Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Magnetic Susceptibility in 2D Superconductor Na_xHfNCl System

Shin-Ichi Shamoto [a], Keigo Iizawa [a], Yusuke Asano [a], Kenji Ohoyama [b] & Tsuyoshi Kajitani [a]

[a] Department of Applied Physics, Faculty of Engineering, Tohoku University, Sendai, 980-8579, JAPAN

[b] Institute for Materials Research, Tohoku University, Sendai, 980-8577, JAPAN

Version of record first published: 27 Oct 2006

To cite this article: Shin-Ichi Shamoto, Keigo Iizawa, Yusuke Asano, Kenji Ohoyama & Tsuyoshi Kajitani (2000): Magnetic Susceptibility in 2D Superconductor Na_xHfNCl System, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 515-520

To link to this article: http://dx.doi.org/10.1080/10587250008026191

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 515-520
Reprints available directly from the publisher
Photocopying permitted by license only

Magnetic Susceptibility in 2D Superconductor Na_xHfNCl System

SHIN-ICHI SHAMOTO[a], KEIGO IIZAWA[a], YUSUKE ASANO[a], KENJI OHOYAMA[b] and TSUYOSHI KAJITANI[a]

[a]*Department of Applied Physics, Faculty of Engineering, Tohoku University, Sendai 980–8579, JAPAN and* [b]*Institute for Materials Research, Tohoku University, Sendai 980–8577, JAPAN*

Superconducting critical temperature, T_c, and the shielding volume fraction, SVF, of layered nitride superconductor Na_xHfNCl have been studied as a function of x, i.e. Na concentration. Although T_c decreases gradually with increasing x from 20.0 K at x=0.11 to 16.5 K at x=0.85, SVF has a sharp peak around x=1/6, where strong coupling between local ordering of Na atoms and Fermi surface instability can be expected. Structural disorder in the samples above x=0.5, observed by powder neutron diffraction, does not affect the superconductivity appreciably. Electronic specific heat coefficient, γ, is estimated to be about 7.7 mJ/mol/K^2 by its difference of magnetic susceptibility between HfNCl and $Na_{0.5}HfNCl$. The γ value is relatively small compared with the high T_c value, revealing double honeycomb lattice system as new potential higher T_c superconductor series by intercalation.

Keywords: 2D superconductor; Na_xHfNCl; magnetic susceptibility; volume fraction; neutron diffraction; Fermi surface nesting

The superconductivity on layered nitrides $Li_x(THF)_yHfNCl$ with T_c=25.5K and Li_xZrNCl with T_c=15K have been discovered by S. Yamanaka et al. [1,2]. The structures of superconducting samples have been found by powder neutron diffraction to be alkali metal intercalated YOF-type, $R\bar{3}m$, which is composed of alternate stacking of double honeycomb lattice of [Zr (or Hf) N] and double triangular Cl lattice [3,4]. According to the structural analyses, the density of states in A_xHfNCl (A; alkali metals) is expected to be higher than that of

A_xZrNCl, indicating why T_c of A_xHfNCl is higher than that of A_xZrNCl [4]. Band structure calculation based on full-potential linearized augmented plane wave (FLAPW) method also supports this tendency [5]. Existence of van Hove singularity at x=0.4 and Fermi surface instability is also suggested by band calculations [5,6], stimulating us to study carrier concentration dependence of physical properties, e.g. superconducting critical temperature (T_c), and shielding volume fraction (SVF).

Here, we report carrier concentration dependence of T_c, the onset critical temperature (T_c^{onset}), and SVF in Na_xHfNCl system in addition to electronic specific heat coefficient (γ) estimated from parallel shift of the temperature dependence of magnetic susceptibility of HfNCl and $Na_{0.5}HfNCl$.

Na_xHfNCl powder with x=0.0-0.85 was prepared as described in the literature [4]. Powder neutron diffraction measurements were carried out using two-axis spectrometers KSD and HERMES at T1 thermal guide of JAERI-JRR3M in Tokai. A pressed pellet was found to have strong preferred orientation, i.e. the pellet-plane normal to c-axis, where HWHM in Gaussian distribution was 30(1) degrees by neutron diffraction measurement, as shown in Fig. 1 (a). The ω scan for 0 0 3 reflection also showed similar result. Magnetization was measured for this kind of pellet samples using a Quantum Design SQUID magnetometer. Magnetic susceptibility of samples with x=0.29 and 0.80 was measured under an applied field parallel to pellet-plane, while pellet-plane of the other samples were set normal to an applied field. After SVF was corrected for a demagnetization effect, SVF of a sample of x=0.80 is in agreement with those of x=0.65 and 0.85, as shown in Fig. 2, proving an accuracy of the correction. The amounts of sodium uptake was determined by an inductively coupled plasma spectrometry (ICP).

