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Phonon Density of States of Double Honeycomb Lattice Superconductors Studied by AGNES

Shin-ichi SHAMOTO, Yoichi KATO, Keigo IIZAWA, Tsuyoshi KAJITANI,
Takeshi KOIWASAKI[1], Masahiro YASUKAWA[1] and Shoji YAMANAKA[1]

Department of Applied Physics, Faculty of Engineering, Tohoku University, Sendai 980-8579, Japan
[1]*Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,*
Higashi-hiroshima 739-8527, Japan

Generalized phonon density of states (GPDOS) of Li_xZrNBr and Na_xHfNCl has been studied by the TOF-type cold neutron spectrometer AGNES with the incident energy of 4.59 meV. Upon Li intercalation in β-ZrNBr, the intensity of GPDOS in enegies ranging from 6 to 14 meV increases, while the intensity around 20 meV decreases, indicating softening of a phonon mode from 18 to 15 meV. The total intensity of GPDOS in Li_xZrNBr system is conserved upon intercalation, whereas it increases in Na_xHfNCl system with increasing x, suggesting co-intercalation of tetrahydrofuran with sodium. The observed low energy phonon modes and Debye temperatures in these double honeycomb lattice superconductors are discussed in conjunction with their superconductivity.

KEYWORDS: neutron scattering, double honeycomb lattice, superconductor, phonon density of states, AGNES

§1. Introduction

Novel layered superconductors, Li_xZrNCl (T_c=14 K),[1)] and $Li_x(THF)_yHfNCl$ (T_c=25 K, THF; tetrahydrofuran C_4H_8O),[2)] possess the double honeycomb lattice of $[ZrN]_2$ or $[HfN]_2$ as a 2 dimensional conducting layer, which is composed of strong covalent network of transition metal and nitrogen.[3)] Electronic density of states in Li_xZrNCl and Na_xHfNCl has been estimated to be small, i.e., $\gamma \leq 3.8$ and 8.8 mJ/mol/K^2, in comparison to their superconducting transition temperatures.[4)] Furthermore, the relationship between T_c and 2 dimensional Fermi temperature estimated by μSR measurement in $Li_x(THF)_yHfNCl$ corresponds well to other high-T_c compounds such as $YBa_2Cu_3O_7$.[5)] There are some similarities between these double honeycomb lattice superconductors and high-T_c cuparates. However, generalized phonon density of states (GPDOS) of these double honeycomb lattice superconductors has not been reported so far. Here, we report the GPDOS of Li_xZrNBr and $Na_x(THF)_yHfNCl$ measured by the TOF-type cold neutron spectrometer AGNES at $T\sim$270 K.

§2. Experimental

β-MNX (where M= Zr, Hf; X= Cl, Br) was prepared by the reaction of ZrH_2(99.7%) or Hf(99.97%) with NH_4X(99.5%) at 650 °C for 30 min under the flow of NH_3 gas (99.9%, 20-50 cc/min). β-MNX phase was purified and separated from the mixture by the chemical vapor transport.[6)] The alkali metal intercalation in β-ZrNX was carried out by dispersing the sample in 15% n-butyllithium solution in hexane in an Ar-filled glove box, while in the case of β-HfNCl the sample was dispersed in Na naphthalene solution of THF. The alkali metal concentration x was determined by an inductively coupled plasma (ICP) spectrometry. An aluminum cell with double cylinders of vanadium foils was used for Na_xHfNCl sample in order to reduce large neutron absorption effect. The neutron scattering measurements were carried out at $T\sim$270 K on the TOF-type cold neutron spectrometer AGNES installed at C3-1-1 cold guide of JAERI-JRR3M in Tokai. 122 detectors were installed in scattering angles between 9 and 130°, where data of 3 detectors (2θ=40, 66 and 80°) were omitted in the present analysis. Each detector efficiency was corrected by using elastic scattering data of vanadium. Time width of time analyzer was set to be 5 μsec at the chopper revolution of about 6300 rpm. The intensity in the energy range 25-30 meV is excluded because of elastic scattering with $\lambda/2$ by graphite monochrometers. For the GPDOS analysis, the data in 2θ range 60-130° were used because of their high detector efficiency. The incident neutron energy was fixed to be 4.59 meV (λ =4.22 Å). Observable energy E range as a function of the scattering vector Q is shown in Fig. 1. Since the E-Q range in the present measurement includes hydrogen dispersion with about 5 Å^{-1} width, the present GPDOS is sensitive to hydrogen atoms. T_c was determined by measuring magnetization of the sample with a Quantum Design SQUID magnetometer, while Debye temperature was estimated from heat capacity data in temperatues ranging from 1.8 to 30 K using a Quantum Design PPMS system.

