



Crystallite size effect on the monoclinic deformation of the bcc crystal structure of chromium



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ABSTRACT

The modulated spin density wave magnetic orderings observed in chromium suggests that the crystal structure of chromium cannot be described by the cubic space group $Im\bar{3}m$. Our experimental studies of polycrystalline and nanocrystalline chromium by synchrotron radiation (SR) and neutron powder diffraction show a hkl-dependent Bragg peak broadening which can be interpreted by the low-symmetry monoclinic space group $P2_1/n$ instead of the high symmetry cubic space group $Im\bar{3}m$. The monoclinic angle is $\beta_m = 90.05(1)^\circ$ and $90.29(1)^\circ$ for polycrystalline Cr and nanocrystalline Cr, respectively. The relative monoclinic distortion observed in chromium is 5 times larger than those reported for several oxides: $BiFeO_3$, $\alpha-Fe_2O_3$, Cr_2O_3 and calcite. The symmetry of the magnetic transverse spin density wave (TSDW) and the longitudinal spin density wave (LSDW) observed in Cr are described by using the superspace groups $P2_1/n(0\beta 0)00$ and $P2_1'/n'(0\beta 0)00$, respectively. These superspace groups describe both the magnetic modulations and the atomic position modulations reported in the literature. The monoclinic symmetry of chromium is a robust effect which is observed in the paramagnetic as well as in the TSDW and LSDW phases.

1. Introduction

The role of symmetry in physics [1] is emphasised by the following statement: “If a system has a certain group of symmetry then any physical observable of that system must also possess the same symmetry”, known as the Neumann’s principle [2]. P. Curie was the first to state [1] that if the observed phenomenon is not invariant under some symmetry operation then the system cannot have this symmetry operation. This concept can be applied to the observation of hkl-dependent Bragg peak broadening in powder diffraction studies [3,4]. According to [3] the hkl-dependent Bragg peak broadening can be interpreted in two ways: (i) by using an anisotropic broadening model within the high symmetry structure model or (ii) by assuming a lower symmetry structure model which leads to reflection splitting induced peak broadening. Both approaches using high-symmetry and low-symmetry models show very similar hkl-dependence and they should lead to similar fit qualities of Rietveld refinements [3]. The conclusion quoted from Ref. [3]: “The refinement results for both possibilities should be carefully considered in combination with possibly available additional information (e.g. results of first-principles calculations) to arrive at adequate conclusions concern-

ing the true symmetry of the material under investigation.” This concept was recently applied to the case of two inorganic oxides: $BiFeO_3$ [5] and $\alpha-Fe_2O_3$ [6]. Both these compounds are believed to have crystal structures described with the high-symmetry trigonal space groups: $R\bar{3}c$ and $R\bar{3}c$, which have a 3-fold rotation axis [001]. The modulated magnetic ordering with modulation vector along [110] in $BiFeO_3$ [7] and the weak ferromagnetic moment perpendicular to [001] in $\alpha-Fe_2O_3$ [8,9] are examples of phenomena which are not invariant under 3-fold rotation, i.e. rotation by 120° or 240° along [001]. The ideas proposed by P. Curie [1] lead to the hypothesis that the crystal structures of $BiFeO_3$ and $\alpha-Fe_2O_3$ cannot be described with trigonal symmetry. Careful high resolution synchrotron radiation (SR) powder diffraction studies of hkl-dependent Bragg peak broadening have shown that the crystal structure of $BiFeO_3$ is described with the low-symmetry monoclinic space group Cc [5] and that of $\alpha-Fe_2O_3$ with the monoclinic space group $C2/c$ [6,10]. These subgroups are obtained by removing the 3-fold rotation operators from the high symmetry trigonal space groups.

In the present paper the same method is applied to chromium which is believed to have a bcc-type cubic crystal structure (space group $Im\bar{3}m$) [11,12] and which shows a spin density wave (SDW). It was

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stated already in the early 1960-ies that the magnetic symmetry of the antiferromagnetic SDW disagrees with the retention of the cubic crystal structure symmetry [13,14]. A search for the evidence of the splitting of X-ray Bragg peaks from polycrystalline Cr for an assumed tetragonal symmetry was performed by Combley [15] in 1968. Careful examination of the linewidths did not show such effects and the upper limit of a tetragonal distortion $c = a(1 + \Delta)$ of Δ was set at 10^{-5} [15]. Dilatometric studies with field cooling and stress cooling of chromium single crystals performed by Steinitz et al. in 1968 [16] have shown that the relative orthorhombic and tetragonal distortions are small: $|\Delta a/a| \approx 20 \times 10^{-6}$. However according to the review by Fawcett [12]: “One should note that the term *cube axis* refers to paramagnetic Cr, the symmetry in the longitudinal SDW phase being tetragonal, while in the transverse SDW phase with a polarizing field along a *cubic axis* perpendicular to Q the symmetry is orthorhombic”.

The transverse spin density wave (TSDW) and the longitudinal spin density wave (LSDW) phases in chromium were analyzed by using the formalism of magnetic superspace groups [17]. The TSDW ordering was described by the orthorhombic superspace group $Immm1'(00\gamma)s00s$ while the LSDW by the tetragonal superspace group $I4/mmm1'(00\gamma)00ss$ [17]. To our best knowledge there are no diffraction studies that would determine the values of the unit cell parameters of chromium in the orthorhombic LSDW state nor in the tetragonal LSDW state so far. Most studies reported that the distortions of the cubic lattice are probably too small to be detected by diffraction methods.

