature behaviour found by Proffen, Neder,

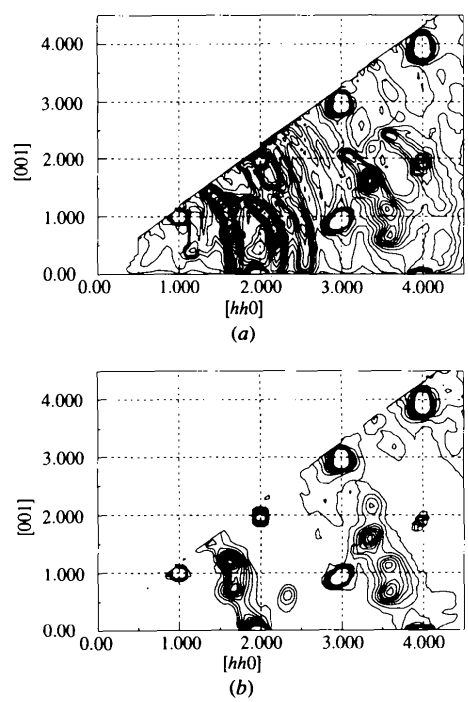
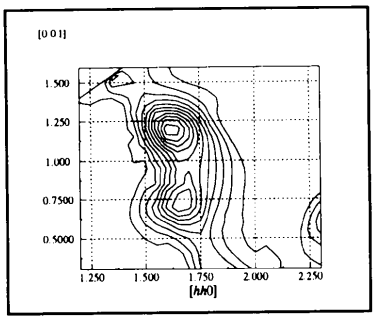
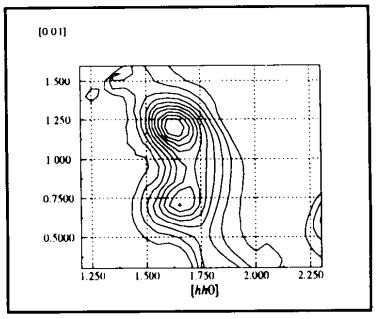


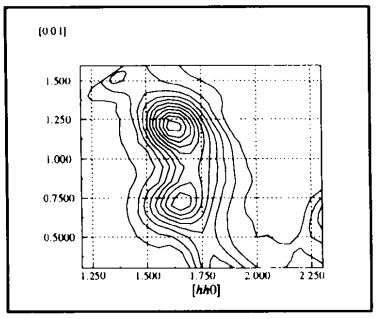
Fig. 1. Measured section of the zeroth layer of the [1$\bar{1}$0] zone of zirconia doped with 15 mol% CaO (CSZ15) at T = 1000 K on the diffractometer SXD, ISIS, using a mirror furnace (Lorenz, Neder, Marxreiter, Frey & Schneider, 1993): (*a*) raw data and (*b*) after background correction. The intensities are given in steps of 20 counts. The lowest intensity level corresponds to 50 counts.



