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The tau-borides τ-$(Fe_{0.54}Ir_{0.46})_{20}Fe_3B_6$ and τ-$(Co_{0.64}Ir_{0.36})_{21}Co_{0.16}B_4B_6$

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ABSTRACT

Two tau-borides, τ-$(Fe_{0.54}Ir_{0.46})_{20}Fe_3B_6$ and τ-$(Co_{0.64}Ir_{0.36})_{21}Co_{0.16}B_4B_6$ were studied by X-ray powder and single crystal diffraction with respect to precise atom site distribution and metal atom ordering. X-ray structure determination for a single crystal of τ-$(Fe_{0.54}Ir_{0.46})_{20}Fe_3B_6$ revealed isotypism with a partially ordered $Cr_{23}C_6$-type (space group $Fm\overline{3}m$, $a = 1.11020$ nm) but with a high degree of random replacement of Fe/Ir atoms in sites 48*h* and 32*f*. X-ray single crystal data for τ-$(Co_{0.64}Ir_{0.36})_{21}Co_{0.16}B_4B_6$ showed a novel low-symmetry structure variant of tau-borides characterized by a noncentrosymmetric distribution of boron tetrahedra and a defect Co-site (space group $F\overline{4}3m$ as a *translationengleiche*, nonisomorphic maximal subgroup of index 2 of $Fm\overline{3}m$, $a = 1.09359$ nm). The crystal structures of both τ-phases are described with nested polyhedra geometrically related to the α-Mn structure. Stability ranges and various structural arrangements of $(MM')_{23}B_6$ phases are discussed.

The crystal structures of $(Fe_{1-x}Ir_x)_3B$ ($x = 0.24$; X-ray single crystal data; Fe_3C-type, space group *Pnma*, $a = 0.5430(2)$, $b = 0.6958(2)$ nm, $c = 0.4654(2)$ nm), and of isotypic $(Fe_{1-x}Rh_x)_3B$ (XPD Rietveld refinement, $x = 0.25$, space group *Pnma*, $a = 0.54560(1)$ nm, $b = 0.69552(1)$ nm, $c = 0.46169(1)$ nm) show both a high degree of randomness in the metal sites.

1. Introduction

Search for novel materials with strong electron correlations turned our attention to M–Ir–B combinations. In several of these systems representatives exist of the $Cr_{23}C_6$-type (so called τ-phases). The crystal structure of $Cr_{23}C_6$ (space group $Fm\overline{3}m$, Cr in 48*h* (0,*y*,*y*) $y = 0.1699$; in 32*f* (x, x, x) $x = 0.38199$; in 8*c* (¼, ¼, ¼); in 4*a* (0,0 0); C in 24*e* (x, 0, 0) $x = 0.2751$ [1, 2]) comprises a remarkably large number of ternary isotypes $(M,M')_{23}B_6$ in boride systems [3–6]. Due to their hardness in combination with magnetically soft behaviour, tau-borides with high magnetic permeability have attracted in the past considerable interest as video head materials [7]. Although metastable binary borides exist ($Fe_{23}B_6$, $Co_{23}B_6$, $Ni_{23}B_6$), M′ elements (M′ may be a transition metal, a main group element or an f-element) act as stabilizers of ternary compounds. The larger M′ metal atoms occupy predominantly the atomic site with the highest coordination number (8*c*, Friauf polyhedron, CN = 16); with increasing M′ content, the M′ atoms may enter the site 4*a* (cubooctahedron, CN = 12). With decreasing differences in atomic radii, the distribution of M and M′ atoms tends towards statistical replacement on atomic sites 48*h* and 38*f* thereby displaying extended homogeneous regions ($(M,Ir)_{23}B_6$, M = Cr, Fe, Mn, Co; $(M,Re)_{23}B_6$, M = Mn, Fe, Co, Ni) [3]. Partial ordering may occur, as in $Re_7Fe_{16}B_6$ (Re atoms preferentially in 8*c* [6]) and $Nb_3Ru_{20}B_6$ (Nb atoms preferentially in 4*a* [8]). For some boride systems, the formation of boron-rich τ-borides has been observed (Co/Ir-, Cr/Ir- and Ni/Al-τ borides) for which the larger boron content has been explained by random partial replacement of metal atoms in the 8*c* site by B_4 tetrahedra (boron in 32*f* site) [9,10,11].

The present work is concerned with the X-ray single crystal characterization of ferromagnetic τ-$(Fe_{0.54}Ir_{0.46})_{20}Fe_3B_6$ and τ-$(Co_{0.64}Ir_{0.36})_{21}Co_{0.16}B_4B_6$ with respect to precise atom site distribution, metal atom ordering and stability of τ-phases. Included also are crystal structure refinements for the ternary phases with Fe_3C-type: $(Fe_{1-x}Ir_x)_3B$ ($x = 0.24$) and the related compound with rhodium.