Chromium is one of the first systems in which a spin-density wave state was discovered by neutron diffraction [18–20]. Between the Néel temperature, $T_N = 311$ K, and the spin flip temperature, $T_{SF} = 122$ K, chromium single crystals show an antiferromagnetic ordering superimposed on a TSDW. The magnetic modulation vector $q_m \approx 0.046$ r.l.u. (the index “m” stands for magnetic) is directed along one of the [100], [010] or [001] directions while the magnetic moments are perpendicular to q_m . At the spin flip transition $T_{SF} = 122$ K the magnetic moments turn by 90° and below T_{SF} they form an antiferromagnetic ordering superimposed on a LSDW, i.e. the moments become parallel to q_m . Early X-ray diffraction (XRD) studies with chromium single crystals [21] have shown that both modulated TSDW and LSDW orderings coexist with a modulation of atomic positions and/or charge distribution described with the modulation vector $q_p = 2q_m$ (the index “p” stands for position). Further neutron diffraction studies with Cr single crystal at 144 K have shown that the TSDW type magnetic ordering has also a third harmonic term $3q_m$ [22]. SR diffraction studies have shown that the second order atomic position and/or charge density wave coexist with the magnetic modulation between T_N and 10 K [23,24]. These SR diffraction studies have also shown the existence not only of the second but also the fourth order harmonics $2q_p = 4q_m$ of the atomic positions and/or charge ordering modulation in chromium single crystals [23,24].

The main motivation of the present paper is to study the hypothetical existence of distortions of the cubic lattice of chromium and their possible changes across the Néel temperature and the spin-flip transition.

2. Experimental

In the present study the following materials were used: commercial polycrystalline chromium samples provided by Riedel (poly-Cr), nanocrystalline chromium (nano-Cr) samples prepared by electrodeposition and studied in Ref. [25] as well as amorphous chromium (am-Cr) prepared by electrodeposition and studied earlier in Ref. [26].

High resolution powder diffraction beamline ID31 at ESRF

The crystal structure and microstructure of poly-Cr were characterized at RT by using high resolution SR powder diffraction at the beamline ID-31 at ESRF [27] at 0.39996 Å. The crystal structure and microstructure of nano-Cr2, nano-Cr3 and nano-Cr4 (used in Ref. [25]) with average crystallite sizes of 29 nm, 31 nm and 65 nm,

respectively, were characterized at RT by using high resolution SR powder diffraction at the beamline ID-31 at ESRF [27]. The wavelengths used were 0.39996 Å, 0.39480 Å and 0.35412 Å. The crystallization process of am-Cr samples (described already in Ref. [26]) was studied by high resolution SR powder diffraction using the ESRF ID-31 beamline [27]. The SR diffraction measurements were performed as a function of time with am-Cr during in situ annealing at 300 °C and 400 °C. The wavelength used was 0.2480 Å.

Neutron TOF diffractometer Polaris at ISIS

The crystal structure and magnetic ordering of poly-Cr were studied by time-of-flight (TOF) neutron diffraction by using the instrument Polaris at ISIS, the UK’s spallation neutron source. The neutron powder diffraction measurements were performed at 473 K (paramagnetic), 150 K (TSDW) and at 50 K (LSDW).

XPDF beamline I15-1 at Diamond Light Source

The crystal structures and microstructures of poly-Cr and nano-Cr2 were characterized by using the XPDF beamline I15-1 at Diamond Light Source. The measurements were performed at RT and 473 K by using the wavelength 0.16167 Å.

Laboratory X-ray powder diffractometer

The changes of the microstructure of poly-Cr due to annealing were studied by powder XRD. The laboratory X-ray powder diffractometer with Seifert ID3003 generator (Mo $K\alpha_{1,2}$ radiation $\lambda_{1/2} = 0.7093$ Å, 0.7136 Å) and high resolution HZG-4 goniometer was used. The powder XRD measurements were performed at RT with poly-Cr samples that were annealed ex-situ in a furnace (in air) at 400 °C, 500 °C and 600 °C for 6 h each. The annealing temperatures are sufficiently high to reduce internal strains and induce possible grain growth. The maximal annealing temperature 600 °C is too low to obtain measurable amounts of chromium oxides [28].

The instrumental resolution of the high resolution powder diffraction beamline ID-31@ESRF and the laboratory X-ray diffractometer were estimated by measuring a powder diffraction pattern of the LaB₆ NIST standard. The instrumental resolution of the neutron TOF diffractometer Polaris and the XPDF I15-1@Diamond beamline was estimated by measuring a powder diffraction pattern of the Si NIST standard.

3. Results for polycrystalline chromium

3.1. Refinement of the cubic bcc structure

The high energy SR diffraction patterns of poly-Cr and nano-Cr2 were measured in PDF-mode at RT and 473 K by using the I15-1@Diamond beamline. The wavelength used was 0.16167 Å and the SR powder diffraction patterns have a high statistical accuracy. In order to characterize the poly-Cr and nano-Cr samples Rietveld refinement was performed by using the Jana2006 programme [29]. The standard cubic bcc crystal structure was assumed. The refinements were successful and the resulting plots are shown in Supplementing Information, Fig. S1. The cubic lattice parameters, a_c at RT are 2.88473(7) Å and 2.88400(15) Å for poly-Cr and nano-Cr2, respectively. For 473 K a_c equals 2.88847(7) Å and 2.88822(15) Å for poly-Cr and nano-Cr2, respectively. The values obtained at RT are very close to the reference values of 2.88300 Å [30] and 2.8843 Å [31].

The high statistical accuracy of the powder SR diffraction patterns obtained at I15-1@Diamond indicate the absence (no more than 0.1% by volume) of phases other than bcc Cr. It is important to note that there are no indications of the presence of chromium hydride phases: the hcp (ϵ) and fcc (γ) [32–34]. One can therefore conclude that poly-Cr and nano-Cr2 are composed of pure bcc chromium and they cannot incorporate much hydrogen in their lattice.

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