Electrical transport in $YNi_{2-x}Cu_xB_2C$

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We have investigated the normal-state conduction mechanism of the superconducting intermetallic compounds, $YNi_{2-x}Cu_xB_2C$ by measuring the electrical resistivity and the thermoelectric power (TEP) of $YNi_{2-x}Cu_xB_2C$ for different Cu concentrations x. The resistivity data show that T_c decreases systematically, and the scattering of electrons by structural disorder seems to increase upon greater Cu substitution. The TEP has a nonlinear temperature dependency, which suggests the modified mixed-valent character (the mixed-valency and the diffusion contribution). However, the discrepancy between TEP data and the best-fit curve of the modified mixed-valent character for the underdoped samples at low temperature indicate that an additional scattering mechanism, such as phonon drag, is involved. [S0163-1829(98)02701-5]

I. INTRODUCTION

The discovery of superconductivity in YNi_2B_2C (Ref. 1) has opened a new research field of quaternary rare-earth transition-metal superconducting and magnetic borocarbides, RM_2B_2C (R: rare-earth metal, M: transiton metal).[2,3] The highest-T_c compound among the intermetallic borocarbide superconductors is known to be $YPb_5B_3C_{0.3}$ with $T_c = 23$ K.[4,5] Several single-particle band-structure calculations have been reported.[6,7] The electronic structure calculations suggest that these materials are in the category of conventional superconductors with metallic and three-dimensional character. Along with the above studies, Lee *et al.*[8] had calculated band structure of YNi_2B_2X (X=B, C, N, and O) by using the linearized muffin-tin orbital band method. The results revealed that the shift of the Fermi level is *rigid-band*-like as the number of conduction electrons increases and in the case of YNi_2B_2C, the Fermi level is located right at the van Hove–like singular density of states (DOS) peak, which consists mainly of Ni $3d$ and Y $4d$ states. Looney *et al.*[9] had studied the dependence of T_c on hydrostatic pressure for Cu-substituted $YNi_{2-x}Cu_xB_2C$ compounds. They found T_c decreases under pressure, which indicates that the intermetallic borocarbides are BCS-like superconductors. The normal-state transport properties of single crystal[10] RNi_2B_2C (R=Y, Ho, Tm) have shown a metallic resistivity and negative thermoelectric power (TEP). In particular, the TEP of Y(Ho)Ni_2B_2C showed the change in slopes at the ''knee,'' which is larger than expected for simple electron-phonon enhancement effects.[11] They have suggested that the observed slope change could be due to the phonon drag effect. We have measured the TEP of polycrystalline YNi_2B_2C and fitted the data with the so-called modified mixed-valency formula. Unlike the single-crystal measurement results of Rathnayaka *et al.*,[10] however, our TEP data showed flatter temperature dependency in high-temperature regions. This could be due to the granular nature of our polycrystalline sample. Kohara *et al.*[12] had regarded YNi_2B_2C as itinerant antiferromagnetic spin fluctuation material, in which $3d$ electronic correlation plays a significant role. The fact that our TEP data could be fitted with the modified mixed-valency formula could be an indirect support for their NMR data interpretation.

In this paper, we present the subsequent results of TEP studies for our polycrystalline samples YNi_2B_2C, which shows a *phonon-drag*-like peak right above T_c.[13] To clarify the observed TEP data, the resistivity and the TEP of the Cu-substituted $YNi_{2-x}Cu_xB_2C$ polycrystalline samples are studied systematically. Our measurements of TEP for $YNi_{2-x}Cu_xB_2C$ provide the additional information on the effect of Cu substitution to Ni site, which can contribute to the investigation of the superconducting mechanism of the intermetallic borocarbide superconductors.