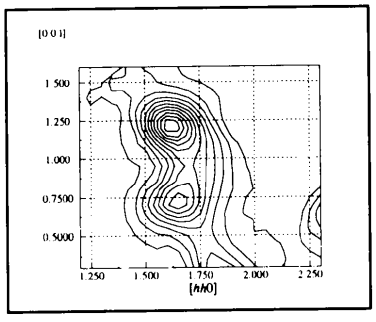
(*a*) $T = 1000\,\mathrm{K}$



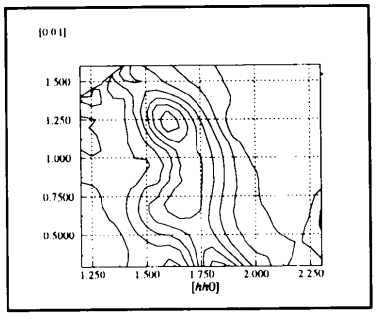
(*b*) $T = 1150\,\mathrm{K}$



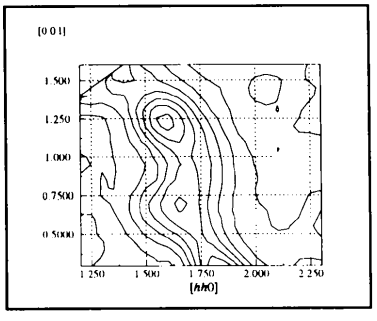
(*c*) $T = 1200\,\mathrm{K}$



(*d*) $T = 1250\,\mathrm{K}$

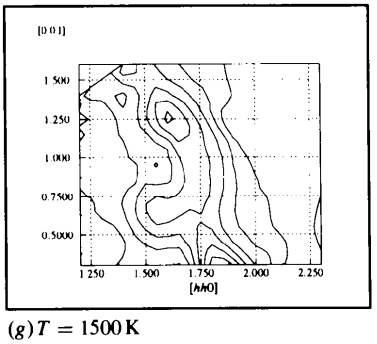


(*e*) $T = 1300\,\mathrm{K}$

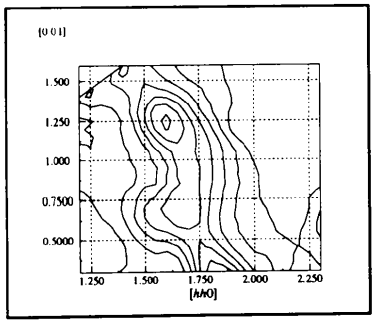


(*f*) $T = 1350\,\mathrm{K}$

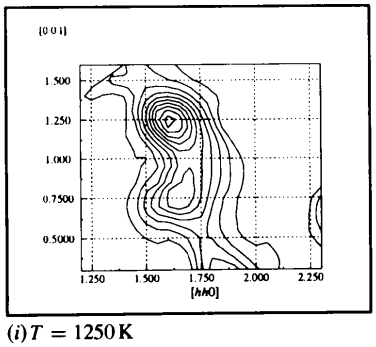
(*a*)–(*g*): Heating
(*h*)–(*j*): Cooling



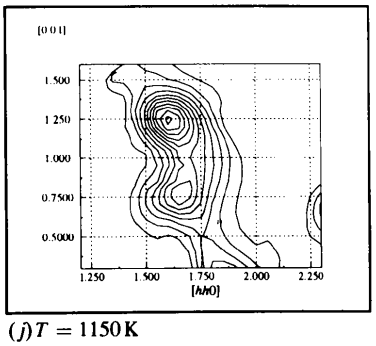
(*g*) $T = 1500\,\mathrm{K}$



(*h*) $T = 1350\,\mathrm{K}$



(*i*) $T = 1250\,\mathrm{K}$



(*j*) $T = 1150\,\mathrm{K}$

Fig. 2. Section around diffuse maxima (1.6 1.6 0.8) and (1.6 1.6 1.2) of CSZ15 at different temperatures. The intensities are given in steps of 20 counts. The lowest intensity level corresponds to 50 counts.

Frey, Keen & Zeyen (1993) and report, based on an interpretation using microdomains, an ordering process between the microdomains supported by an enhanced ionic motion at high temperatures, *i.e.* an increase of the correlation length from 25 Å at room temperature to 60 Å at 1000 K. Kahlert, Frey, Boysen & Lassak (1995) interpret the decrease of correlations at temperatures above 1200 K by the higher mobility of the oxygens and a subsequent dissolution of the microdomains.

The aim of the present work is the study of the temperature dependence of the diffuse scattering of zirconia within the temperature range of the previously reported drop in diffuse intensity. In our recent study of the diffuse scattering of zirconia at room temperature (Proffen, Neder & Frey, 1996) the combination of neutron and X-ray scattering experiments gave additional information on the defect structure, *i.e.* the structure of the microdomains. On the basis of this experience high-temperature neutron *and* X-ray scattering experiments were carried out.

