Structural Behavior of Non-Oxide Perovskite Superconductor

MgCNi$_3$ at Pressures up to 32 GPa

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Abstract

We report the pressure dependence of the structural parameters of the non-oxide perovskite superconductor MgCNi$_3$ up to 32 GPa using a diamond anvil cell and synchrotron x-rays at room temperature. The structure of the compound remains in the Pm-3m cubic symmetry throughout the pressure range. The bulk modulus $B_0 = 156.9 \pm 0.2$ GPa with $B'_0 = 9.8$ obtained by fitting the pressure-volume data is in good agreement with theoretical calculations reported earlier. An anomalous shift of the (111) and (200) lines observed above 9 GPa indicates a possible local short range distortion that is consistent with earlier studies.
I. INTRODUCTION

The recent discovery of superconductivity in the Ni rich perovskite MgCNi$_3$ with a transition temperature $T_c = 8.5$ K has triggered intense research towards the search for superconducting materials in the intermetallic family. The observation of superconductivity in this compound is unusual and surprising as Ni has strong magnetic behavior due to partially filled $d$ states. The domination of Ni $3d$ bands inferred from band structure calculations emphasizes a strong hybridization between the Ni $3d$ and C $2p$ electrons, and the non-ferromagnetic ground state of MgCNi$_3$ is consequence of a reduced Stoner factor due to this hybridization. Neutron diffraction experiments performed at low temperatures down to 2 K show no sign of ferromagnetic order indicating the absence of magnetic anomalies around the transition temperature. Ignatov et al., performed Ni $K$-edge x-ray absorption measurements and reported distortions in the Ni$_6$ octahedra below 70 K which favour a low symmetry crystal structure. The ferromagnetic spin fluctuations observed in the NMR experiments, and the unusual quasi two dimensional van-Hove singularity (vHs) reported by Rosner et al., suggest that MgCNi$_3$ lies in the proximity of a ferromagnetic boundary. There are still open questions regarding the role of spin fluctuations and/or lattice instabilities on the origin of superconductivity in this system.

Even though it is reported that the density of states shows normal behavior under pressure up to 20 GPa, $T_c$ shows an increase as a function of pressure. The possible reason behind the rise in $T_c$ has been attributed to either a reduction in the spin fluctuations or an increase in the electron-phonon interaction followed by a structural transition. The recent temperature dependent inelastic neutron scattering studies give evidence for a lattice instability in the low frequency Ni phonon modes. Still, there have been no detailed structural studies on this system to clarify the structural stability at high pressure, with the exception of an energy dispersive x-ray diffraction (EDXRD) report by Youlin et al. In order to investigate the structural properties under pressure, we have performed high pressure x-ray diffraction experiments on this compound and discuss the results in detail in the following sections.
II. EXPERIMENTAL

The sample used in the experiments was synthesized by the conventional solid state reaction method reported earlier. The x-ray diffraction patterns recorded at ambient conditions showed the compound crystallizes in the cubic perovskite phase with a minor impurity of unreacted Ni (2-5%). The cell parameter obtained at ambient conditions, \( a = 3.8100(\pm0.0004) \text{ Å} \), matches well with the reported values in the literature. The AC susceptibility and four probe resistivity measurements showed the \( T_c \) onset around 8 K.

High pressure experiments were performed using a Merrill-Bassett type diamond anvil cell (DAC) with a culet diameter of 400 \( \mu \text{m} \) at Sector 16 IDB, HPCAT, Advanced Photon Source (APS), Chicago. The sample in powder form was loaded with tiny ruby chips in a 185 \( \mu \text{m} \) hole drilled in a stainless steel gasket with a preindentation to 65 \( \mu \text{m} \). We performed three experimental runs up to 32 GPa: two with silicone fluid pressure transmitting medium and another with Flourinet (FC70) to examine effects of pressure medium on the results. The diffraction images were recorded using an imaging plate. In all the experimental runs the typical beam size was 20x20 \( \mu \text{m}^2 \), and the exposure time for each pattern was 10-20 sec. The pressure in the DAC has been determined using the standard ruby fluorescence method. The diffraction images were integrated using the Fit2D software and the structural refinement has been done using RIETICA (LHPM) Rietveld package and JADE.

III. RESULTS AND DISCUSSION

The crystal structure of MgCNi\(_3\) is a three dimensional network with the Ni atoms crystallographically located at \( 3c (0;1/2;1/2) \), Mg at \( 1a (0;0;0) \) and C at \( 1b (1/2;1/2;1/2) \) adopting the Pm-3m cubic space group symmetry. The Ni atoms occupy the position of the negative halide atoms in the common perovskite structure, and form a metallic Ni\(_6\) octahedra framework. The superconducting properties are strongly dependent on the atomic position of Ni, which in turn governs the Ni-C bonding and Ni-Ni hopping.