§3. Results and Discussion

Powder neutron diffraction patterns, i.e., the elastic component of the AGNES data, of β-ZrNBr and $Li_{0.19}ZrNBr$ at $T\sim$270 K are shown in Fig. 2, indicating the increase of c lattice parameter from 29.2 to 29.6 Å by Li intercalation. Their GPDOS is shown in Fig. 3. Both of β-ZrNBr with the weight of 8.85 g and $Li_{0.19}ZrNBr$ with 8.50 g have been measured for 47 hours. As for low energies below 25 meV, the GPDOS increased at energies

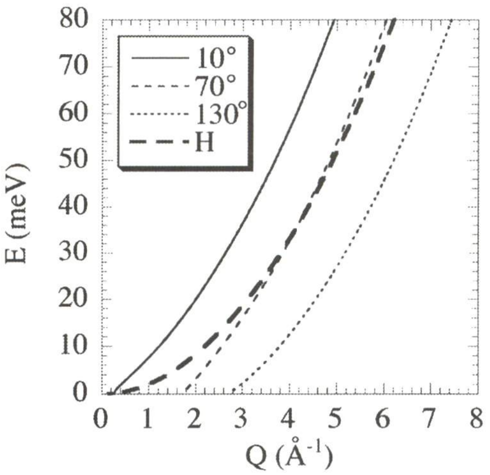

Fig. 1. Relation between energy E and scattering vector Q for 2θ=10, 70 and 130° in an energy gain side of the present measurement by AGNES. Recoil dispersion by a hydrogen atom is also shown by a wide broken line H.

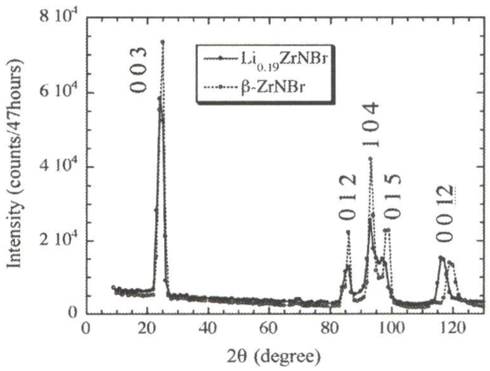

Fig. 2. Powder neutron diffraction patterns of β-ZrNBr and $Li_{0.19}ZrNBr$ by AGNES at $T\sim$270 K.

from 6 to 14 meV, whereas it decreased around 20 meV, indicating phonon softening from E=18 to 15 meV. At high energies, softening of a phonon mode from E=64 to 60 meV can be seen upon intercalation, although the error bars are large. Phonon modes at high energies are composed mainly of nitrogen vibration because of its light mass and strong force constant with neighboring atoms, while low energy phonon modes include zirconium and bromine vibrations. Since alkali metals, i.e., Li and Na, have small total cross section, their contribution to GPDOS can be neglected. Upon Li intercalation, Zr atoms are known to move towards nitrogen layer away from Br layer[7] as in the case of $Li_{0.16}ZrNCl$.[3] Furthermore, electrons are supplied in a conduction band which is formed by $[ZrN]_2$ double honeycomb lattice.[8] According to these facts, the softened phonon from E=18 to 15 meV would be the Zr-Br vibrational mode.

