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Effect of substituting Fe and Ru for Ni on the thermopower of $MgCNi_3$

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The intermetallic perovskite $MgCNi_3$ is a superconductor with a $T_c=7$ K. Substitution of Fe and Ru for Ni decreases T_c monotonically as the doping concentration is increased. Here we report thermopower measurements $S(T)$ on $MgCNi_3$, $MgCNi_{3-x}Fe_x$, and $MgCNi_{3-x}Ru_x$. For $MgCNi_3$ the thermopower is negative, $-12.5\ \mu V/K$, at 300 K. The absolute value of S decreases as x increases in $MgCNi_{3-x}Fe_x$ and $MgCNi_{3-x}Ru_x$. The sign of S changes from negative to positive at low temperatures for values of $x>0.01$. These data show that the carriers in $MgCNi_3$ are electrons, and by increasing x and decreasing temperature, the participation of hole carriers clearly increases. The influence of the magnetic moments of the Fe atoms on the thermopower is not visible.

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INTRODUCTION

$MgCNi_3$ is an unusual superconductor.[1] The high proportion of Ni atoms in the unit cell suggests the possibility of magnetic interactions, but so far this has not been observed. The simple intermetallic perovskite structure makes this compound attractive for study and there are many papers dedicated to theoretical considerations, i.e., band-structure calculations. Analysis of the calculated electronic structure has shown a large narrow density-of-states peak located very close to the Fermi energy (E_F).[2–8] The presence of this peak was confirmed by photoemission and x-ray spectroscopy experiments.[6,9] Since the peak is located just below E_F, chemical substitution in $MgCNi_3$ is expected to significantly change its electronic properties. Numerous efforts have been made to hole dope $MgCNi_3$ in an attempt to shift the Fermi level, thereby increasing the density of states at E_F. An increase in T_c or the appearance of ferromagnetism was expected. Previous studies have focused on the partial substitution of Co,[10,11] Fe,[10,12] Mn,[13] and Ru[14] for Ni, the introduction of carbon deficiencies into the structure,[15,16] and on the partial substitution of B for C.[17] In all cases, T_c was found to decrease and ferromagnetism was not observed. Doping on the Mg site, which also causes a decrease of T_c, seems to be the most difficult (discussed in Ref. 18). Recently, three new compounds in which Mg was completely replaced by Zn,[18] Ga,[19] and In[20] ($GaCNi_3$, $ZnCNi_3$, and $In_{0.95}CNi_3$) were reported.

Negative values for the Hall coefficient and thermopower indicate that the carriers in $MgCNi_3$ are electron-type.[21] The effect of Fe and Ru substitution for Ni on the superconducting transition temperature T_c in $MgCNi_3$ is quite different.[12] The superconductivity in $MgCNi_{3-x}M_x$ is suppressed more slowly in the Ru-substituted compounds than in the Fe-substituted compounds. This is most likely because the Fe atoms act as magnetic impurities that break the superconducting Cooper pairs. Since Ru is a nonmagnetic metal, the observed changes in the T_c of $MgCNi_{3-x}Ru_x$ are expected to be primarily due to a band-structure (i.e., electron count) effect.[12] Therefore, studies of the transport properties of $MgCNi_3$ substituted with Fe and Ru are highly valuable. The elements Fe and Ru are from the same column in the periodic table and both substitutions are expected to decrease the electron concentration by the same amount. Measurement of the thermopower is a sensitive tool, which can be used to monitor changes in the electronic properties of a material. In this communication, we report the results of our thermopower measurements $S(T)$ on $MgCNi_3$, $MgCNi_{3-x}Fe_x$, and $MgCNi_{3-x}Ru_x$. We show that the Fe and Ru substitutions affect $S(T)$ similarly despite having a much different influence on T_c.

