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Pressure Effect and Neutron Scattering Study on A_x HfNCl (A; Alkali Metals and Organic Molecules)

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The transition temperature of Na_xHfNCl (T_c^{max}=20.0 K) is found to be lower than that of $Li_{0.5}THF_yHfNCl$ (T_c=24.0 K). Pressure effect on $Na_{0.3}HfNCl$ (T_c=19.4 K) is found to be small, i.e., dT_c/dP =-0.013(6) K/kbar. Powder neutron inelastic scattering on $Na_{0.3}HfNCl$ shows the increase in $S(Q,E)$ at anomalous high energy, i.e., about 30 meV, in comparison with 2Δ~8 meV with decreasing temperature from 25 to 10 K.

Layered superconductors, A_xZrNCl (T_c~15 K) (A;alkali metals and organic molecules) and $Li_x(THF)_yHfNCl$ (T_c~25.5 K) have been discovered by Yamanaka et al. [1,2]. These crystal structures are found to have a fairly flat double honeycomb lattice as a conducting plane [3,4], leading to an unique band structure. The conduction band filled by small number of electrons has 3-fold nesting condition [5,6]. Larger density of states for A_xHfNCl is estimated than that for A_xZrNCl based on the distance between the nearest neighbor Zr or Hf atoms. This result coincides with that of FLAPW band calculation [5]. Pauli paramagnetic susceptibility of these compounds also supports this tendency [7]. However, recent result by μSR measurement indicates that there is some magnetic ordering in the parent HfNCl sample below 100 K [8] in contrast to ZrNCl [3].

The powder samples of Li_xZrNCl and A_xHfNCl has been prepared by the methods described in the literatures [1,2]. AC susceptibility was measured at various pressures, which were applied by using the clamp piston cylinder type apparatus with Fluorinert FC-75 (3M) as the pressure medium. Powder neutron inelastic scattering measurements for neutron incident energy E_i=110 meV were carried out using MARI spectrometer at the ISIS pulsed neutron source at the Rutherford Appleton Laboratory. The amounts of alkali metals uptake were determined by an inductively coupled plasma spectrometry.

Although some band calculations emphasize the importance of van Hove singularity at a certain x-value [9], the transition temperature, T_c, of Na_xHfNCl decreased gradually from 20.0 K to 16.5 K with increasing x from 0.11 to 0.85 [7]. The maximum T_c of 20.0 K in Na_xHfNCl is obviously lower than the T_c of 24.0 K in $Li_{0.5}(THF)_{0.2}HfNCl$, where both of our samples were prepared by the same procedure except for the difference of alkali metals. It should be noted that both superconductors have the similar superconducting onset transition temperature, i.e., 25.0-25.5 K. In contrast to this result, the difference of T_c between Na_xZrNCl (T_c^{max}=15 K) and Li_xTHF_yZrNCl (T_c^{max}=15 K) can be ignored. This phenomenon will be discussed in details in the literature [10]. The decease of T_c for the present HfNCl system is expected to be due to the local structural disorder, possibly in connection with the Fermi surface nesting. We have studied the pressure effect on T_c of $Na_{0.3}HfNCl$ as shown in

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Fig. 1. Pressure effect for $Na_{0.3}HfNCl$ (T_c=19.4 K) is found to be dT_c/dP =-0.013(6) K/kbar. It contrasts with the large pressure effect (0.2 K/kbar) [11] on $La_{2-x}Sr_xCuO_4$, probably due to the reduction of the local structural disorder. The competition between the increase of band width and the lattice hardening would be the reason of this small pressure effect on $Na_{0.3}HfNCl$.

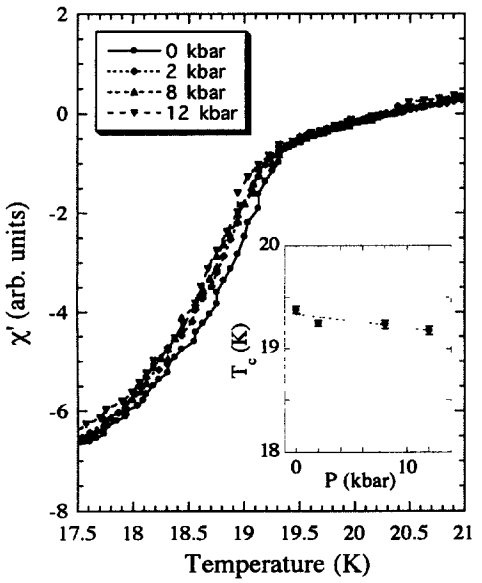

Fig. 1. Temperature dependence of AC magnetic susceptibility at various pressures. Inset: T_c plotted against the applied pressure.

Fig. 2 shows $S(Q,E)$ spectra of $Na_{0.3}HfNCl$ at Q=5.3-6.9 A^{-1}. The intensity at 15 and 30 meV increased with decreasing temperature from 25 to 10 K. This kind of increase has been observed in 44 meV phonon of $YBa_2Cu_3O_7$ [12], indicating a common feature in high-T_c compounds. Although the phonon energy in $YBa_2Cu_3O_7$ coincides with E~2Δ, the energy of 30 meV observed here was much higher than the energy at 2Δ~8 meV in Na_xHfNCl [7]. This is very anomalous, since the only phonon with E~2Δ is expected to have some anomaly according to the superconducting gap formation.

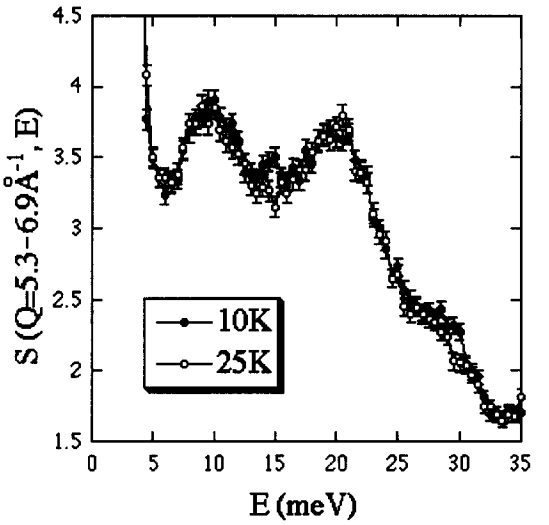

Fig. 2. Energy dependence of $S(Q,E)$ of $Na_{0.3}HfNCl$ at 10 and 25 K integrated from Q=5.3 to 6.9 A^{-1}.

In summary, pressure effect on $Na_{0.3}HfNCl$ is found to be small. Powder neutron inelastic scattering on $Na_{0.3}HfNCl$ shows the increase in $S(Q,E)$ at anomalous high energy, i.e., about 30 meV, in comparison with 2Δ~8 meV, with decreasing temperature from 25 to 10 K.

[1] S. Yamanaka et al., Adv. Mater. **8** (1996) 771.
[2] S. Yamanaka et al., Nature **392** (1998) 580.
[3] S. Shamoto et al., Physica C **306** (1998) 7.
[4] S. Shamoto et al., J. Phys. Chem. Solids **60** (1999) 1431.
[5] I. Hase et al., Phys Rev B **60** (1999) 1573.
[6] R. Weht et al., unpublished.
[7] S. Shamoto et al., Molecular Crystals and Liquid Crystals in press (ISIC X).
[8] Y.J. Uemura et al., ibid.
[9] C. Felser et al., J. Mater Chem. **9** (1999) 451.
[10] S. Yamanaka et al. in preparation.
[11] M. Sato et al., Chem. Lett. (1987) 1039.
[12] M. Arai et al., Phys. Rev. Lett. **69** (1992) 359.