Experimental report

04/10/2019

Proposal: **7-01-424** **Council:** 4/2015

Title: INS Studies of Layered Copper-Nickel Cyanides to Probe Order, Disorder and Negative Thermal Expansion

Research area: Physics

This proposal is a new proposal

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Samples: $Ni(CN)_2$
$(Cu_{0.10}Ni_{1.90})(CN)_4$
$(Cu_{0.25}Ni_{1.75})(CN)_4$
$(Cu_{0.33}Ni_{1.67})(CN)_4$
$(Cu_{0.50}Ni_{1.50})(CN)_4$
$(CuNi)(CN)_4$

Instrument	Requested days	Allocated days	From	To
IN6	6	6	17/09/2015	23/09/2015
IN4	6	0		

Abstract:

We aim to obtain phonon spectra on a series of new two-dimensional layered compounds, $(Cu_xNi_{2-x})(CN)_4$ and the related parent material, $Ni(CN)_2$. These materials show a range of thermal expansion behaviours: the magnitude of both the negative thermal expansion (NTE) and positive thermal expansion (PTE) effects can be tuned by varying the copper content of the mixed-metal cyanide, even though the substitution has little apparent effect on the structure. For example, $CuNi(CN)_4$ shows significant intralayer NTE combined with very high PTE in the third dimension (both effects are larger than those in the parent $Ni(CN)_2$) whereas $(Cu_{0.50}Ni_{1.50})(CN)_4$ shows zero NTE. We wish to determine the reasons for these behaviours by examining the differences between the phonon density of states for the different compositions.

Phonon dynamics in the layered negative thermal expansion compounds $Cu_xNi_{2-x}(CN)_4$

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This study explores the relationship between phonon dynamics and negative thermal expansion (NTE) in $Cu_xNi_{2-x}(CN)_4$. The partial replacement of nickel (II) by copper (II) in $Ni(CN)_2$ leads to a line phase, $CuNi(CN)_4$ ($x = 1$), and a solid solution, $Cu_xNi_{2-x}(CN)_4$ ($0 \leqslant x \leqslant 0.5$). $CuNi(CN)_4$ adopts a layered structure related to that of $Ni(CN)_2 (x = 0)$, and interestingly exhibits two-dimensional (2D) NTE which is ~1.5 times larger. Inelastic neutron-scattering (INS) measurements combined with first-principles lattice dynamical calculations provide insights into the effect of Cu^{2+} on the underlying mechanisms behind the anomalous thermal behavior in all the $Cu_xNi_{2-x}(CN)_4$ compounds. The solid solutions are presently reported to also show 2D NTE. The INS results highlight that as the Cu^{2+} content increases in $Cu_xNi_{2-x}(CN)_4$, large shifts to lower energies are observed in modes consisting of localized in- and out-of-plane librational motions of the CN ligand, which contribute to the NTE in $CuNi(CN)_4$. Mode Grüneisen parameters calculated for $CuNi(CN)_4$ show that acoustic and low-energy optic modes contribute the most to the NTE, as previously shown in $Ni(CN)_2$. However, mode eigenvectors reveal a large deformation of the $[CuN_4]$ units compared to the $[NiC_4]$ units, resulting in phonon modes not found in $Ni(CN)_2$, whose NTE-driving phonons consist predominately of rigid-unit modes. The deformations in $CuNi(CN)_4$ arise because the d^9 square-planar center is easier to deform than the d^8 one, resulting in a greater range of out-of-plane motions for the adjoining ligands.

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I. INTRODUCTION

Many layered compounds exhibit interesting physical properties arising directly from their two-dimensional (2D) nature. Metallic films, magnetic layers, 2D conductors, and superconductors are the basis of thin-film technology [1]. The ability of layered compounds to form intercalated systems has also resulted in many electrochemical and catalytic uses [2]. In some cases, 2D compounds exhibit the abnormal property of negative thermal expansion (NTE), which has potential uses in applications requiring a targeted thermal response, and in composite materials requiring overall zero thermal expansion. Several transition-metal cyanides exhibit NTE and many investigations have been carried out to understand the atomistic mechanisms behind the abnormal thermal behavior. Examples include $Zn(CN)_2$ and $Cd(CN)_2$ [3], which exhibit three-dimensional (3D) isotropic NTE along with high-temperature CuCN, AgCN, and AuCN, which exhibit one-dimensional (1D) NTE [4]. More recently, the behaviors of mixed-metal cyanides, such as $Cu_xAg_{1-x}CN$, $ZnAu_2(CN)_4$, $ZnNi(CN)_2$, and $Ag_3Co(CN)_6$, as well as many other Prussian blue analogs, have been studied [5–9].

$Ni(CN)_2$ is an example of a well-studied layered transition-metal cyanide exhibiting 2D NTE [10–14]. It has a structure consisting of sheets of square-planar $[Ni(C/N)_4]$ units, which lack long-range stacking order. The compound has thermal expansion coefficients, α_a of $-6.5 \times 10^{-6}\,K^{-1}$ and α_c of $+69 \times 10^{-6}\,K^{-1}$, where *a*, *b* is the in-plane lattice parameter and *c* is normal to the layers. These lead to an overall volume expansion coefficient, α_V of $+48 \times 10^{-6}\,K^{-1}$. Replacing half of the Ni^{2+} ions with Cu^{2+} to form $CuNi(CN)_4$ results in an isostructural compound with a smaller interlayer separation and more pronounced 2D NTE [$\alpha_a = -9.7(8) \times 10^{-6}\,K^{-1}$] [11]. The α_c and α_V coefficients are also correspondingly larger compared to those of $Ni(CN)_2$, and their values increase with temperature [11]. The metal atoms alternate within the sheets as in a checkerboard and, unlike in $Ni(CN)_2$, in which the cyanide ligands show "head-to-tail" disorder, the cyanide ligands in $CuNi(CN)_4$ are completely ordered with the carbon end bonding to Ni [11]. A single sheet of $CuNi(CN)_4$ is shown in Fig. 1. The mechanism behind the observed NTE in the two compounds is key to understanding how the addition of Cu enhances the phenomenon.

The first insight into the mechanism of 2D NTE in $Ni(CN)_2$ was found by Reverse Monte Carlo (RMC) fitting of total neutron-diffraction data by Goodwin *et al.* [12]. Results yielded five dispersionless phonon modes below 4.1 meV involving rigid rotations and translations of the $[Ni(C/N)_4]$ units, four of which forced the C and N atoms out of plane. The four vibrations produce a rippling effect of the layers, which has the net effect of bringing the Ni atoms closer together, while at the same time pushing neighboring layers further apart.

Inelastic neutron scattering (INS) provided a direct way of probing phonon dynamics in $Ni(CN)_2$ [13]. Measurements were combined with *ab initio* density-functional theory (DFT) calculations carried out using a single nickel-cyanide layer, neglecting the head-to-tail disorder of the cyanide ligands. The calculated phonon density of states accurately reproduced

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