X-ray diffraction patterns collected at several pressures are shown in the Fig. 1. In general the diffraction lines observed can be clearly indexed to the cubic structure. When analyzing the pressure data after the first run and refining the structural parameters, we noticed a strong deviation from the systematic shift of the (111) and (200) lines under pressure above
8 GPa (Fig. 2). The (111) line tends to stay at low angles and (200) shifts rapidly to higher angles with increasing pressures. As the cubic perovskites are very sensitive to the uniaxial stress distributions around the sample environment, usually one expects uneven shifts and splittings, even pressure induced changes to rhombohedral symmetry if a non-hydrostatic stress develops during the glassy transformation of the pressure transmitting medium\[15, 16\]. Since our recent high pressure experiments found the silicone fluid medium (poly dimethyl siloxane with a viscosity of 1 cst) to be nearly hydrostatic at least up to 10 GPa\[17\], the effect of non-hydrostatic stress on the sample in the first run is expected to be less pronounced below 10 GPa. To see whether these anomalies are due to the pressure medium or intrinsic local distortions associated with structural modifications, we decided to repeat the experiments (Run 2 with silicone fluid and Run 3 with Fluorinert - FC70). The hydrostatic limit of Fluorinert (FC70) has been recently reported to be 0.55 GPa\[18\]. Thus when using Fluorinert pressure medium, one might expect the anomalous line shifts to appear at a lower pressure relative to silicone fluid if the cause of the shifts is due to the solidification of the pressure medium. The results of the refinements of the data obtained from Run 2 and 3 showed similar behavior observed in Run 1 around 8 GPa which showed that the stress distributions due to change in the pressure medium are not significant. This indicates that there are intrinsic local distortions from the ideal cubic structure.
MgCNi$_3$ is isostructural to the well known Bi$_{1-x}$K$_x$BiO$_3$ (BKBO) superconductor which has $T_c = 30$K. Structural distortions in BKBO have been studied in detail by Braden et al., and they have shown that the rotational instability of the BiO$_6$ octahedra leads to a tetragonal distortion.$^{[19]}$ A non-cubic layered structure for BKBO is further reported by Klinkova et al.$^{[20]}$ As MgCNi$_3$ and BKBO both have breathing instabilities and structural similarities, we carefully examined the high pressure x-ray diffraction patterns of MgCNi$_3$ for super cell reflections and splits in diffraction lines for possible structural transitions. The spectra showed no considerable line broadening and no super cell reflections or splittings up to the highest pressure achieved in this experiment. These observations lead us to conclude that the distortions are associated with a change in the short range structural order. The Rietveld refinement is confined to pressures less than 9 GPa for cubic symmetry and at higher pressures we have obtained the cell parameters by fitting the peak positions using JADE. The $P – V$ data are fitted to the Birch-Murnaghan equation of state given by

FIG. 2: Rietveld refinement for the diffraction pattern collected for MgCNi$_3$ at 0.6 GPa in Run 1. The residuals are $R_{wp}=1.2\%$ and $\chi^2 = 1.1$. The upper panel shows the diffraction lines (111) and (200) after refinement using cubic symmetry in Run 3 at 10.6 GPa. The solid line represents the calculated spectrum and open symbols represent the observed data.
FIG. 3: $P - V$ data for MgCNi$_3$. The open symbols represent EDXRD data from Ref. 11.

This fit yields a bulk modulus of $B_0 = 156.9 \pm 0.2$ GPa with a pressure derivative $B'_0 = 9.8$. The $P - V$ data are shown in Fig. 3. The bulk modulus obtained in our experiment agrees well with the theoretical value estimated earlier [8] and is a factor of 1.7 smaller than the reported value in the EDXRD experiment [11]. The possible reason for the high value of the bulk modulus in the EDXRD experiment may be due to the inaccuracy in estimating the ambient unit cell volume, pressure determination using the internal calibrant and/or the distortions induced on the unit cell due to non-hydrostatic stress coupled with local distortions as there is no use of pressure medium reported. The bulk modulus of MgCNi$_3$ is comparable to MgB$_2$, high $T_c$ superconducting compounds and other oxide perovskites and it is more compressible than its two dimensional borocarbide analogues such as YNi$_2$B$_2$C$_2$ [11, 21-26]. Our experimental results reflect the fact that the Ni-Ni and Ni-C bonding in MgCNi$_3$ are softer than ternary borocarbides and the Bi-O bonds in bismuthates. We have listed the bulk moduli value of some perovskites with elemental Ni in Table 1 for comparison.
| Compound      | Structure       | $T_c$ (K) | $B_0$ (GPa) | $B'_0$ | Ref.     |
|--------------|-----------------|----------|-------------|--------|---------|
| MgCNi$_3$    | Cubic, Pm-3m    | 8        | 156         | 9.9    | this work |
| MgCNi$_3$    | Cubic, Pm-3m    | 8        | 267         | 4      | 11      |
| MgB$_2$      | Hexagonal, P6/mmm | 40      | 151         | 5      | 21      |
| YNi$_2$B$_2$C | Tetragonal, I4/mmm | 15    | 200         | -      | 22      |
| TbNi$_2$B$_2$C | Tetragonal, I4/mmm | 0.3   | 136-196     | -      | 23      |
| Ni           | Cubic, Fm-3m    | -        | 177-187     | -      | 24      |
| Ba$_0.6$K$_{0.4}$BiO$_3$ | Cubic, Pm-3m | 30      | 200         | 4      | 25      |
| BaBiO$_3$    | Tetragonal, P-42 m | -      | 215         | 4      | 25      |
| BaTiO$_3$    | Cubic, Pm-3m    | -        | 135         | 6.4    | 26      |
| KNbO$_3$     | Cubic, Pm-3m    | -        | 146         | 5      | 26      |

TABLE I: Bulk modulus data and other physical properties of some perovskites and borocarbides.

In conclusion we have performed high pressure x-ray diffraction measurements on the non-oxide perovskite MgCNi$_3$ up to 32 GPa. The determined bulk modulus is in excellent agreement with the theoretical value predicted earlier by TB-LMTO calculations. Even though the results show no structural phase transitions, we have noticed a pressure induced distortion which may be associated with a change in the short range order of the crystal structure. Detailed extended x-ray absorption (EXAFS) measurements under pressure are under way to understand the pressure induced changes in this system.

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