The mechanical relaxation study of polycrystalline MgC$_{1-x}$Ni$_3$

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Abstract

The mechanical relaxation spectra of a superconducting and a non-superconducting MgC$_{1-x}$Ni$_3$ samples were measured from liquid nitrogen temperature to room temperature at frequency of kilohertz. There are two internal friction peaks (at 300 K labeled as P1 and 125 K as P2) for the superconducting sample. For the non-superconducting one, the position of P1 shifts to 250 K, while P2 is almost completely depressed. It is found that the peak position of P2 shifts towards higher temperature under higher measuring frequency. The calculated activation energy is 0.13 eV. We propose an explanation relating P2 to the carbon atom jumping among the off-center positions. And further we expect that the behaviors of carbon atoms maybe correspond to the normal state crossovers around 150 K and 50 K observed by many other experiments.
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The superconductivity has been found in intermetallic compounds of the general formula MgC$_{1-x}$Ni$_3$ [1], which has the antiperovskite structure. Many researches have been focused on the possible magnetism or magnetic instability due to a large amount of Ni in this compound [2-5]. The MgC$_{1-x}$Ni$_3$ band structure displays a characteristic very large and narrow peak in the density of states (DOS) just below the Fermi energy [6,7]. Then it is expected that the magnetic interaction still exists in MgC$_{1-x}$Ni$_3$ and there are magnetic fluctuations in superconducting MgC$_{1-x}$Ni$_3$ [8], which is reminiscent of the LnNi$_2$B$_2$C family [9].

Another aspect of MgC$_{1-x}$Ni$_3$ is the possibility of conventional phonon-coupled paring [6,10]. The light element, carbon, might play an important role on the superconductivity in MgC$_{1-x}$Ni$_3$ in the frame of electron-phonon coupling. This viewpoint is also associated with the recently found MgB$_2$ compound with the superconducting transition temperature about 40 K [11]. The light element boron results in the high phonon frequency, and hence the higher transition temperature.

There are some unresolved questions in the normal state such as the crossover behavior located around 50 K and the “knee” near 150 K [8,12,13]. It is also found that the superconductivity is critically dependent on the carbon concentration in MgC$_{1-x}$Ni$_3$. When $1-x$ is smaller than about 0.85, the superconductivity is completely suppressed and the “knee” near 150 K disappears. While when $1-x$ is larger than 0.85 both the superconductivity and the “knee” recover. In this report, we measured the mechanical relaxation spectra of a superconducting ($x \approx 0$) and a non-superconducting ($x \approx 0.2$) MgC$_{1-x}$Ni$_3$. The comparative study would throw some insights into the mechanism for the superconductivity of MgC$_{1-x}$Ni$_3$.

Two ceramic samples of MgC$_{1-x}$Ni$_3$ with different carbon content were prepared by conventional method as described in Ref. 12. Resistance of the samples was measured by the standard four-probe technique and the result was shown in figure 1. The transition temperature $T_C$ of the superconducting MgC$_{1-x}$Ni$_3$ sample is 7 K.

Internal friction ($Q^{-1}$) and modulus ($Y$) of the mechanical relaxation spectra were mea-
sured by Frequency-Modulation-Acoustic-Attenuation (FMAA-I) equipment made in the University of Science and Technology of China. The dimensions of the rectangular bars of the samples are $\sim 5 \times 1 \times 0.2 \text{mm}^3$ with resonant frequencies from 2600 to 4100 Hz.

The mechanical relaxation spectra of a superconducting and a non-superconducting samples on heating, with the rate about 1 K/min, were shown in figure 2. For the superconducting sample, there are two internal friction peaks (at 300 K labeled as P1 and 125 K as P2). With increasing the measured frequency, the position of P2 shifts towards higher temperature, which is shown in figure 3. Then it is expected that P2 may be due to the thermally activated process. The calculated activation energy $U = 0.13eV$ and the pre-exponential factor $\nu_0 = 2.9 \times 10^9 \text{Hz}$, by a fit of the Arrhenius relation $2\pi f_p = \nu_0 \exp(-U/T_p)$, where $f_p$ is the resonant frequency and $T_p$ peak temperature. But P1 does not show clear shift within experimental errors. For the non-superconducting sample, P2 is nearly completely suppressed and P1 has shifted towards 250 K.

The relative changes of modulus of the two samples $\Delta Y/Y$, which can be obtained by the following formula $\Delta Y/Y = (f^2 - f_0^2)/f_0^2$, are also shown in the figure 2, where $f$ is the resonant frequency, and $f_0$ the resonant frequency at 81 K. No clear softening point (local minimum) of modulus was observed in our measured temperature range, which indicates there is no lattice instability. It is consistent with the powder diffraction experiment results [14], which shows that the lattice parameter and the Debye-Waller factors for individual atoms decrease smoothly with decreasing temperature, and no unusual change of the structure parameters near $T_C$. This is different to the case for superconducting BKBO with the perovskite structure, where structure instability was observed [15,16]. On the other hand, there are modulus defects corresponding to P1 and P2 peaks for the superconducting sample. But only one modulus defect appears around 260 for the non-superconducting one.