EXPERIMENT

Two series of 0.5 g samples with nominal compositions: $Mg_{1.2}C_{1.5}Ni_{3-x}Ru_x$ (x=0, 0.005, 0.01, 0.02, 0.03, 0.05, and 0.1) and $Mg_{1.2}C_{1.5}Ni_{3-x}Fe_x$ (x=0, 0.005, 0.01, 0.015, 0.02, 0.025, 0.05) were synthesized. The starting materials were Mg flakes (99% Aldrich Chemical), Ni sponge (99.9% Johnson Matthey and Alfa Aesar), glassy carbon spherical powder (Alfa Aesar), Ru powder (99.95% Alfa Aesar), and Fe powder (99.5% Alfa Aesar). Previous studies on $MgCNi_3$ indicated the need to employ excess magnesium and carbon in the synthesis in order to obtain optimal carbon content.[1,15] The excess Mg is vaporized during the course of the reaction (though it sometimes forms MgO in the final product).[15] After thorough mixing, the starting materials were pressed into pellets, wrapped in zirconium foil, placed on an Al_2O_3 boat, and fired in a quartz tube furnace under a 95% Ar/5% H_2 atmosphere. The initial furnace treatment began with a half hour at 600 °C, followed by 1 h at 900 °C. After cooling, the samples were reground, pressed into pellets, and placed back in the furnace under identical conditions at 900 °C. The latter step was repeated two additional times. Following the heat treatment, the samples were analyzed with powder x-ray diffraction using Cu $K\alpha$ radiation. The resulting material contains only one intermetallic phase, stoichiometric $MgCNi_{3-x}M_x$, plus a small proportion of elemental carbon.[15]

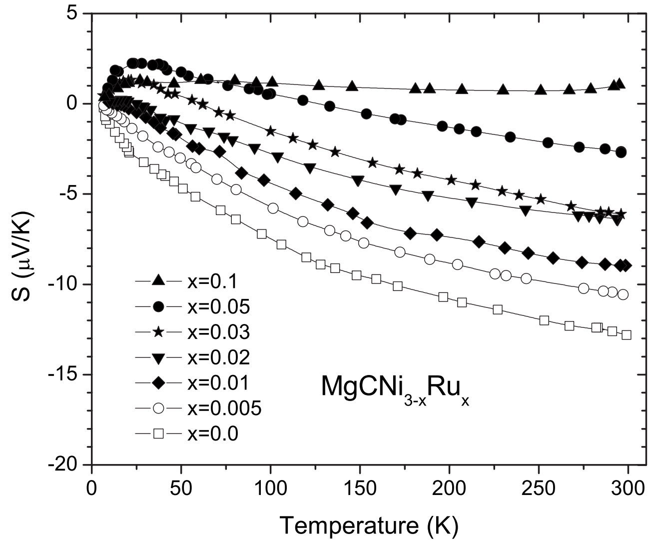

FIG. 1. Temperature dependence of the thermopower $S(T)$ for all $MgCNi_{3-x}Ru_x$ samples, with x=0, 0.005, 0.01, 0.02, 0.03, 0.05, and 0.1.

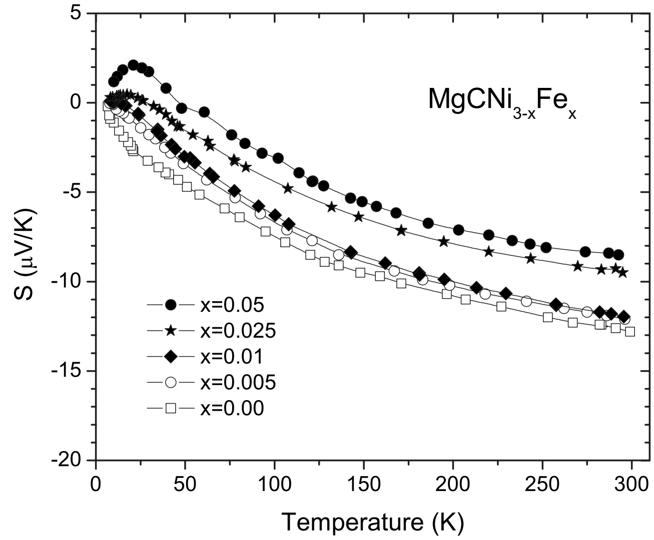

FIG. 2. Temperature dependence of the thermopower $S(T)$ for all $MgCNi_{3-x}Fe_x$ samples with x=0, 0.005, 0.01, 0.025, and 0.05.

Because no transition metal excess is needed for synthesis, and x in both $MgCNi_{3-x}Ru_x$ and $MgCNi_{3-x}Fe_x$ is far below the solubility limit, the nominal Ru and Fe contents correspond to the real doping level.

