Ni-site Doping Effect of New Antiperovskite Superconductor ZnNNi₃

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Abstract. A new superconductor ZnNNi₃ with Tc of about 3 K has the same anti-perovskite-type such as MgCNi₃ and CdCNi₃. For this new superconductor, we have studied the Ni-site doping effect with the formula of ZnNNi₃₋ₓMₓ. The dopant elements M are chosen to be Cu, Co, Fe, Mn, Cr, and V. In Mn and Fe doping, only by x=0.05 doping, the superconductivity rapidly disappears. The superconductivity survives in V, Cr, Co, and Cu cases up to x=0.1, 0.3, 0.5 and 0.05 doping, respectively. This result suggests that the magnetic character is associated with the origin of superconductivity. Interestingly, in Co-doping case, the superconductivity and ferromagnetism coexist at low temperature. It has been revealed that form EPMA analysis the coexistence is originated from the spatial phase separation of superconducting ZnNNi₃ and ferromagnetic ZnN(Co₂₋ₓNiₓ), suggesting the existence of miscibility gap of ZnN(Ni, Co)₃ solid solution.

1. Introduction
Since the discovery of the superconductivity in antiperovskite MgCNi₃, having a superconducting temperature (Tc) of ~ 8 K [1], a lot of experiments about antiperovskite superconductor has been performed in the context of the involvement of ferromagnetism and superconductivity. MgCNi₃ includes a lot of ferromagnetic Ni and has a structural similarity with f.c.c. elemental Ni, implying the involvement between ferromagnetism and superconductivity in MgCNi₃. In order to elucidate the origin of superconductivity in MgCNi₃, several experiments to reveal the superconducting-gap symmetry have been carried out [2-6], but the consensus has not been obtained so far. After the discovery of MgCNi₃, two new antiperovskite superconductors CdCNi₃ [7, 8] and ZnNNi₃ [9, 10] has been discovered. In this paper, Ni-site doping effect of most recently discovered antiperovskite superconductor ZnNNi₃ is reported.

2. Experimental
The samples were prepared with elemental Zn, Ni, V, Cr, Mn, Fe, Co, and Cu powders. The powders were weighed with nominal compositions of Zn₁₋ₓNiₓ₋₃Mₓ, (M=V, Cr, Mn, Fe, Co, and Cu), and mixed, then pressed into pellets. The extra Zn was added to compensate vaporizing quantity. Except for M=Cu with x=0.2 sample, the pellets were sintered in NH₃ gas at 400 °C for 3 h, 520 °C for 5h, and finally 600 °C for 5 h until the samples became single phases, with intermediate grindings. For M=Cu with x=0.2, NH₃-50% and H₃-50% mixed gas was needed to obtain the single phase sample. NH₃ gas decomposes to chemically active hydrogen and nitrogen at high temperature and active
nitrogen penetrates into the sample and the sample is nitrified. This has been known as an effective method to make 3d-transition metal nitride [11-13].

X-ray diffraction patterns were obtained employing CuKα radiation. Magnetization was measured by using Quantum Design SQUID magnetometer with zero field cooling (ZFC) procedure.

3. Result and discussion
X-ray results revealed that all samples are synthesized as single phases (not shown). The diffraction patterns can be indexed with simple cubic structure and the lattice parameters are determined to be about 3.76 Å for all samples except for M=Cu with x=0.2 sample, and 3.68 Å for M=Cu (x=0.2) sample. The nitrogen contents, which are estimated from the sample weight changes, are almost the same to be ~ 1 for all samples except for M=Cu (x=0.2) sample. In M=Cu (x=0.2) sample, the nitrogen content is estimated to be ~ 0.5. This is consistent with the fact that NH3~50% and H2~50% mixed gas was needed to obtain single phased sample.