2. Experimental and measurements

The samples used for neutron and X-ray scattering experiments with nominal composition $Zr_{0.85}Ca_{0.15}O_{1.85}$ were taken from a single charge supplied by Djevahirdjan Corporation, Switzerland. The transparent crystals were grown by the skull-melting technique. The volume of the crystal used for the neutron measurements was *ca* 0.8 cm^3. The size of the X-ray sample was *ca* $200 \times 150 \times 150\ \mu m^3$.

The neutron measurements were carried out on the time-of-flight instrument SXD at the neutron spallation source ISIS, RAL. The sample was heated by a mirror furnace (Lorenz, Neder, Marxreiter, Frey & Schneider, 1993), which was adapted to the instrument SXD. This furnace operates under oxidizing atmosphere and yields temperatures up to 2300 K. The wavelength range 0.25–8 Å could be used. The extended diffuse scattering was measured with a ZnS-scintillating position-sensitive detector (PSD) with 64×64 elements at a distance of 120 mm, providing an angular resolution of $\Delta(2\theta) = 1.4°$. A great advantage of this setup is the possibility of measuring large sections of reciprocal space without any movement of the furnace or sample. The disadvantage of such an arrangement is that it is hard to shield a large two-dimensional PSD placed close to the sample from sources of background. Air scattering and scattering from the mirror furnace itself are therefore not an insubstantial part of the diffraction pattern. The collected data were corrected for the spectral distribution as determined by a vanadium scan and for background scattering by an empty scan, which was carried out with the furnace and the ceramic tubes (Al_2O_3) used as a sample holder at 1250 K. The data for each element at the given scattering angle θ were transformed into momentum space by $Q = (m_n/h)(L)(2\sin\theta)(1/t)$, with L = total neutron flight path, t = flight time, m_n = neutron mass and h = Planck's constant. Fig. 1 shows the observed section of the zeroth layer of the $[1\bar{1}0]$ zone between the [110] and [111] directions at a temperature of 1000 K, without and with applied background correction. The area used for the data evaluation (see next section) around the diffuse maxima (1.6 1.6 0.8) and (1.6 1.61.2) can be seen in Fig. 2 for all measured temperatures.

For the X-ray measurements a Weissenberg camera with special heating equipment was used (Adlhart, Tzafaras, Sueno, Jagodzinski & Huber, 1982). In our previous experiment (Proffen, Neder, Frey, Keen & Zeyen, 1993) we found an irreversible change of the zirconia sample while heating *in vacuuo*, which was not observed at ambient atmosphere. For this reason the original, X-ray transparent, graphite heating element of the camera was replaced by a platinum heating element