GPDOS of β-HfNCl, $Na_{0.27}HfNCl$ and $Na_{0.75}HfNCl$ at $T\sim$270 K is shown in Fig. 4. For HfNCl and $Na_{0.75}HfNCl$, sample can and sample weight (about 8 g) were similar to each other. These two data normalized by their measuring times (107 hours for β-HfNCl and 45.5 hours for $Na_{0.75}HfNCl$) are compared. The strongest peak around 20 meV in GPDOS of β-HfNCl contrasts with that of β-ZrNBr, indicating the contribution of Cl atom with large scattering cross section. In two energy regions of 0-20 and 30-70 meV, the intensity increased appreciably with increasing x.

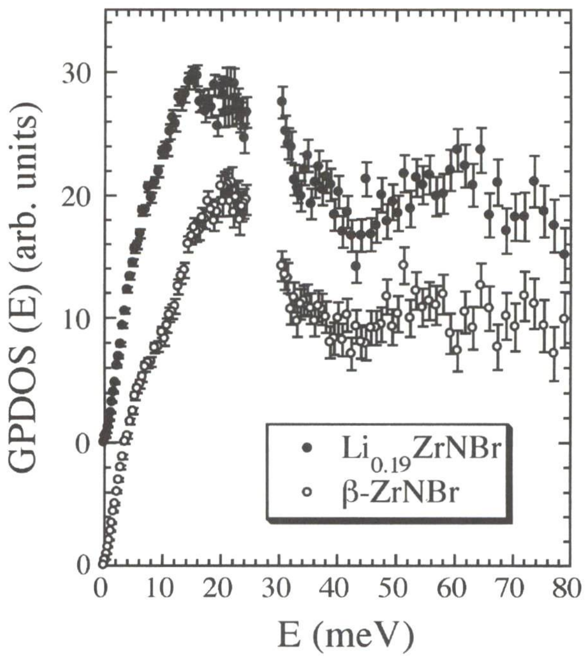

Fig. 3. GPDOS of β-ZrNBr and $Li_{0.19}ZrNBr$ at $T\sim$270 K.

Table I summarizes $\sum_j(\sigma_c+\sigma_i)_j/M_j$ values for atoms, where σ_{cj} denotes coherent scattering cross section of jth atom, σ_{ij} is incoherent scattering cross section of jth atom and M_j is atomic mass of jth atom. Although there is not much meaning of σ_c in non-Bravais crystals, it could be a guide for possible intensity of specific atoms to GPDOS. In other words, it assumes that one phonon branch is composed of one atom vibration in a unit cell. $(\sigma_c+\sigma_i)/M$ for Na atoms is not large enough to explain the increase of total GPDOS intensity of Na intercalated samples in Fig. 4, suggesting co-intercalation of organic molecule THF with sodium. GPDOS of inorganic compounds, such as high-T_c cuprates, is observed up to about 100 meV, while stretching vibrations of hydrogen, such as $=CH_2$, are around 300 meV. Therefore, the intensity of THF may be spread up to high energies,

Table I. Relative possible intensity of atoms to GPDOS.

Atoms	$\sum_j \sigma_{cj}/M_j$	$\sum_j \sigma_{ij}/M_j$	$\sum_j (\sigma_c+\sigma_i)_j/M_j$
Li	0.07	0.13	0.20
Na	0.07	0.07	0.14
THF	16.1	637.0	653.1
HfNCl	1.15	0.20	1.35
ZrNBr	0.93	0.04	0.97