II. EXPERIMENT

$YNi_{2-x}Cu_xB_2C$ ($x=0-0.29$) samples were prepared by an arc-melting method under argon gas atmosphere. The ingot was melted several times to ensure better homogeneity. Samples, sealed in quartz tube under vacuum, were annealed at 1050 °C for 10 h and cooled down to room temperature over a period of 2 h. The sample characterizations were performed by using an x-ray diffractometer, a scanning electron microscope, and a SQUID magnetometer. The x-ray diffraction patterns (see Fig. 1) show that all these $YNi_{2-x}Cu_xB_2C$ samples are predominantly single phase having centered-tetragonal structure, although there exists some trace of a satellite shoulder at the foot of the (112) peak. As indicated in Fig. 1, the lattice parameters a and c/a estimated from the XRD data do not change appreciably upon the Cu substitution up to $x=0.29$. This is different from the results of Pt-substituted YNi_2B_2C.[14] The $Y(Ni_{1-x}Pt_x)_2B_2C$ shows that the lattice parameters a and c increase substantially upon the Pt substitution. The corresponding unit-cell volume increases linearly with increasing Pt concentration. Such an expansion of the unit-cell volume was attributed to the larger ionic size of Pt^{2+} (1.06 Å) compared with that of Ni^{2+} (0.78 Å). On the other hand, the Co-substituted YNi_2B_2C, $Y(Ni_{1-x}Co_x)_2B_2C$

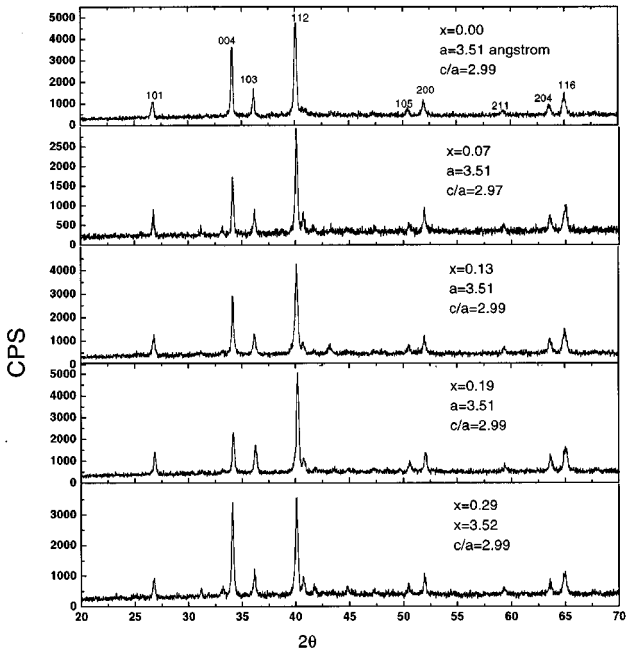

FIG. 1. X-ray diffraction patterns on powered $YNi_{2-x}Cu_xB_2C$ samples.

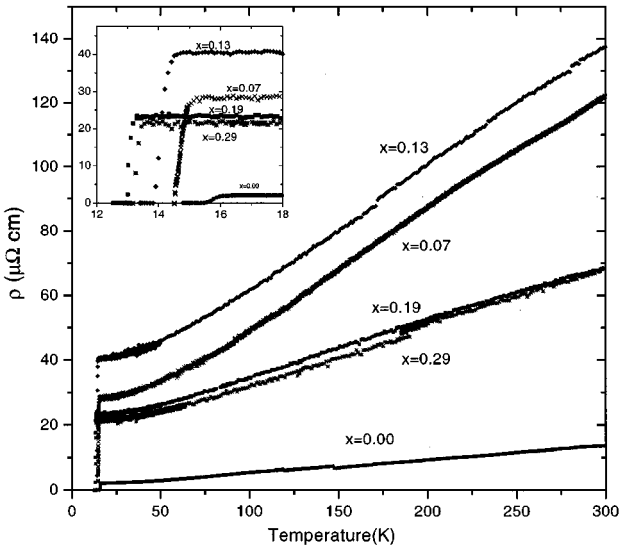

FIG. 2. The resistivity for $YNi_{2-x}Cu_xB_2C$ compounds. The inset shows the resistivity near the superconducting transition temperature in these samples.