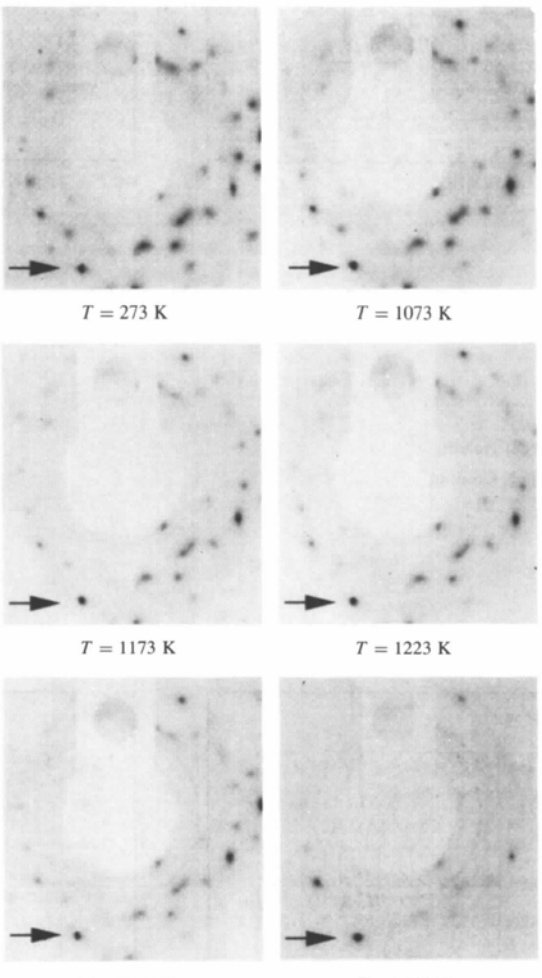


Fig. 3. X-ray photographs at a fixed ω-position of CSZ15 using a heating Weissenberg camera (Adlhart, Tzafaras, Sueno, Jagodzinski & Huber, 1982) at different temperatures (Mo $K\alpha$ radiation, quartz monochromator exposure time 8 h). The black arrow marks a Bragg reflection used for reference.

to allow high-temperature measurements in an oxidizing atmosphere. Consequently, the observable scattering was limited to a small cone given by the hole in the heating element for the primary beam. The diffuse scattering shown in Fig. 3 was recorded at a fixed ω position with an exposure time of 8 h. At temperatures above 1173 K powder rings are visible, which can be indexed as pure platinum. In this temperature range the heating element starts to evaporate and recrystallizes on the surface of the sample.

3. Data evaluation and results

Two basic features of the diffuse scattering can be recognized: diffuse maxima corresponding to a superstructure wavevector of $\pm(0.4\ 0.4\ \pm0.8)$ and underlying broad diffuse bands. To learn about the temperature behaviour of the diffuse maxima, a profile of the strongest intensity concentration at (1.6 1.6 1.2) scanned perpendicularly to the underlying diffuse band was fitted with a symmetric Gaussian. An example fit for the measurement at T = 1200 K is shown in Fig. 4. The measured section around these diffuse maxima is too small to fit the diffuse maxima and the underlying diffuse band by two-dimensional Gaussians, as seen in Proffen, Neder, Frey, Keen & Zeyen (1993), while the diffuse maxima at higher Q vectors became too weak at high temperatures for a quantitative analysis. Table 1 contains the results for the neutron measurements, *viz.* one background parameter,

Table 1. *Results of fitting the neutron data*

Temperature (K)	Background	Integral intensity	FWHM	Goodness-of-fit
Heating				
1000	23 (5)	47 (4)	0.265 (9)	5.5
1150	24 (4)	45 (3)	0.261 (4)	4.9
1200	26 (6)	47 (3)	0.268 (8)	5.0
1250	32 (6)	46 (3)	0.261 (9)	5.6
1300	44 (7)	30 (3)	0.29 (2)	5.7
1350	46 (8)	31 (3)	0.30 (1)	5.5
1500	54 (9)	25 (5)	0.30 (3)	8.8
Cooling				
1350	47 (7)	30 (5)	0.30 (1)	5.2
1250	24 (8)	41 (4)	0.27 (1)	5.8
1150	23 (7)	44 (4)	0.275 (9)	5.5

the integrated intensity, the half-width FWHM of the diffuse maximum perpendicular to the diffuse band and the goodness-of-fit. The intensity displayed is corrected for a temperature factor using values published by Lorenz, Frey, Schulz & Boysen (1988). The resulting temperature dependence of the integrated intensity of the diffuse maximum at (1.6 1.6 1.2) is shown in Fig. 5. The full circles and squares mark intensities measured while heating and cooling, respectively. As in our previous study (Proffen, Neder, Frey, Keen & Zeyen, 1993) a strong and fully reversible decrease of the intensity of the diffuse maxima can be observed under ambient atmosphere. In our recent experiment the range of this intensity 'drop' could be narrowed to a smaller temperature range between 1250 and 1300 K. As the general behaviour corresponds to the results of our previous elastic neutron measurements (Proffen, Neder, Frey, Keen & Zeyen, 1993), the major part of the observed diffuse intensities can be assumed to be elastic. The half-width of the diffuse maximum (Fig. 6) shows an insignificant increase as a function of temperature.