In figure 4, the prediction of Debye theory, $Q^{-1} = \frac{\Delta}{T(1 + \omega^2 \tau^2)}$, is compared with P2 peak, where $\Delta$ is the relaxation strength, $\omega = 2\pi f$, and $\tau = \nu_0^{-1} \exp(U/T_p)$. It is clear that the prediction is much narrower than the experiments. So, the Cole-Cole law [17], $Q^{-1} =$
\( \Delta \text{Im}[\frac{1}{1+\omega^\alpha}] \), is used to fit the experimental results. In the fitting, background internal
friction, \( Q_B^{-1} = 4.5 \times 10^{-6} T + 7.6 \times 10^{-4} \), that may originate from the low temperature tail
of P1 peak etc., is firstly subtracted. The fitted \( \alpha = 0.52 \) that means there exist strong
 correlations between the relaxation units [18].

Due to both the small activation energy and small pre-exponential factor of the relaxation
time of P2 peak, \( U = 0.13eV \) and \( \nu_0 = 2.9 \times 10^9 \) Hz, we expect that it is related to the
off-center hoping of carbon atoms [19]. Usually, the perovskite oxide presents the ferroelectricity, which is due to the ordering of off-center light ions in the octahedral structure. In
\( \text{MgC}_{1-x}\text{Ni}_3 \), light element carbon locates in the center of octahedron. Then carbons might
posses the off-center configurations and hop among the off-center sites. It should be noted
that this off-centered configuration does not alternate the average crystalline symmetry and
average symmetry of carbon atoms when no ordering takes place. Then it is not easy to be
observed by other experiments. This kind of off-center hopping leads to mechanical energy
loss and modulus defect, and the activation energy and the pre-exponential factor are usually
small, such as the off-center relaxation process of oxygen atoms in \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) [20].

P2 peak is observed only in superconducting sample, and in non-superconducting samples
it is largely depressed. This might provide some important information on the superconduct-
ing in \( \text{MgC}_{1-x}\text{Ni}_3 \). Ren et al. [12] investigated the structure feature of a series of \( \text{MgC}_{1-x}\text{Ni}_3 \)
in detail. They observed two different phases of \( \text{MgC}_{1-x}\text{Ni}_3 \), non-superconducting \( \alpha\)-
\( \text{MgC}_{1-x}\text{Ni}_3 \) phase and superconducting \( \beta\)-\( \text{MgC}_{1-x}\text{Ni}_3 \) phase. Due to the smaller lattice
parameter of \( \alpha\)-\( \text{MgC}_{1-x}\text{Ni}_3 \) phase, the off-center configurations would be suppressed. It is
consistent with the result that P2 is depressed in the non-superconducting sample.

The off-center configurations will be smeared with the increase of temperature and conse-
quently, there will be a crossover point somewhat above P2 peak temperature (~125 K). This
might correspond to the “knee” near 150K observed in the resistivity, thermal power and
thermal conductivity in superconducting \( \text{MgC}_{1-x}\text{Ni}_3 \) [12,13]. Moreover, there exist strong
correlations among the off-center carbon atoms as mentioned above, which will lead to their
ordering at low temperature. Whether this ordering is related to the electronic crossover near 50 K [8,13] needs further studies in superconducting MgC$_{1-x}$Ni$_3$.

As to the P1 peak, due to its appearing in both superconducting and non-superconducting samples, it is speculated that it may be related to the jumping of carbon vacancies between different octahedrons. Usually, this kind of jumping process is almost impossible in perovskite, but MgC$_{1-x}$Ni$_3$ is the so-called anti-perovskite, where nickel atoms, other than oxygen ones, form the octahedrons, so that the binding to the center atoms is weak. Moreover, carbon is light element that is easy to jump. Furthermore, the nickel atoms nearest to the carbon vacancies shift from the idealized positions [21], which will increase the mobility of carbon vacancies and create local distortions. As a result, internal friction peak and modulus defect is observed.

In summary, we have measured the mechanical relaxation spectra of superconducting and non-superconducting MgC$_{1-x}$Ni$_3$ samples from liquid nitrogen temperature to room temperature. A thermally activated relaxation peak is observed around 125K in superconducting sample. We expect that it should be due to the off-center hopping of carbon atoms. This internal friction peak is almost fully depressed in non-superconducting samples. This indicates that this process is closely related to the superconductivity in MgC$_{1-x}$Ni$_3$. The other peak near 300K, which appears in both superconducting and non-superconducting samples, is speculated to be related to the jumping of carbon vacancies between different octahedrons.

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Figure Captions

Figure 1. Reduced resistance $R/R_{300K}$ of a superconducting ($x \approx 0$) and a non-superconducting ($x \approx 0.2$) MgC$_{1-x}$Ni$_3$ samples vs temperature $T(K)$.

Figure 2. Internal friction ($Q^{-1}$) and reduced modulus ($\Delta Y/Y_{81K}$) of the mechanical relaxation spectra of a superconducting and a non-superconducting MgC$_{1-x}$Ni$_3$ samples from liquid nitrogen temperature to room temperature.

Figure 3. The internal friction spectra ($Q^{-1}$) of the P2 peak for the superconducting MgC$_{1-x}$Ni$_3$ sample with the resonant frequency 2605 and 4098 Hz, respectively.

Figure 4. A fit of Cole-Cole law (solid line) to the P2 peak. The dashed line is the prediction of the Debye theory.
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$Q^{-1} \times 10^3$ vs. $T$ (K)

- $f = 2605$ Hz
- $f = 4098$ Hz

P$_2$
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![Graph showing the relationship between Q^-1 - Q_B^-1 and T (K). The graph includes a peak at around 120 K with labels for Debye Theory and Cole-Cole Law.](image-url)