

and containing no secondary phases. The Knoop indentation hardness tests showed that the hardness of NPD is as high as 120-130 GPa, which is equivalent to or even higher than those of single-crystal diamonds. High temperature hardness tests using Knoop indenters prepared from NPD specimens demonstrated that the hardness of NPD at high temperatures ($>800\text{ }^{\circ}\text{C}$) is about 2 times higher than those of single-crystal diamonds. The extremely high hardness is believed to be due to the blocking effect of dislocation movement (development of plastic deformation) at grain boundaries. The data from wear tests using a diamond wheel indicated that the wear rate of NPD is less than one-tenth of those of conventional polycrystalline diamond containing metal binders. These salient characteristics permit us to apply the large NPD to a wide field of industrial and scientific applications such as high-precision cutting tools, abrasion-resistant materials, optical windows, high-pressure anvils and so on.

Keywords: diamond, high pressure, nanostructures

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Crystal structure and lattice dynamics of high-pressure scandium trihydride

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In contrast to yttrium and rare-earth trihydrides, scandium trihydride is thermally unstable at ambient conditions and forms only under high hydrogen pressure [1]. Now scandium trihydride and trideuteride powder samples are synthesised under high pressure of gaseous hydrogen or deuterium and studied by neutron diffraction at ambient pressure and 95 K. Scandium trihydride is studied by inelastic neutron scattering at 20 K in the energy range 4-250 meV and compared to yttrium trihydride. The neutron diffraction investigation shows that hydrogen in ScH₃ occupies distorted tetrahedral and octahedral interstitial positions in the hexagonal close-packed metal lattice with the axial ratio of $c/a = 1.815$, which is typical of the YH₃ and HoH₃ structures. The displacements of the octahedral hydrogen atoms in ScH₃ demonstrate no ordering therefore the ScH₃ structure is described within space group $P6_3/mmc$. Inelastic neutron scattering shows that this is the symmetry of the mean lattice whereas the local structure is similar to that of yttrium and holmium trihydrides.

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Keywords: neutron structure analysis, metal hydride structures, high-pressure synthesis

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The structural study in Pd₂Mn alloy

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Pd-Mn alloy system has complicated phases and structures. It presents α_1 , β_1 , β_2 , and β_3 phases among 20-60 at. % Mn. There are few reports on the β_2 phase (Pd₂Mn), so that more detailed X-ray experiment should be performed for understanding of the structural characteristics. We have made a slice of multicrystal Pd-Mn alloys, which have 31.2, 33.4, and 34.7 at. % Mn. All the samples are quenched into ice water from 800°C after heated for two days, and then annealed from 600°C after heated for one month. Rietan-2000 is used to analyze the diffraction data for both quenched and annealed samples. Quenched samples show fcc structures and are considered to be in disorder states. The 33.4 at. % Mn sample annealed from 600°C is confirmed to be in β_2 phase, in which the space group is $Pnma$, and the atomic positions are Mn (1/8, 1/4, 1/12), Pd (I) (1/8, 1/4, 5/12), and Pd (II) (1/8, 1/4, 3/4), by the Rietveld analysis fitness of $R_{wp}=2.75$, and $S=1.46$. However, the atomic positions from our experiments are Mn (0.157, 0.25, 0.098), Pd (I) (0.148, 0.25, 0.416), and Pd (II) (0.083, 0.25, 0.757), a little shifted from the ideal positions. These shifts are considered to be from the distortions against the nearest Mn-Mn or Pd-Pd atom pairs. Our previous research shows in disordered states, a Pd or Mn atom tends to have an unlike nearest neighbour atom. The nearest neighbour's distances are 3.11Å for Mn-Mn, 2.81Å for Pd-Pd, and 2.60Å for Mn-Pd atoms pairs. The 31.2 and 34.7 at. % Mn samples annealed from 600°C present two phases of β_2 and DO₂₃. The in-situ diffraction measurements and the DSC thermal analysis are also on plan for understanding the process details of order-disorder phase transition.

Keywords: X-ray diffraction, alloy phases, Rietveld analysis

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Crystal structure and thermal property of ionic liquid-H₂O mixtures

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By simultaneous X-ray diffraction and DSC (Differential Scanning Calorimetry) method, crystal structure and thermal property of ionic liquid (IL)-H₂O mixtures were investigated. The IL used in this study is N,N-diethyl-N-methyl-N-2-methoxyethyl ammonium tetrafluoroborate. H₂O concentration, x , are 0.0 - 12.0 mol% H₂O. Anomalous phase diagrams are obtained both on cooling and heating. In-situ observations were performed using 3 kW X-ray generator (RINT-Ultima 3, Rigaku Co., Japan). On cooling, pure IL is crystallized at -30 °C. Two kinds of crystal structures (orthorhombic and monoclinic) are determined. With increasing H₂O concentration, crystallization temperature, T_c , decreased up to 6.66 mol%. At 6.66 mol%, no exothermal peak was observed on cooling. In addition, no Bragg peaks appeared. A pure amorphous state is realized at 6.66 mol%. Above 6.66 %, two phase coexistence of amorphous and crystal were formed. Therefore, 6.66 % (x_c) is regarded as the crossover point. On heating, cold crystallization occurred above x_c with the distinct exothermal peak on DSC measurements. The cold crystallization temperature, T_{cc} , was almost constant ($x_c < x < 12\%$). Crystal structures are the same ($0 < x < 12\%$). Moreover, no peak broadening of Bragg reflection appeared along the radial direction. At x_c , crystallization was completely suppressed on cooling. "Two dynamic components" in Raman spectrum suggest the two different