To analyse the X-ray high-temperature data in a quantitative way, the X-ray photographs were scanned with a standard flat bed scanner (Proffen & Hradil, 1993). Further processing was carried out by fitting a two-dimensional Gaussian to a selected diffuse maximum, which shows no contamination by the platinum powder

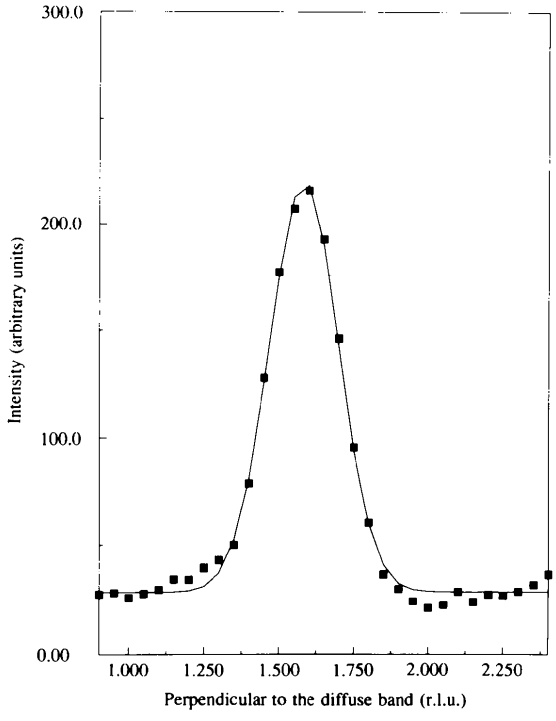


Fig. 4. Typical fit of SXD data (here at T = 1200 K); full squares are observed intensities perpendicular to the diffuse band and the solid line represents the calculated function.

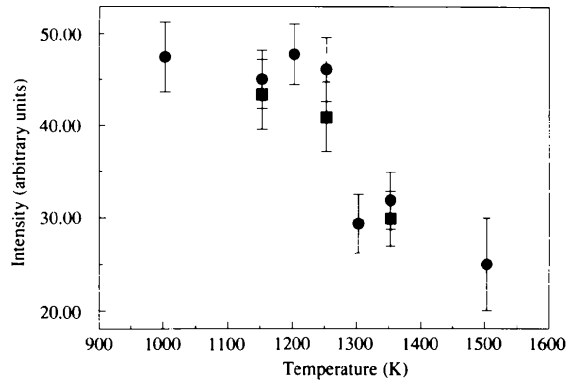


Fig. 5. Temperature dependence of the integrated intensity of the diffuse maximum (1.6 1.6 1.2) of CSZ, measured on SXD. The full circles mark temperature points during heating, the full squares while cooling.

Table 2. *Results of fitting the X-ray data*

Temperature (K)	Background	Integral intensity	$FWHM_a$	$FWHM_b$	Goodness-of-fit
273	42.5 (7)	7280 (470)	26.6 (4)	21.9 (3)	4.2
1073	43.4 (9)	6780 (440)	21.3 (3)	17.8 (4)	3.4
1173	54.1 (7)	6010 (420)	17.1 (1)	14.8 (2)	3.6
1223	48.5 (7)	5080 (430)	18.5 (4)	15.8 (6)	3.5
1273	53.9 (8)	5240 (410)	20.9 (4)	17.9 (3)	3.4
1423	53.1 (3)	2210 (500)	25.3 (9)	22.6 (4)	2.1