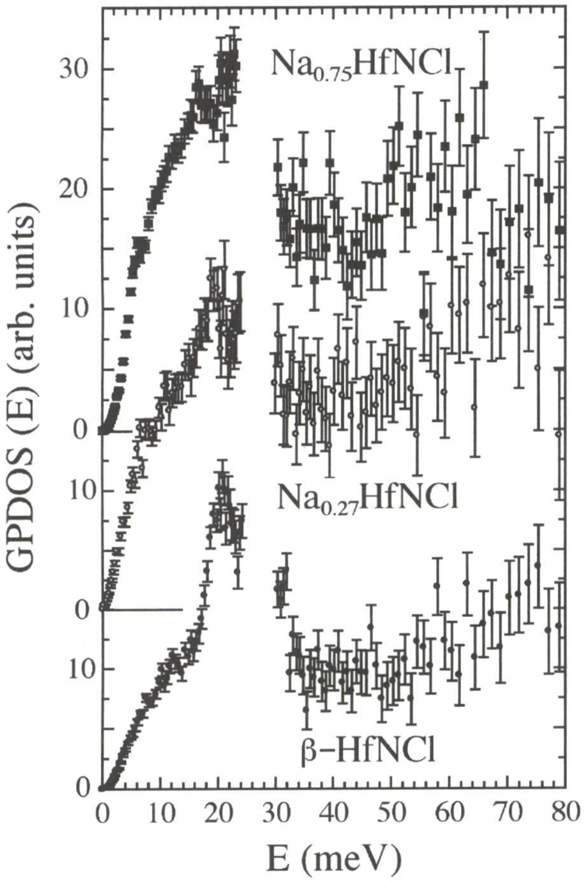

Fig.4. GPDOS at $T\sim270$ K for the samples β-HfNCl, $Na_{0.27}HfNCl$ and $Na_{0.75}HfNCl$.

leading to the small contribution of THF to the energy range in Fig. 4. The *c*-axis parameters at $x=0$, 0.27 and 0.75 were 27.7, 29.7 and 30.1+33.1 Å(two phase mixture), respectively. The elongation of *c*-axis upon Na intercalation is somewhat larger than that of Li_xZrNBr, in comparison to the difference in ionic radii between Li^+ and Na^+ ions, i.e., 0.74 and 1.02 Å. Extra weight for Na_xHfNCl estimated by ICP analysis also increased with increasing x. Therefore, we conclude that this weight is due to co-intercalation of THF, where the content, y, of THF in $Na_x(THF)_yHfNCl$ would be 0.11 and 0.23 for the samples with $x=0.27$ and 0.75, respectively. Since *c*-axis of $Na_x(THF)_yHfNCl$ is much smaller than that of $Li_x(THF)_yHfNCl$, THF molecules would align parallel to $[HfNCl]_2$ blocks. It might be related to existence of a gap in the x range from 0.3 to 0.5 for samples prepared under various intercalation conditions.[4)]

At low energies there were humps at E=7, 15.5, 18 and 21 meV in ZrNBr spectrum, while in HfNCl spectrum they can be observed at E=12 and 21 meV. In Li_xZrNCl (x<0.16), peaks were observed at E=13, 21 and 24 meV.[9)] Debye temperature θ_D estimated from heat capacity measurement at low temperature is expected to reflect these phonon energies. The θ_D values in $Li_{0.19}ZrNBr$, $Na_{0.2}HfNCl$ and $Li_{0.2}ZrNCl$ were 218, 232 and 280 K, respectively. There seems to be some relationship between the lowest phonon energies and Debye temperatures in MNCl system. It would be owing to the similarity of cross sections between Zr and Hf. The ratio of electronic density of states at the Fermi surface, $N(0)$, is estimated from interatomic distances between the nearest neighbor transition metal atoms, leading to $N(0)_{ZrNBr}$: $N(0)_{ZrNCl}$: $N(0)_{HfNCl}$= 1.00(1) : 0.98(2) : 1.15(3).[7)] If an attractive interaction V is given for the T_c^{onset} value, i.e., 14.5 K, of $Li_{0.19}ZrNBr$ in the simple BCS formula with θ_D and $N(0)$, other T_c^{onset} values of Li_xZrNCl and Na_xHfNCl, i.e., 15.5 and 23.5 K, can be evaluated with the same V to be 17.5 and 22.5 K, respectively. The agreement between the observed T_c^{onset} values and those evaluated with θ_D indicates that the mechanism of superconductivity through the medium of phonon would be common in the double honeycomb lattice superconductors.

§4. Summary

GPDOS of Li_xZrNBr (x=0 and 0.19) and $Na_x(THF)_yHfNCl$ (x=0, 0.27 and 0.75) has been measured by the TOF-type cold neutron spectrometer AGNES at $T\sim270$ K. In Li_xZrNBr system, softening of phonon from 18 to 15 meV, which was assigned to Zr-Br vibrational mode, has been observed upon Li intercalation. In Na_xHfNCl system, co-intercalation of THF was found from total intensity increase in GPDOS.

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