Superconductivity was characterized by zero-field cooling ac magnetization (H_{ac}=3 Oe, f=10 kHz) performed at a 5 Oe dc field in the temperature range 1.9–8 K (PPMS—Quantum Design). Thermoelectric power measurements were performed in the temperature range 7–300 K by a steady-state mode using a semiautomatic instrument fitted into the transport liquid-helium Dewar.[22] The sample was clamped between two spring-loaded Cu blocks with heaters attached. A pair of platinum thermometers (HY-CAL Engineering, EL-700-U, Pt-1000 Ω) was used to detect the temperature differences between the blocks. Special attention has been paid to limit any errors that might occur in the detection of small temperature differences. The blocks were insulated from the surroundings so that a thermal difference could be produced by the heaters. The quality of the thermal contact between the sample and the Cu blocks was tested by electrical resistance measurements and only values below 2 Ω were accepted. A calibration of the equipment was performed using a Pb (6*N*) sample.[23]

RESULTS AND DISCUSSION

The temperature dependence of the thermopower $[S(T)]$ of $MgCNi_3$, $MgCNi_{3-x}Ru_x$, and $MgCNi_{3-x}Fe_x$ are presented in Figs. 1 and 2, respectively. For $MgCNi_3$ the thermopower has a negative value in the temperature range 7–300 K and exhibits metallic character. The room-temperature thermopower is $S(300\text{ K})=-12.8\ \mu\text{V/K}$ and its magnitude is larger than that previously reported by Lin *et al.* ($-9.2\ \mu$V/K).[21] The absolute value of the thermopower $|S|$ decreases as Fe and Ru are substituted for Ni. This indicates that changes in the density of states at the Fermi energy $g(E_F)$, dominate over the influence of decreasing charge concentration n on the $|S|$. Assuming a constant value of $g(E_F)$, a decrease in n should cause an increase in $|S|$ according to the equation: $S(T)=(2\pi^2k_B^2/3)[g(E_F)/n\cdot|e|]T$. However, $|S|$ decreases with doping and this supports the suggestion that the $g(E)$ peak close to the Fermi energy is smeared by elemental substitution; as a result, $g(E_F)$ decreases. The same conclusion was derived from the superconducting properties of the $MgCNi_{3-x}M_x$ (M=Fe, Ru). In this case, T_c also decreases as the doping level increases.[12]

At low temperatures $S(T)$ changes sign from negative to positive and, for $MgCNi_{3-x}Ru_x$, this effect is visible in the concentration range: $0.01\leq x\leq 0.05$. For high Ru concentrations, such as $MgCNi_{2.9}Ru_{0.1}$, $S(T)$ remains positive in the whole temperature range. Strong influence of the doping on $S(T)$ is clearly visible in Fig. 3, which shows the derivative of the thermopower with respect to temperature versus temperature (dS/dT vs T). Above 50 K, dS/dT is negative and increases with temperature for $MgCNi_3$ and $MgCNi_{2.95}M_{0.05}$. Below 50 K, the dS/dT curve drops in the case of $MgCNi_3$ and rapidly increases in the doped samples. This opposite behavior indicates that the substitution of Fe or Ru causes large changes in the band structure of $MgCNi_3$. It also suggests a strong increase of hole participation in band conductivity.

Figure 4 illustrates the different effects of Fe and Ru doping of $MgCNi_3$ on the thermopower at 20 K ($S_{20\text{ K}}$) and the superconducting transition temperature (T_c). Superconductivity is suppressed more rapidly in the Fe-substituted samples than in the Ru-substituted samples (see the inset). It is shown in Ref. 12 that magnetic susceptibility (χ) in the normal state increases with Fe doping and decreases with Ru doping. This suggests that Fe acts as a magnetic impurity and breaks apart the Cooper pairs. This effect was predicted by Abrikosov and Gorkov,[24] and was observed in many intermetallic superconductors.[25] The main panel of Fig. 4 shows the thermopower at 20 K for the Fe- and Ru-substituted

