Experimental report

25/11/2019

Proposal:	**7-01-471**	**Council:**	4/2018

Title: Tuning phonon dynamics in the novel anomalous thermal expansion candidates, tertiary mixed-metal cyanides CuxAgyAu1-x-yCN

Research area: Materials

This proposal is a new proposal

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Samples:
Cu1/2Ag1/6Au2/6
Cu1/3Ag1/3Au1/3CN
Cu1/4Ag1/4Au1/2CN
Cu1/6Ag1/6Au2/3CN

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	7	4	01/10/2018	05/10/2018

Abstract:

The group 11 metal cyanides exhibit 1-D negative thermal expansion along the direction of M-CN chains they consist of. We have been exploring the possibility of tuning this property by varying the metal composition and have synthesised for the first time a set of tertiary mixed-metal cyanides with the general formula Cu_xAg_yAu_1-x-yCN. We would like to collect their phonon spectra to study how their dynamics changes with composition, and as a function of temperature. This will be combined with ab initio phonon calculations to establish the influence hetero-metallophilic interactions have, both along the chain and across the metal planes, on the nature and the evolution of phonons.

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Anomalous thermal expansion in one-dimensional transition metal cyanides: Behavior of the trimetallic cyanide $\mathrm{Cu_{1/3}Ag_{1/3}Au_{1/3}CN}$

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The structural dynamics of a quasi-one-dimensional (1D) mixed-metal cyanide, $\mathrm{Cu_{1/3}Ag_{1/3}Au_{1/3}CN}$, with intriguing thermal properties is explored. All the current known related compounds with straight-chain structures, such as group 11 cyanides CuCN, AgCN, AuCN, and bimetallic cyanides $M_xM'_{1-x}\mathrm{CN}$ (M, $M' =$ Cu, Ag, Au), exhibit 1D negative thermal expansion (NTE) along the chains and positive thermal expansion (PTE) perpendicular to them. $\mathrm{Cu_{1/3}Ag_{1/3}Au_{1/3}CN}$ exhibits similar PTE perpendicular to the chains, however PTE, rather than NTE, is also observed along the chains. In order to understand the origin of this unexpected behavior, inelastic neutron scattering measurements were carried out, underpinned by lattice-dynamical density-functional-theory (DFT) calculations. Synchrotron-based pair-distribution-function analysis and $^{13}\mathrm{C}$ solid-state nuclear-magnetic-resonance measurements were also performed to build an input structural model for the lattice dynamical study. The results indicate that transverse motions of the metal ions are responsible for the PTE perpendicular to the chains, as is the case for the related group 11 cyanides. However, NTE along the chain due to the *tension effect* of these transverse motions is not observed. As there are different metal-to-cyanide bond lengths in $\mathrm{Cu_{1/3}Ag_{1/3}Au_{1/3}CN}$, the metals in neighboring chains cannot all be truly coplanar in a straight-chain model. For this system, DFT-based phonon calculations predict small PTE along the chain due to low-energy chain-slipping modes induced by a *bond-rotation effect* on the weak metallophilic bonds. However the observed PTE is greater than that predicted with the straight-chain model. Small bends in the chain provide an alternative explanation for thermal behavior. These would mitigate the *tension effect* induced by the transverse motions of the metals and, as temperature increases and the chains move further apart, a straightening could occur resulting in the observed PTE. This hypothesis is further supported by unusual evolution in the phonon spectra, which suggest small changes in local symmetry with temperature.

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I. INTRODUCTION

Negative thermal expansion (NTE) is a counterintuitive phenomenon which can manifest in 1, 2, or 3 dimensions [1]. Understanding the dynamical mechanisms behind the phenomenon provides valuable information that helps to design other NTE compounds or even zero-thermal-expansion composites. NTE is often observed in transition-metal cyanides as the diatomic, linear, cyanide ligand provides a degree of flexibility that allows for low-energy transverse modes that give rise to the *tension effect* [1]. Well-known examples include high-temperature (HT) CuCN, $\mathrm{Ni(CN)_2}$ and $\mathrm{Zn(CN)_2}$ [2–4]. In each case, partial substitution of the metal ions resulting in $\mathrm{Cu}_x\mathrm{Ag}_{1-x}\mathrm{CN}$, $\mathrm{Cu}_x\mathrm{Ni}_{1-x}\mathrm{(CN)_4}$ and $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{(CN)_2}$, alters the magnitude of the observed NTE [5–7].

The group 11 metal cyanides form quasi-one-dimensional (1D) materials consisting of linear M-CN chains packed together in a hexagonal arrangement [8]. AgCN, AuCN, and HT-CuCN all exhibit 1D NTE parallel to their linear chains, and large positive thermal expansion (PTE) perpendicular to them [2]. The same directional behavior is observed for the bimetallic cyanides, such as $\mathrm{Cu_{1/2}Au_{1/2}CN}$, $\mathrm{Ag_{1/2}Au_{1/2}CN}$ and $\mathrm{Cu}_x\mathrm{Ag}_{1-x}\mathrm{CN}$ ($0 \leqslant x \leqslant 1$), with varying magnitudes [5]. This work explores the thermally induced anomalous dynamical behavior of the trimetallic cyanide, $\mathrm{Cu_{1/3}Ag_{1/3}Au_{1/3}CN}$.

The compounds mentioned above adopt one of the two structure types shown in Fig. 1 [8]. In the AuCN structure, the metal ions in neighboring chains are aligned, resulting in coplanar metal sheets. In the AgCN structure, the chains are offset by 1/3 of the interchain metal-to-metal distance. The difference between the structures of AuCN and AgCN specifically was previously attributed to the aurophilic bonding present in AuCN [8]. Structural analysis of the bimetallic cyanides showed that all the Au-containing cyanides adopt the AuCN structure [5]. In these compounds, metals have both like and unlike nearest neighbors perpendicular to the chains and there is no long-range metallic ordering within the metal planes. Nonetheless, it appears that metallophilic interactions, either between very small fractions of neighboring Au ions

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