shows little variations of the lattice parameters a and c in the range $0<x<0.1$ where the main decrease of T_c occurs.[15] Only at the high concentration regime, were significant lattice parameter changes observed. The small variation at low concentration could be due to the similar ionic size of Co and Ni. The observed small change in lattice parameters a and c in our $YNi_{2-x}Cu_xB_2C$ samples up to $x=0.29$ shown in Fig. 1 could also be understood from the fact that the ionic size of Cu and of Ni are not substantially different. The electron diffraction investigations (backscatterd electron images and EPMA) confirms that the Cu precipitation does not exist. Instead, the Cu is substituted to the Ni vacancy site initially. The standard four-probe method was used for the electrical resistivity measurement and the differential thermocouple was used for the TEP measurement. Details of the measurement techniques were published elsewhere.[16]

III. RESULT AND DISCUSSION

In Fig. 2 the temperature dependence of the resistivity and the superconducting onset T_c for $YNi_{2-x}Cu_xB_2C$ samples are shown. At high temperature, the electrical resistivity $\rho(T)$ is linear in T. But for all these samples, there is a low temperature ''knee'' in $\rho(T)$. T_c has its maximum value ($T_c^{\max}=15.9$ K) for the pure YNi_2B_2C and it decreases systematically upon Cu substitution. From the experimentally observed T_c and the McMillan's empirical formula[17] for T_c, we can obtain the electron-phonon coupling constant for different Cu concentrations. Here we have set $\Theta_D=348$ K as the effective Debye temperature of the polycrystalline samples and taken the assumed Coulomb pseudopotential parameter $\mu^*=0.13$. The calculated results (see Table I) show that these compounds are found to be in the intermediate coupling limit with $\lambda=0.87-0.96$. In terms of the power law, $(\rho-\rho_0)=aT^p$, where ρ_0 is the residual resistivity just above T_c, the exponent p, which describes $(\rho-\rho_0)$ for $T_c\leqslant T\leqslant 0.1\Theta_D$, varies systematically from 2.22 to 2.00 (see Table I). Doniach[18] has postulated the existence of strong spin fluctuation scattering in a narrow-band intermetallic compounds and shows that, as in the dilute alloy case,[19] the resistivity varies as T^2 near $T=0$ and goes through a linear T-dependence region at higher temperatures. Our resistivity data of $YNi_{2-x}Cu_xB_2C$ samples show similar temperature dependencies in the normal state ($T_c\leqslant T\leqslant 300$ K). We will discuss this in connection with the mixed-valency later. As shown in Fig. 2, the values of ρ_0/ρ_{RT} become bigger as the Cu concentration increases. Since the ρ_0/ρ_{RT} represents approximately the relative size of structural scattering of electrons (and also roughly phonons), the observed enhancement of ρ_0/ρ_{RT} in $YNi_{2-x}Cu_xB_2C$ indicates the larger structural disorder of the sample upon Cu substitution.

The temperature dependence of TEP of the $YNi_{2-x}Cu_xB_2C$ sample for different x is shown in Fig. 3. The negative sign of TEP indicates that the charge carriers in these samples are electronlike. For pristine and underdoped samples, there is a hump right above T_c characteristic of the phonon drag effect. This hump disappears gradually with increasing Cu concentration. A replacement of 15 at % Ni by Cu results in large changes of the TEP: the phonon drag contribution disappears entirely. The phonon drag effect of TEP presumably results from certain sheets of the Fermi surface allowing for (intraband) normal process at low temperature. The disappearance of this TEP peak upon the substitu-

TABLE I. The onset T_c, electron-phonon coupling constant (λ), best-fit parameter (p) ($\rho-\rho_0=aT^p$), and ρ_0/ρ_{RT} values for $YNi_{2-x}Cu_xB_2C$ samples.

