Experimental report

14/01/2016

Proposal: DIR-117 **Council:** 10/2012

Title: Pressure-dependent Structural PhaseTransitions in Cyanide Framework Compound Ni(CN)2

Research area: Physics

This proposal is a new proposal

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Samples: Ni(CN)2

Instrument	Requested days	Allocated days	From	To
D20	3	3	05/08/2013	08/08/2013

Abstract:

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New insights into the compressibility and high-pressure stability of $Ni(CN)_2$: a combined study of neutron diffraction, Raman spectroscopy, and inelastic neutron scattering

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Abstracts

Nickel cyanide is a layered material showing markedly anisotropic behaviour. High-pressure neutron diffraction measurements show that at pressures up to 20.1 kbar, compressibility is much higher in the direction perpendicular to the layers, *c*, than in the plane of the strongly chemically bonded metal-cyanide sheets. Detailed examination of the behaviour of the tetragonal lattice parameters, *a* and *c*, as a function of pressure reveal regions in which large changes in slope occur, for example, in *c*(*P*) at 1 kbar. The experimental pressure dependence of the volume data is fitted to a bulk modulus, B_0, of 1050 (20) kbar over the pressure range 0–1 kbar, and to 124 (2) kbar over the range 1–20.1 kbar. Raman spectroscopy measurements yield additional information on how the structure and bonding in the $Ni(CN)_2$ layers change with pressure and show that a phase change occurs at about 1 kbar. The new high-pressure phase, (Phase PII), has ordered cyanide groups with sheets of D_{4h} symmetry containing $Ni(CN)_4$ and $Ni(NC)_4$ groups. The Raman spectrum of phase PII closely resembles that of the related layered compound, $Cu_{1/2}Ni_{1/2}(CN)_2$, which has previously been shown to contain ordered C≡N groups. The phase change, PI to PII, is also observed in inelastic neutron scattering studies which show significant changes occurring in the phonon spectra as the pressure is raised from 0.3 to 1.5 kbar. These changes reflect the large reduction in the interlayer spacing which occurs as Phase PI transforms to Phase PII and the consequent increase in difficulty for out-of-plane atomic motions. Unlike other cyanide materials e.g. $Zn(CN)_2$ and $Ag_3Co(CN)_6$, which show an amorphization and/or a decomposition at much lower pressures (~100 kbar), $Ni(CN)_2$ can be recovered after pressurising to 200 kbar, albeit in a more ordered form.

Keywords: neutron diffraction, crystallographic aspects of phase transformations, neutron inelastic scattering, Raman spectroscopy, phonons in crystal lattice

(Some figures may appear in colour only in the online journal)