2. Experimental details

All samples, each of a total amount of about 0.5–1 g, were prepared by argon arc-melting elemental pieces of transition metals (Alfa Aesar, purity >99.9 mass%) and crystalline boron (Alfa Aesar, 98%). To assure homogeneity, the samples were re-melted several times. A part of each alloy was wrapped in Mo-foil, sealed in an evacuated silica tube and heat-treated for 10 days at 970 °C prior

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to quench by submerging the capsules in cold water. X-ray powder diffraction data were collected from as-cast and annealed alloys employing a Guinier–Huber image plate system with monochromatic Cu $K_{\alpha 1}$ radiation ($8^\circ < 2\theta < 100^\circ$). Single crystals were mechanically isolated from the crushed alloys, which were melted in a BN-crucible in a high vacuum furnace with a W-metal heater and slowly cooled to 970 °C, kept there for 24 h, and quenched by shutting off the power to the furnace. Inspections on an AXS-GADDS texture goniometer assured high crystal quality, unit cell dimensions and Laue symmetry of the specimens prior to the X-ray intensity data collections on a four-circle Nonius Kappa diffractometer equipped with a CCD area detector employing graphite monochromated Mo K_α radiation ($\lambda = 0.071069$ nm). Orientation matrices and unit cell parameters were derived using the program DENZO [12]. No absorption corrections were performed because of the rather regular crystal shapes and small dimensions of the investigated specimens. The structures were solved by direct methods and were refined with the SHELXL-97 program [13,14]. Quantitative Rietveld refinements of the X-ray powder diffraction data were performed with the FULLPROF program [15].

3. Results

3.1. The crystal structure of $(Fe_{0.54}Ir_{0.46})_{20}Fe_3B_6$

Single crystal X-ray intensities with systematic extinctions for a face centered Bravais lattice only are compatible with the space groups $Fm\overline{3}m$, $F\overline{4}3m$ and $F432$. Intensity statistics [16] on $|E^2\text{-}1| = 0.946$ favoured a centrosymmetric space group and an initial structure solution was obtained in $Fm\overline{3}m$. Positions of the Fe and Ir atoms, located from direct methods, are consistent with the $Cr_{23}C_6$-type structure. The position of the boron atom was derived from difference Fourier synthesis. The structure was refined by full-matrix least-squares methods on F^2 with anisotropic displacement parameters for the metal atoms but isotropic temperature factors for boron. Refinement of the occupancy factors clearly indicated a statistical occupation of sites 48*h* and 32*f* by iridium and iron atoms, whereas the two remaining sites, 8*c* and 4*a*, are exclusively occupied by iron atoms. Results of the refinement, which converged to $R1 = 0.028$ with residual electron densities smaller than ± 4100 e/nm^3, prove isotypism with the structure type of $Cr_{23}C_6$ and are summarized in Table 1.

Atomic coordinates and site occupancies, as obtained from the single crystal study, were taken as the basis for the Rietveld analyses of X-ray powder diffraction data for $(Fe_{0.54}Ir_{0.46})_{20}Fe_3B_6$. Consistent with the single crystal analysis, the sites 48*h* and 32*f* were also found in XPD to be occupied by a mixture of Fe/Ir atoms. Although the refinement on isotropic thermal parameters revealed slightly higher values for iron atoms in 8*c* and 4*a*, refinement of occupancy parameters indicate full occupation of these sites by Fe atoms. Thus the refinement proceeded smoothly to low residual values ($R_F = \sum|F_o - F_c|/\sum F_o = 0.034,\ R_I = \sum|I_o - I_c|/\sum I_o = 0.062$) displaying reasonable atom displacement parameters.

The crystal structure of $(Fe_{0.54}Ir_{0.46})_{20}Fe_3B_6$ belongs to the branch of tau-borides with a high degree of Fe/Ir substitution on the metal sublattice, i.e. random mixtures of Ir and Fe-atoms occupy the atomic sites 32*f* and 48*h* with coordination numbers (CN) 13 and 14 thereby forming tetragonal anti-prisms which are occupied by boron atoms as well as empty cubes around vacant center position in 4*b* (½,½,½). It is worthy to note, however, that for $(Fe_{0.54}Ir_{0.46})_{20}Fe_3B_6$ the site 8*c* (center of the CN = 16 Friauf polyhedron) and the site 4*a* (center of the CN = 12 cuboctahedron) are both exclusively occupied by the smaller but more electropositive Fe-atoms. This is perfectly in line with the observation that in most tau-borides the more electropositive element occupies the site 8*c* and eventually also site 4*a*, although the electropositive elements usually are also the atoms larger in size. In an earlier study X-ray intensity photographs have been used to derive the Fe/Ir atom site distribution throughout the large homogeneity field $Fe_{15.4-10}Ir_{7.6-13}B_6$ [3,10]. A comparison of calculated and visually observed intensities yielded the formula $(Fe_{0.62}Ir_{0.38})_{20}Fe_3B_6$ for the Fe-rich τ-boride whereas with increasing Ir-content Ir atoms were found to enter the 4a, 8c sites as shown for $(Fe_{0.48}Ir_{0.52})_{23}B_6$ [3,10].