	$x=0.00$	$x=0.07$	$x=0.13$	$x=0.19$	$x=0.29$
T_c	15.89	14.93	14.35	13.47	13.20
λ	0.96	0.93	0.91	0.88	0.87
p	2.22	2.14	2.04	2.02	2.00
ρ_0/ρ_{RT}	0.21	0.24	0.29	0.31	0.33

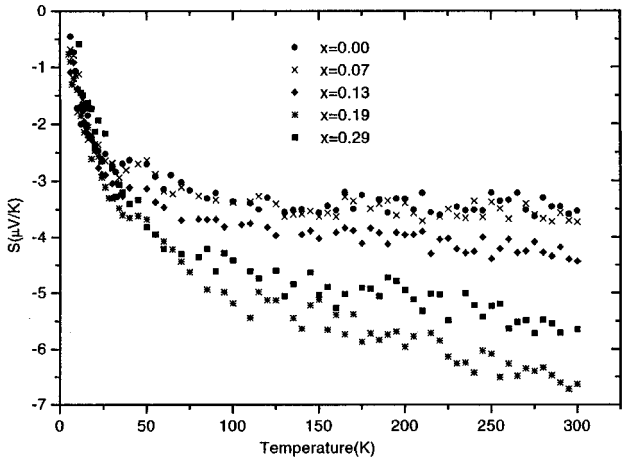

FIG. 3. The temperature dependence of TEP for $YNi_{2-x}Cu_xB_2C$ samples.

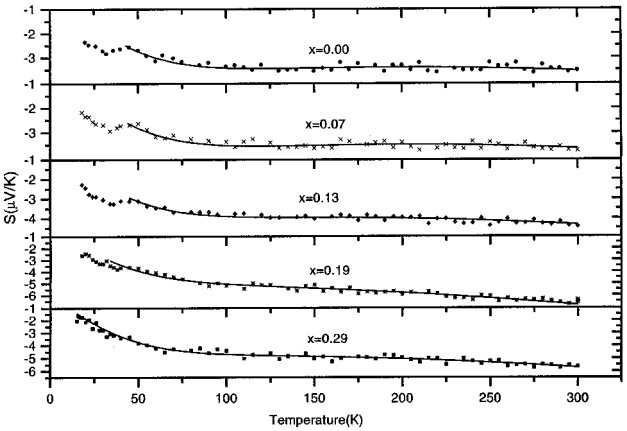

FIG. 4. Best-fit (solid lines) curves for $YNi_{2-x}Cu_xB_2C$ samples corresponding to Eq. (2).

tion of 15 at % Ni by Cu indicates that these sheets might be Ni derived. But it is not surprising in view of the fact that the residual resistivity ratio ρ_0/ρ_{RT} of these compounds increases continuously as dopant concentration x increases from 0 to 0.29 (shown in Table I). Thus as the scattering of electrons and of phonons by structural disorderness increases, the phonon heat current is reduced and there is a reduction in momentum transferred to the electron, i.e., of the phonon drag effect. The electron diffusion TEP S can be written as the standard Mott's formula:

$$S=-\frac{\pi^2 k_B^2 T}{3|e|}\left(\frac{d\ \ln\ \sigma(\varepsilon)}{d\varepsilon}\right)_{\varepsilon=\varepsilon_F}. \tag{1}$$

If the Fermi level is located at one side of the singular DOS peak, the TEP would be 20–30 μV/K,[20] ignoring the T dependence of relaxation time scale. However, the observed small electron diffusion TEP in Fig. 3 is perhaps a consequence of these materials located at the top of the peak in DOS predicted by the band-structure calculations.[8]