Powder diffraction patterns of Na_xHfNCl system varied with increasing x, as shown in Fig. 1 (b). Parent compound, β-HfNCl, had SmSI-type structure [3], while $Na_{0.29}HfNCl$ compound had Na intercalated YOF-type one [3,4],

where full occupation of Na at 3a site corresponds to the chemical formula $Na_{0.5}HfNCl$. This structural phase transition is explained by sliding of $[HfNCl]_2$ slabs [3]. By further intercalation, part of $Na_{0.80}HfNCl$ sample became amorphous. It should be noted that T_c and SVF did not change appreciably with increasing x through 0.5, as shown in Fig. 2. It is conceivable

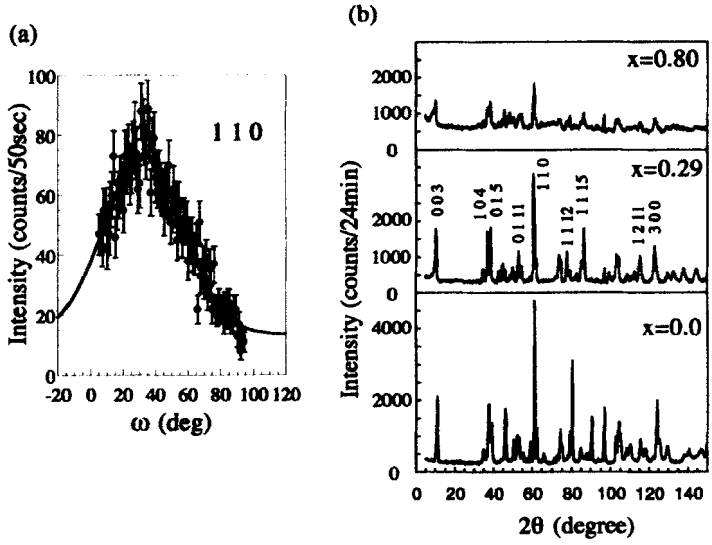

FIGURE 1 (a) ω scan for 1 1 0 reflection of a Na_xHfNCl pellet, where an axis normal to the pellet-plane is set in a scattering plane. Although the range of ω scan was limited by KSD spectrometer, the background intensity was substantially identical to that of θ-2θ scan. (b) Powder neutron diffraction patterns of Na_xHfNCl samples with x=0, 0.29, and 0.8 at T=4 K. Wavy high background and relatively low peak intensities for the sample with x=0.80 indicates its partial disorder.

that excess sodium atoms sit outside of conducting planes $[HfN]_2$, i.e. in the Cl bilayers, to retain the electronic state. Therefore, partial structural disorder in $Na_{0.80}HfNCl$ could be explained in terms of random slips of $[HfNCl]_2$ slabs. It also suggests 2D superconductivity of this system, i.e. short out of plane

coherence length, ξ_c. Although T_c decreased gradually with increasing x from 20.0 K (x=0.11) to 16.5 K (x=0.85), SVF had a sharp peak around x=1/6, where penetration depth might decrease anomalously. Partial de-intercalation of the x=0.29 sample by slow oxidation, i.e. exposing a sample to air at about 250 K for about 1 month, resulted in an increase of SVF (from 18% to 28% at 5K),

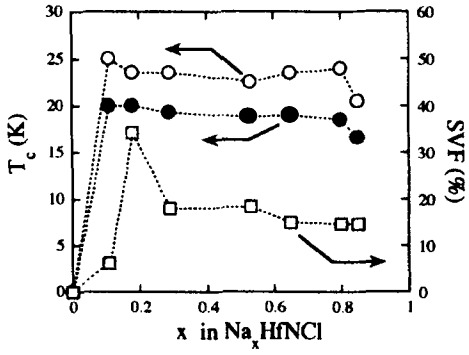

FIGURE 2 Superconducting critical temperature (●), the onset temperature (○) and the shielding volume fraction (□) of Na_xHfNCl as a function of x.

while the sample with x=0.80 treated in the same way showed only small change in SVF (from 14% to 12% at 5K). These results also support the sharp peak of SVF around x=1/6, which corresponds to 1/3 occupancy of Na atom at 3a site. In this case, ordering of Na atoms could take place, resulting in the formation of superlattice with the superlattice vectors, $\mathbf{a}_1'=2\mathbf{a}_1+\mathbf{a}_2$ and $\mathbf{a}_2'=-\mathbf{a}_1+\mathbf{a}_2$ where $\mathbf{a}_1$ and $\mathbf{a}_2$ are original unit vectors. These superlattice translation vectors, $\mathbf{a}_1'$ and $\mathbf{a}_2'$, correspond almost perfectly to three-fold nesting vectors ($\boldsymbol{Q}=2\boldsymbol{k}_F$) [6], indicating strong coupling between Fermi surface instability and local ordering of Na atoms. However, this kind of static Fermi surface instability is considered to reduce T_c and SVF. The result of SVF was opposite. On the other hand, the static Fermi surface instability might explain the reason why maximum T_c in Na_xHfNCl was lower than that in $Li_x(THF)_yHfNCl$, i.e. 25.5K, where double