3.2. The crystal structures of $(Fe_{1-x}Ir_x)_3B$, $x = 0.24$ and isotypic $(Fe_{1-x}Rh_x)_3B$, $x = 0.25$

Binary "Fe_3B" is known to exist as a metastable phase in several structure modifications depending on the heat treatment and cooling conditions (Fe_3C-type, space group *Pnma*, $a = 0.5428$ nm, $b = 0.6699$ nm, $c = 0.4439$ nm; Ni_3P-type, space group $I\overline{4}$, $a = 0.8655$ nm, $c = 0.4297$ nm; Ti_3P type, space group $P4_2/n$, $a = 0.8648$ nm, $c = 0.4314$ nm [18]). The crystal structures of stable phases $(Fe_{1-x}Ir_x)_3B$ and $(Fe_{1-x}Rh_x)_3B$ were reported earlier [19] as the result of an electronic stabilizing effect of metal atoms M = Mo, W, Re, Ru, Rh, Ir, Pd, Pt on the formation of $(Fe,M)_3B$ phases within a structural sequence $Ni_3P \rightarrow Ti_3P \rightarrow Fe_3C$-type. Hitherto the isotypism of $(Fe_{1-x}Ir_x)_3B$ and $(Fe_{1-x}Rh_x)_3B$ with Fe_3C-type was established from powder X-ray film data only. In order to gain detailed data on atom site distribution, the crystal structure of $(Fe_{1-x}Ir_x)_3B$ was refined in the present work from single crystal data which converged to a low reliability factor $R1 = 0.022$ with residual electron densities as small as 2080/-2160 e/nm^3. Results are compiled in Table 2. The structure refinement confirmed the Fe_3C-type yielding random occupancies of metal atomic sites by mixtures of iron and iridium atoms. The disorder in the two metal atom sites (8*d* and 4*c*) was also established from a Rietveld refinement revealing the Fe/Ir site occupancies consistent with the data obtained from the single crystal. The isotypism with Fe_3C-type, as well as the disorder of Fe/Rh atoms in the metal sites was also confirmed from Rietveld refinement of X-ray powder data for $(Fe_{1-x}Rh_x)_3B$ with $x = 0.25$ (Table 2).

A maximum equilibrium content of Fe in Fe_3C-type $(Co_{1-x}Fe_x)_3B$ was reported earlier (at 900 °C, $0 \le x \le 0.367$, $a = 0.5318$ nm, $b = 0.6635$ nm, $c = 0.4425$ nm for $x = 0.367$) [19]. For $(Fe_{1-x}Ni_x)_3B$, the solubility of Ni was established from rapidly quenched amorphous alloys: $0.4 \le x \le 0.7$, $a = 0.545$ nm, $b = 0.672$ nm, $c = 0.449$ nm (Fe-ich boundary) and $a = 0.535$ nm, $b = 0.669$ nm, $c = 0.446$ nm (Ni-rich boundary) [20]. In case of Rh and Ir, the Fe_3C-type structures were found to form at $x = 0.24$ and $x = 0.25$ for $(Fe_{1-x}Ir_x)_3B$ and $(Fe_{1-x}Rh_x)_3B$ respectively. The increasing M-radii of $(Fe_{1-x}M_x)_3B$, (M = Rh, Ir) infer slightly larger M–M and M–B distances ($d_{M-M} = 0.2564(1)–0.2905(1)$ nm, $d_{M-B} = 0.211(1)–0.279(1)$ nm and $d_{M-M} = 0.2589(1)–0.2900(1)$ nm, $d_{M-B} = 0.2126(4)–0.2791(5)$ nm for Rh and Ir compounds respectively) (Table 3) as compared to the binary Fe_3B isotype ($d_{Fe-Fe} = 0.2426–0.2835$ nm, $d_{Fe-B} = 0.1981–0.2807$ nm). With boron atoms in edge-connected triangular metal atom prisms, there are no boron–boron contacts in the structure.

3.3. The crystal structure of $(Co_{0.64}Ir_{0.36})_{21}Co_{0.16}B_4B_6$

Similarly to $(Fe_{0.54}Ir_{0.46})_{20}Fe_3B_6$, the intensity pattern of a crystal obtained from the alloy with nominal composition Co_2IrB_2 indicated an F-centered unit cell. Laue symmetry and systematic extinctions were consistent with cubic space groups $Fm\overline{3}m$, $F\overline{4}3m$ and F432. However, contrary to $(Fe_{0.54}Ir_{0.46})_{20}Fe_3B_6$, the intensity statistics with $|E^2\text{-}1| = 0.769$ did not clearly indicate centrosymmetry. The structure was solved by direct methods in space