On the other hand, the mixed-valence compounds and heavy fermions have an increasing ρ versus T curve that can follow a Fermi-liquid T^2 law at lower temperature. Now we try to compare the present data with those of the mixed-valence system because this permits one to reconcile the resistivity data qualitatively. Doniach's theory[14] of spin fluctuations in narrow-band intermetallic compounds gives support to this possibility and can be used as a basis for arguments in its favor. To obtain the best fit, we use the modified mixed-valence form [here, the αT term is the diffusive TEP given as Eq. (1)]

$$S=\frac{AT}{B^2+T^2}+\alpha T, \tag{2}$$

where α, A, B^2 are given by

$$\alpha=\frac{\pi^2 k_B^2}{3|e|}\eta(\varepsilon_F),\quad A=\frac{2(\varepsilon_0-\varepsilon_F)}{|e|},$$

$$B^2=3\frac{(\varepsilon_0-\varepsilon_F)^2+\Gamma^2}{\pi^2 {k_B}^2}$$

and $\eta(\varepsilon_F)$ is the DOS per charge carrier at the Fermi level. We have fitted the TEP results of our samples with Eq. (2) and the results are presented in Fig. 4. It should be mentioned that for the superconducting samples we have not considered the points near T_c for fittings, because the sharp drop in TEP near T_c may be originated from the thermodynamic superconducting fluctuation. The best-fit parameters A, B, and α obtained for different samples are presented in Table II. The $(\varepsilon_0-\varepsilon_F)$ and Γ values are also given in the same table. The $(\varepsilon_0-\varepsilon_F)$ values are one-tenth of those obtained by Gottwick *et al.*[21] for intermatallic compounds, $CeNi_x$ and Ferro *et al.*[22] for $YBa_2Cu_3O_{6.8}$ single crystal. But if we assume that the Fermi level in YNi_2B_2C is located at the top of the singular DOS peak, these results for $YNi_{2-x}Cu_xB_2C$ samples could be reasonable. The results also show that $(\varepsilon_0-\varepsilon_F)$ and Γ values decrease upon the Cu concentration.

TABLE II. The fitting parameters and the corresponding $\eta(\varepsilon_F)$, $(\varepsilon_0-\varepsilon_F)$, Γ values for $YNi_{2-x}Cu_xB_2C$ compounds.

	$x=0.00$	$x=0.07$	$x=0.13$	$x=0.19$	$x=0.29$
α (μV/K^2)	−0.0069	−0.0071	−0.0093	−0.0170	−0.0133
A (μV)	−479.63	−492.61	−505.24	−550.28	−555.16
B (K^2)	86.80	86.60	83.62	80.67	80.54
$\eta(\varepsilon_F)$ (states/eV carrier)	−0.0285	−0.0291	−0.0381	−0.0698	−0.0546
$(\varepsilon_0-\varepsilon_F)$ (meV)	−0.2398	−0.2463	−0.2726	−0.2751	−0.2776
Γ (meV)	13.53	13.50	13.04	12.58	12.56

It is expected that with increasing carrier (electron) concentration, the Fermi energy should go up with respect to the top of the band. Therefore if ε_0 is fixed in position, the above result suggests that ε_F increases with increasing carrier density, which is consistent with the increasing behavior of $\eta(\varepsilon_F)$ as shown in Table II. Following the Cu replacement, the atomic Cu($3d^{10}4s^1$) states instead of Ni($3d^8 4s^2$) are regarded as valence electrons in the band calculations. This consideration can explain the systematic decrease of half width of resonance (Γ) as x increases.

IV. CONCLUSION

In summary, we have proposed that the TEP in $YNi_{2-x}Cu_xB_2C$ seems to be commonly dominated by the mixed valency and the diffusion contribution as well. The microscopic origin of the mixed valency seems unclear but the three-dimensional antiferromagnetic spin fluctuations could be important in understanding the observed temperature dependence of TEP. As the Cu concentration increases, the superconductivity tends to be suppressed resulting in lower T_c and the *phonon-drag*-like hump disappears gradually. We suggest that the role of the observed *phonon-drag*-like hump right above T_c could be relevant for explaining the superconducting transition mechanism.

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