rings that appear at higher temperatures (see later in this section). The local principle a and b axes of the Gaussian are rotated with respect to the underlying x and y axes of the scanned film by an angle α. The diffuse maximum was therefore fitted by two parameters for the position, two half-width parameters $FWHM_a$ and $FWHM_b$ and one parameter for the peak intensity. The flat background is described by one additional parameter. For all refinements of the high-temperature data the angle α was kept fixed at its room temperature value of $\alpha = 34°$. A typical result of this procedure for the X-ray measurements at a temperature of 1073 K is shown in Fig. 7. Table 2 contains the results of the X-ray refinements, *viz.* one background parameter, the integrated intensity, the half-widths $FWHM_a$ and $FWHM_b$ in the principle a and b directions of the Gaussian and the goodness-of-fit. As for the neutron case, the integrated intensities are corrected for temperature factors (B values from Lorenz, Frey, Schulz & Boysen, 1988). The temperature dependence of the integrated X-ray intensity of the diffuse maximum is shown in Fig. 8. A strong decrease of the diffuse intensity can easily be seen between 1273 and 1423 K, in accordance with the neutron measurements. The slight decrease visible at lower temperatures is due to absorption by the platinum evaporating from the heating element and covering the sample at temperatures above 1173 K. The strongly texturized Pt-powder rings do not allow any subtraction of this disruptive scattering from the data. Fortunately, direct comparision of the measurements at 1273 and 1423 K shows that the amount of contamination by platinum at 1273 and 1423 K is almost

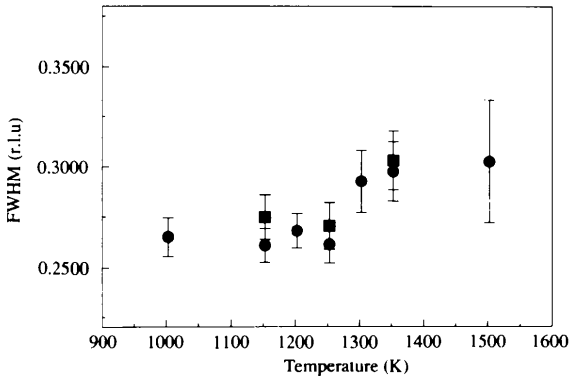


Fig. 6. Temperature dependence of the FWHM of the diffuse maximum (1.6 1.6 1.2) of CSZ measured on SXD. The full circles mark temperature points measured while heating, the full squares while cooling.

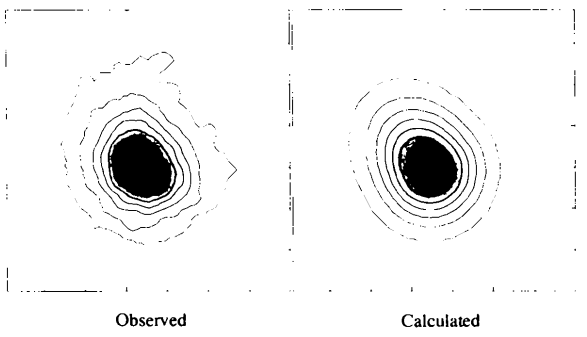


Fig. 7. Typical fit (here at T = 1073 K) of a two-dimensional Gaussian to scanned X-ray data.

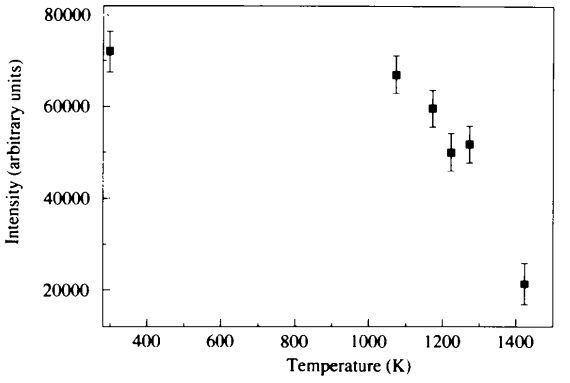


Fig. 8. Temperature dependence of the integrated intensity of a diffuse maximum of CSZ15 measured with X-rays.