kind of molecular properties of water: one is to disturb crystallization, while other is to promote crystallization. The competition between them can generate a pure amorphous state. Furthermore, lattice relaxation occurs around the boundary between crystal domains and the amorphous solid, since sharp Bragg peaks are observed at any phases.

Keywords: ionic materials, DSC/XRD, phase transitions and structure

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Debye-Waller factors and quantum phase transition in KH_2PO_4

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KDP (KH_2PO_4) is a typical ferroelectrics, in which the proton distribution changes through the phase transition. We measured scattering intensity from the single crystal by using neutron 4-circle diffractometer (FONDER) installed at JRR3M in JARERI, Tokai. The crystal structures at different temperatures between 10 and 300K are refined. The Debye-Waller factors are determined carefully. Though the transition temperature, the factors for K, P and O change without noticeable anomaly and approach the zero temperature values. However, the proton's factor along the double-well axis shows discontinuous behavior indicating the modification of the hydrogen bonding. The figure shows U_{11} vs. temperature; U_{11} of the split atom H changes continuously. The temperature dependence is compared with a quantum model of the structural phase transition. The phase transition mechanism seems to be not a typical order-disorder or displacive type but a quantum type transition

Keywords: neutron structure determination, Debye-Waller factor, quantum wells

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Lattice instability of FeNi and Fe_3Pt Invar alloys

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Elastic diffuse scattering of neutrons was found around various Bragg peak positions for typical Invar alloys, $\text{Fe}_{1-x}\text{Ni}_x$ ($0.35 < x < 0.6$), ordered $\text{Fe}_{72}\text{Pt}_{28}$ and disordered $\text{Fe}_{72}\text{Pt}_{28}$ alloys. Diffuse scattering intensities depend on temperature and Ni concentrations and increase with decreasing temperature and decrease with increasing Ni concentrations. The pattern of diffuse scattering intensity changes from peak to peak. The reasonable agreement with observed diffuse peak patterns was obtained for the analysis using Huang diffuse scattering for the nucleus of an anisotropic defect. Since all of these Invar alloys are located close to the phase boundary of fcc-bcc martensitic transformation, Huang diffuse scattering is considered to be due to the formation of premartensitic embryos.

From the comparison of calculated diffuse scattering intensities in reciprocal lattice space with those for a simplified model, actual lattice deformation of embryos in real space was determined. The lattice deformation is described as a shear wave propagating along the [1 1 0] direction and with the [1 -1 0] polarization vector. From these data, the early stage of fcc-bcc martensitic transformation in Fe and Fe alloys is discussed. Since the regions of temperatures and Fe concentrations for which diffuse scattering are observed coincide with those for which the Invar anomalies are observable, the formation of premartensitic embryos seems to be strongly related to the Invar effects for these alloys.

Keywords: invar alloys, Huang diffuse scattering, premartensitic phase

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Photoinduced disorder-to-incommensurate order phase transition in an Fe(II) spin crossover complex

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Molecular multistability has attracted an increasing interest in the context of functional molecular materials. The possibility of switching between different stable states under external perturbation like temperature, pressure or light excitation allows to tune and control the macroscopic properties (magnetic, electronic, optic) of the system. In the solid state, the coupling between purely molecular aspects and intermolecular interactions may lead to collective phenomena, i.e. photo-induced phase transitions [1]. Spin crossover (SCO) materials are typical examples of such photo-switchable molecular systems [2]. We investigate the light-induced switching process in the SCO complex $\{\text{Fe}(\text{abpt})_2[\text{N}(\text{CN})_2]_2\}$, through time and temperature dependent photo-crystallographic measurements. Upon laser light excitation, an unprecedented collective long range ordering of the dicyanamide $[\text{N}(\text{CN})_2]$ groups develops, resulting in a displacive modulation of the crystal structure with wavevector $q = 0.331(2)a^* + 0.658(2)b^* - 0.000(3)c^*$, incommensurate with the underlying reciprocal crystal lattice. The corresponding structural analysis of the metastable HS phase is performed under the superspace group approach, using JANA [3]. A lattice structural instability is evidenced as the basis for the disorder-to-incommensurate order phase transition. A Frenkel-Kontorova-like model of competing interactions within two layer subsystems is proposed to elucidate the origin of the incommensurability.

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Keywords: solid-state phase transformations, incommensurate ordering, photochemistry