As shown in figure 1, with only x=0.05 doping the superconductivity rapidly disappears and is strongly suppressed, respectively for M=Mn and Fe samples. The superconductivity survives up to x=0.1, 0.3 and 0.05 for M=V, Cr and Cu samples, respectively. It should be noted that for Cu (x=0.05) and Cr (x=0.1) doping the \( T_c \) even increase. The origin of this increase of \( T_c \) is unclear. It is necessary to investigate how the electronic structure modified by doping. As mentioned above in M=Cu with x=0.2 sample, N content is supposed to be not 1 but 0.5 and the lattice constant is much smaller than other samples, consequently the electronic structure may be strongly modified, therefore the origin of pair breaking mechanism of this sample is quite different from those of other samples.

![Figure 1. Temperature dependences of magnetic susceptibility \( \chi \) for ZnNi\(_{3-x}\)M\(_x\). The superconducting volume fractions are about 60-170 % except for M=Mn, Fe and Cu (x=0.2), showing the bulk nature of superconductivity.](image)

In classical BCS superconductor, the pair breaking effect by magnetic impurity is mainly dominated by de Gennes factor \((g-1)^2J(J+1)\), where \( g \) is Landé g-factor and \( J \) is magnetic moment of magnetic impurity. Supposing naively that the magnetic moments of dopant elements comes from those of unpaired electrons in 3d orbitals, de Gennes factors are calculated to be 3.25, 8.75, 8.75, 6, and 0 for V,
Cr, Mn, Fe, and Cu, respectively (assuming $g=2$). In this case, the degree of pair breaking effect is expected in the order of Mn, Cr, Fe, V, and Cu. This expectation is roughly consistent with the experiment except for M=Cr and Co. Namely, comparing at the same doping level of $x=0.05$, the superconductivity almost disappears for M=Mn and Fe but survive for M=V and Cu. In M=Mn case, the superconductivity is expected to be destroyed similarly to M=Mn and Fe cases. However, the superconductivity survives even with $x=0.3$ doping. Moreover, $T_c$ even increases for $x=0.1$ sample. This suggests that the superconductivity in this system might not be a simple BCS type but a kind of exotic one probably associated with magnetic character.

In M=Co, the interesting result was obtained. The superconductivity survives up to $x=0.5$ doping. (see figure 2). Moreover, the superconductivity coexists with ferromagnetism as shown in M-H curves for $x=0.25$ sample at above and below $T_c$ (see inset of fig. 2). The origin of this coexistence has been found to be the spatial phase separation of ferromagnetic ZnN(Co$_{2.6}$Ni$_{0.4}$) and superconducting ZnNNi$_3$ with microscopic domain size by EPMA study, suggesting the existence of miscibility gap of ZnN(Ni, Co)$_3$ solid solution in low Co concentration region. Ferromagnetic ZnN(Co$_{2.6}$Ni$_{0.4}$) and superconducting ZnNNi$_3$ have the same crystal structure and almost the same lattice constant. Therefore, the ferromagnet–superconductor granular contact is realized and the nature of ferromagnet–superconductor grain boundary is expected to be good. This indicates the possibility of useful device for example π-junction quantum bit and magnetoresistance device and so on.

In summary, we have studied the Ni-site doping effect for ZnNNi$_3$, using V, Cr, Mn, Fe, Co, and Cu. In Mn and Fe doping, the superconductivity rapidly disappears but survives in V, Cr, Co, and Cu cases up to $x=0.1$, 0.3, 0.5 and 0.05 doping, respectively. This behavior is not consistent with classical BCS case, suggesting that the magnetic character is associated with the origin of superconductivity. In Co doping case, the superconductivity and ferromagnetism coexist at low temperature. It has been
revealed that form EPMA analysis the coexistence of superconductivity and ferromagnetism is originated from spatial phase separation of superconducting ZnNNi$_3$ and ferromagnetic ZnN(Co$_{2.6}$Ni$_{0.4}$). This can be regarded as a good quality ferromagnet-superconductor granular contact that is possible candidate for useful devise.

**Acknowledgements**

This work was partly supported by a Grant-in-Aid for Scientific Research from The Ministry of Education, Culture, Sports, Science and Technology, Japan and by Research Institute of Yokohama National University.

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