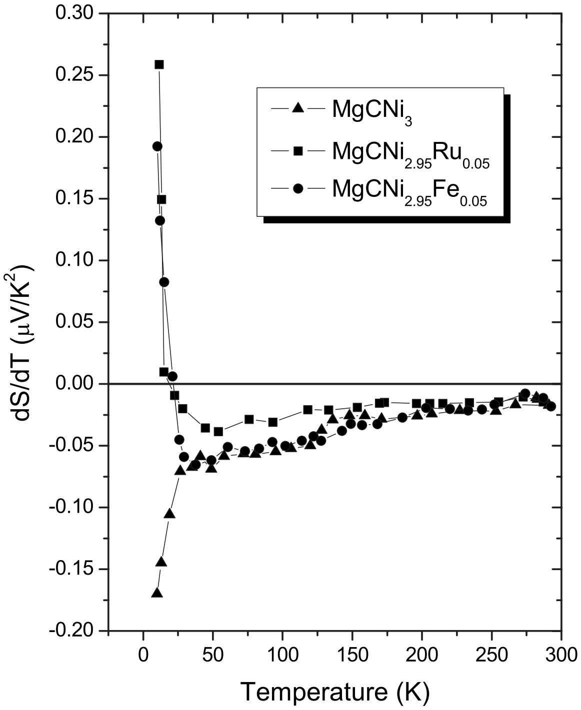

FIG. 3. Derivative dS/dT vs temperature for $MgCNi_3$, $MgCNi_{2.95}Fe_{0.05}$, and $MgCNi_{2.95}Ru_{0.05}$.

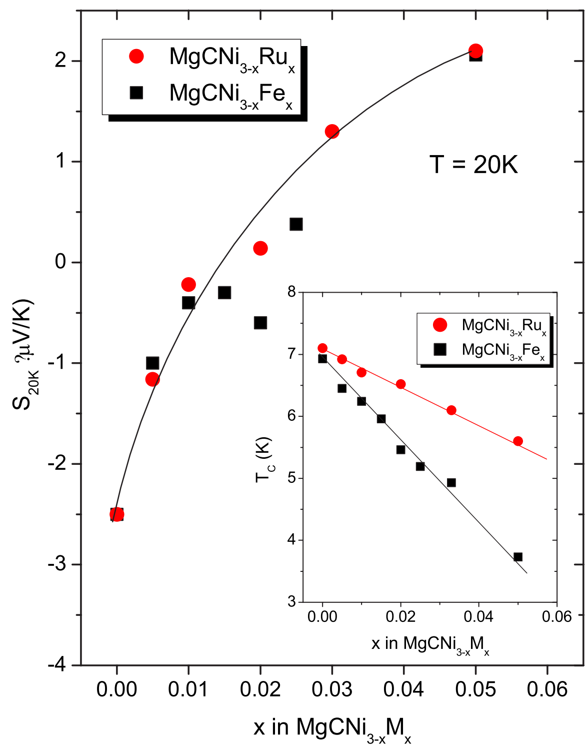

FIG. 4. (Color online) Thermopower at 20 K, $S_{20\ K}$, and the superconducting transition temperature T_c (inset) in $MgCNi_{3-x}M_x$ (M=Ru, Fe) as a function of doping x.

samples. Interestingly, although T_c decreases in a different way, the thermopower increases in a similar manner for both $MgCNi_{3-x}Ru_x$ and $MgCNi_{3-x}Fe_x$. The same effect is also observed in $Mg_{1-x}Mn_xB_2$ and $Mg_{1-x}Al_xB_2$, where Mg is partially substituted by the magnetic atoms and the nonmagnetic atoms.[26]

CONCLUSIONS

Our measurements of the temperature dependence of the thermopower $S(T)$ of $MgCNi_3$, $MgCNi_{3-x}Fe_x$, and $MgCNi_{3-x}Ru_x$ show that the substitution of Fe and Ru causes an increase of the participation of hole-type carriers. This effect is especially strong at low temperatures. The magnetic moments of the Fe atoms do not appear to have an effect on the $S(T)$ of $MgCNi_{3-x}Fe_x$. This is in contrast to the strong dependence of the superconducting transition temperature on the Fe concentration. The thermopower changes greatly with Fe and Ru substitutions, especially at low temperatures. The Fermi energy in $MgCNi_3$ is located at the slope of $g(E)$. Therefore, it is expected that hole doping should increase both T_c and $|S|$. Previous studies of $MgCNi_{3-x}M_x$, M=Co, Mn, Fe, Ru, and MgC_xNi_3 and $MgC_{1-x}B_xNi_3$ have shown the opposite effect, namely, decreasing T_c. It is illustrated here that $|S|$ also decreases with the Fe and Ru doping. This supports the suggestion that the $g(E)$ peak close to the Fermi energy is smeared by elemental substitution and, as a result, $g(E_F)$ decreases.