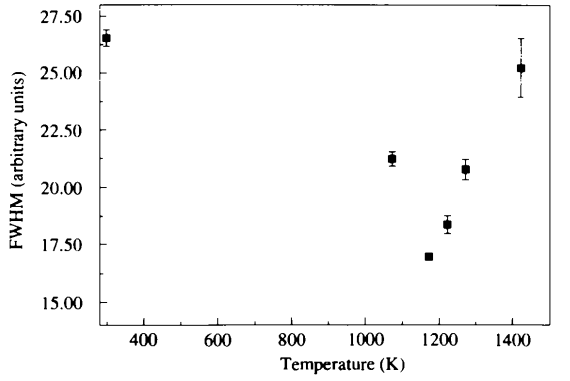


Fig. 9. Temperature dependence of the half-width $FWHM_a$ of a diffuse maximum of CSZ15 measured with X-rays.

equal. Subsequently, the strong decrease of the observed intensity in this temperature range is mainly due to a decrease in the intensity of the diffuse scattering itself and not an effect of absorption by platinum covering the sample. In contradiction to the results of the neutron measurements the temperature dependence of the half-widths $FWHM_a$ and $FWHM_b$ of the diffuse maximum (Fig. 9) show a minimum at 1173 K. The intensity of the Bragg reflection marked by an arrow in Fig. 3 shows that the observed behaviour of the intensity and the half-width of the diffuse maximum cannot be traced back to small displacements of the sample during heating. Summarizing, the integrated intensity of the diffuse maxima shows a strong decrease at $T \sim 1275$ K in the neutron as well as in the X-ray case, whereas the half-width shows a different behaviour: an almost constant half-width in the neutron case and a minimum at $T \sim 1173$ K in the X-ray case. A tentative interpretation of this result is given in the next section.

4. Discussion

Diffuse neutron as well as X-ray intensities of calcium-stabilized zirconia can be well described by a correlated distribution of two types of microdomains based on a single and a paired oxygen vacancy with relaxed neighbours (Proffen, Neder & Frey, 1996). Generally, we observed that this diffuse scattering is very similar in a wide range of concentrations from 4 to 15 mol% CaO (Proffen, Neder, Frey, Keen & Zeyen, 1993). This can be understood by an inhomogeneous crystal material, which contains areas with a certain concentration of oxygen vacancies necessary for the proposed correlated distribution of microdomains and areas without ordered oxygen vacancies. Different concentrations of CaO result in different regions with correlated microdomains. The temperature dependence of the intensity of the diffuse maxima shows a strong decrease between 1250 and 1300 K, but is still observable up to the highest temperature of 1500 K achieved in this experiment. In the same temperature range of this anomaly other unusual observations were reported: large anisotropic phonon line-widths measured by inelastic neutron scattering (Strauß *et al.*, 1995) and a deviation from the Arrhenius behaviour of the ionic conductivity (Strickler & Carlson, 1964). Furthermore, this temperature interval corresponds to the approximate limit of the stability field of the fluorite structure in the phase diagram (Hellmann & Stubican, 1983). The correlation length remains almost unchanged at room temperature and for temperatures above 1300 K. In our model of an inhomogeneous crystal the amount of correlated microdomains decreases strongly within the temperature range 1250–1300 K, but the correlation length remains almost unaffected. This results in a strong increase of the amount of 'free' oxygen vacancies separated from the correlated microdomains, which explains the increase in ionic conductivity found by Strickler & Carlson (1964).

As mentioned above the half-width of the diffuse maxima shows a minimum only for the X-ray measurements as a function of temperature. This minimum corresponds to an increase of the correlation length from 25 Å at room temperature to 32 Å at 1173 K. We conclude from this behaviour an increased correlation between the cations in this temperature range, whereas the correlation for the oxygen sublattice remains almost unaffected. One should be aware that the strong scatterers in the X-ray case are the cations (Zr,Ca) compared with the oxygens, whereas the scattering power of all these ions are comparable in the neutron case. The ordering of the cations might be facilitated by a higher mobility at this temperature which allows Zr to occupy more of the preferred seven-coordinated sites. The ordering of the oxygens may be prevented by the large calcium ions which hinder the mobility of the oxygens (Kahlert, Frey, Boysen & Lassak, 1995). For proof of this tentative model additional high-temperature X-ray measurements are necessary.

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