honeycomb lattice could be relaxed by co-intercalation of organic molecules, THF. The x-values below 0.6 in the present study were close to 1/6, 1/4, and 1/2, which correspond to 1/3, 1/2, and 1 as an occupancy of Na atom at 3a site. Therefore, all T_c values in this system could be reduced by this Fermi surface instability. If T_c values were scaled by the maximum value of T_c, i.e. 20.0K, the present x-dependence of scaled T_c was similar to that of A_xZrNCl [8], where no effect of co-intercalation of organic molecules was found. This could be due to the low density of states and a flat hard honeycomb lattice in A_xZrNCl system, resulting in a weak Fermi surface nesting effect. The effect of van Hove singularity on T_c and SVF has not been observed in the present study, probably because we could not get any sample around x=0.4.

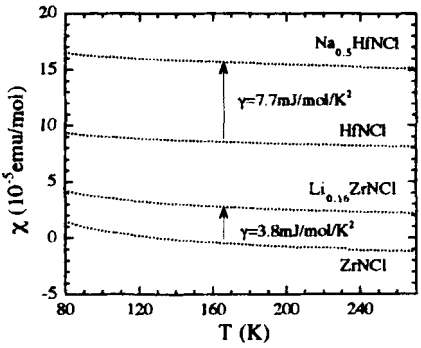

FIGURE 3 Temperature dependence of magnetic susceptibility for ZrNCl, $Li_{0.16}ZrNCl$, HfNCl, and $Na_{0.5}HfNCl$ under H=1 T. The γ values evaluated from the parallel shifts are shown, which can be regarded as the sum of Pauli paramagnetic susceptibility and Van Vleck paramagnetic susceptibility approximately.

Fig. 3 shows the temperature dependence of magnetic susceptibility of Na_xHfNCl with x=0 and 0.5 and Li_xZrNCl with x=0 and 0.16. The estimated γ values for $Na_{0.5}HfNCl$ and $Li_{0.16}ZrNCl$ were 7.7 mJ/mol/K^2 and 3.8 mJ/mol/K^2, respectively. It is reasonable that A_xHfNCl with larger γ than

that in A_xZrNCl exhibited higher T_c than that of A_xZrNCl, although the absolute γ value was smaller than 45mJ/mol/K^2 of A_3C_{60} superconductors with similar T_c,revealing double honeycomb lattice system as new potential higher T_c superconductor series. Regardless of alkali metal and co-intercalation of THF, these values agreed well with the γ values, 7.9 mJ/mol/K^2 and 3.7 mJ/mol/K^2, estimated from superconducting critical fields, H_c, e.g. 1600 Oe for $Li_{0.48}(THF)_yHfNCl$ and 930 Oe for $Li_{0.16}ZrNCl$ [7], respectively, assuming superconducting energy gap, $2\Delta=4.5\ k_BT_c$ for both compounds. It suggests that Van Vleck paramagnetism can be neglected in the present analyses.

In summary, we found a sharp peak in the SVF around x=1/6 for Na_xHfNCl, where strong coupling between local ordering of Na atoms and Fermi surface instability can be expected. Structural disorder in the samples above x=0.5, observed by powder neutron diffraction, does not affect the superconductivity appreciably. The γ value of A_xHfNCl, i.e. 7.7 mJ/mol/K^2, was small in comparison with its high T_c value, revealing double honeycomb lattice system as new potential higher T_c superconductor series by intercalation.

We thank Profs. S. Yamanaka, M. Sato, T. Takahashi and W. E. Pickett, Drs. T. Yokoya and I. Hase for fruitful discussions, Profs. Y. Syono and M. Kikuchi for providing the opportunity for using SQUID magnetometer, Messrs. S. Kawano and K. Nemoto for their sincere technical assistance.

References

[1] S. Yamanaka, K. Hotehama and H. Kawaji, Nature **392,** 580 (1998).

[2] S. Yamanaka, H. Kawaji, K. Hotehama and M. Ohashi, Adv. Mater. **8,** 771 (1996).

[3] S. Shamoto, T. Kato, Y. Ono, Y. Miyazaki, K. Ohoyama, M. Ohashi, Y. Yamaguchi and T. Kajitani, Physica C, **306,** 7 (1998).

[4] S. Shamoto, K. Iizawa, M. Yamada, K. Ohoyama, Y. Yamaguchi and T. Kajitani, J. Phys. Chem. Solids in press (1999).

[5] I. Hase and Y. Nishihara, Phys. Rev. B to be submitted (1999).

[6] R. Weht, A. Filippetti and W. E. Pickett, to be submitted (1999).

[7] S. Yamanaka, Meeting Abstracts of the Physical Society of Japan, **53**-2, Part 3, 638 (1998) [in Japanese].

[8] H. Kawaji, K. Hotehama, S. Yamanaka, Chem. Mater. **9,** 2127 (1997).