ACKNOWLEDGMENTS

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[1] T. He, Q. Huang, A. P. Ramirez, Y. Wang, K. A. Regan, N. Rogado, M. A. Hayward, M. K. Haas, J. J. Slusky, K. Inumara, H. W. Zandbergen, N. P. Ong, and R. J. Cava, Nature (London) **411**, 54 (2001).
[2] S. B. Dugdale and T. Jarlborg, Phys. Rev. B **64**, 100508(R) (2001).
[3] J. H. Shim, S. K. Kwon, and B. I. Min, Phys. Rev. B **64**, 180510(R) (2001).
[4] A. Szajek, J. Phys.: Condens. Matter **13**, L595 (2001).
[5] D. J. Singh and I. I. Mazin, Phys. Rev. B **64**, 140507(R) (2001).
[6] I. R. Shein, A. L. Ivanovskii, E. Z. Kurmaev, A. Moewes, S. Chiuzbian, L. D. Finkelstein, M. Neumann, Z. A. Ren, and G. C. Che, Phys. Rev. B **66**, 024520 (2002).
[7] J. L. Wang, Y. Xu, Z. Zeng, Q. Q. Zeng, and H. Q. Lin, J. Appl. Phys. **91**, 10, 8504 (2002).
[8] H. Rosner, R. Weht, M. D. Johannes, W. E. Pickett, and E. To-

satti, Phys. Rev. Lett. **88**, 027001 (2002).

[9] I. G. Kim, J. I. Lee, and A. J. Freeman, Phys. Rev. B **65**, 064525 (2002).

[10] T. G. Kumary, J. Janaki, A. Mani, S. M. Jaya, V. S. Sastry, Y. Hariharan, T. S. Radhakrishnan, and M. C. Valsakumar, Phys. Rev. B **66**, 064510 (2002).

[11] M. A. Hayward, M. K. Haas, A. P. Ramirez, T. He, K. A. Regan, N. Rogado, K. Inumaru, and R. J. Cava, Solid State Commun. **119**, 491 (2001).

[12] T. Klimczuk and R. J. Cava, Solid State Commun. **132**, 379 (2004).

[13] A. Das and R. K. Kremer, Phys. Rev. B **68**, 064503 (2003).

[14] T. Klimczuk, V. Gupta, G. Lawes, A. P. Ramirez, and R. J. Cava, Phys. Rev. B **70**, 094511 (2004).

[15] T. G. Amos, Q. Huang, J. W. Lynn, T. He, and R. J. Cava, Solid State Commun. **121**, 73 (2002).

[16] L. Shan, K. Xia, Z. Y. Liu, H. H. Wen, Z. A. Ren, G. C. Che, and Z. X. Zhao, Phys. Rev. B **68**, 024523 (2003).

[17] T. Klimczuk, M. Avdeev, J. D. Jorgensen, and R. J. Cava, Phys. Rev. B **71**, 184512 (2005).

[18] M.-S. Park, J. Giim, S.-H. Park, Y. W. Lee, S. I. Lee, and E. J. Choi, Supercond. Sci. Technol. **17**, 274 (2004).

[19] P. Tong, Y. P. Sun, X. B. Zhu, and W. H. Song, Phys. Rev. B **73**, 245106 (2006).

[20] P. Tong, Y. P. Sun, X. B. Zhu, and W. H. Song, Solid State Commun. **141**, 336 (2007).

[21] S. Y. Li, W. Q. Mo, M. Yu, W. H. Zheng, C. H. Wang, Y. M. Xiong, R. Fan, H. S. Yang, B. M. Wu, L. Z. Cao, and X. H. Chen, Phys. Rev. B **65**, 064534 (2002).

[22] T. Plackowski, C. Sulkowski, J. Karpinski, J. Jun, and S. M. Kazakov, Phys. Rev. B **69**, 104528 (2004).

[23] R. B. Roberts, Philos. Mag. **36**, 91 (1977).

[24] A. A. Abrikosov and L. P. Gorkov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960) [Sov. Phys. JETP **12**, 1243 (1961)].

[25] For example, in K. Rogacki, B. Batlogg, J. Karpinski, N. D. Zhigadlo, G. Schuck, S. M. Kazakov, P. Wägli, R. Puźniak, A. Wiśniewski, F. Carbone, A. Brinkman, and D. van der Marel, Phys. Rev. B **73**, 174520 (2006).

[26] K. Rogacki, C. Sulkowski, K. Oganisian, N. D. Zhigadlo, S. Katrych, and J. Karpinski (unpublished).