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Properties of $MgCNi_3$ Superconductor

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The present invited article describes the properties of superconducting $MgCNi_3$ with T_c (*ca.* 8 K) having a simple cubic perovskite structure with space group Pm-3m and lattice parameter a *ca.* 3.812 Å. Its conduction electrons are derived from the partially filled Ni d-states that typically lead to the ferromagnetism in metallic Ni and many Ni-based binary alloys. It has electron type carriers in the normal state. The T_c increases with the increase of x in MgC_xNi_3 but generally decreases due to the Ni site doping by Co, Fe, Mn, Cu etc. Again, the T_c is found to increase with the increase of external pressure. The electronic contribution is slightly higher than the lattice one in its normal state thermal conductivity. The specific heat and tunneling spectroscopic studies indicate that this is an s-wave BCS-type weak/moderate coupling type-II superconductor.

Key Words: $MgCNi_3$ superconductor, Structure, Resistivity, Specific heat, Pressure effect.

INTRODUCTION

The $MgCNi_3$ superconductor has a perovskite structure[1] like $CaTiO_3$ with the equivalence of Ca to Mg, Ti to C and O to Ni. The high proportion of Ni shows that the magnetic interactions play a dominant role. It is not large enough to induce the magnetic instability in it but is associated with its superconducting properties[2]. ^{13}C NMR studies[3] suggest that the electronic states reach a modestly mass enhanced Fermi-liquid like states prior to the superconducting transition. Lattice distortion associated with charge density waves (CDW) or long range antiferromagnetic (AF) ordering consistent to spin density waves (SDW) is not revealed[1] in $MgCNi_3$. The single-phase perovskite structure in MgC_xNi_3 is found only in narrow range of carbon content ($0.88 < x < 1.0$). The doping of Ni site by Cu and Co decreases the T_c significantly[4,5]. The present article discusses the synthesis and properties of $MgCNi_3$ superconductor.

EXPERIMENTAL

Synthesis of $MgCNi_3$

The MgC_xNi_3 samples with $x = 0.9$-1.5 are prepared by using the raw materials as Mg flakes, fine Ni powder and glassy carbon spherical powder[1,6,7]. The starting materials are properly mixed and pressed into pellets. The pellets are placed into a Ta foil, put in an alumina boat and fired in a quartz tube furnace under a mixed gas of 95% Ar and 5% H_2 environment. The samples are heat treated at 600°C for 0.5 h and followed by one hour at 900°C. These are cooled, grounded,

pressed and heated at 900°C for one more hour. Owing to the volatility of Mg, 20% excess of its stoichiometric ratio is added to the initial mixture[1,7]. Chemical doping as well as diffusion of metallic particles in $MgCNi_3$ has been reported by several groups[7]. Most of the groups dope on the Ni site[7]. However, the doping effect on Mg site is also studied[7]. The preparation technique is over all conventional type.

RESULTS AND DISUCSSION

Structure of $MgCNi_3$

$MgCNi_3$ superconductor possesses the classical cubic perovskite structure with the space group Pm-3m and the lattice constant[1,2] a *ca.* 3.81221 Å at 295 K. The neutron diffraction study[1,2] shows that the formula for the superconducting phase is $MgC_{0.96}Ni_3$ for the nominal composition $MgC_{1.25}Ni_3$. This is due to the small amount of unreacted graphite found in the sample[1,2]. The atomic positions are: Mg 1a (0, 0, 0); C 1b (0.5, 0.5, 0.5) and Ni 3c (0, 0.5, 0.5) respectively with temperature factors 0.90(3), 0.54(4) and 0.75(1) $Å^2$. Regular domains, with an average size as small as *ca.* 4 nm, appear commonly in the superconducting phase[7]. Introduction of carbon vacancies has significant effects on the positions of the Ni atoms. Electronic structure of $MgC_{1-x}Ni_3$ with X-ray photoemission spectroscopy and X-ray absorption spectroscopy show that overall band structure is in reasonable agreement with band structure calculations[8] including the existence of von Hove singularity near E_F.

In $MgCNi_{3-x}Co_x$ system[5], the lattice parameter decreases slightly with increasing x. The *in situ* high-pressure energy dispersive X-ray diffraction has shown that the structure of $MgCNi_3$ is stable[7] under a pressure *ca.* 22 GPa. $MgCNi_3$ has the perovskite structure over the whole temperature range and no structural or long-range magnetic ordering transitions are observed. There are no unusual changes of the structural parameters near T_c.

Properties of $MgCNi_3$

1) Electrical properties

The upper part of Fig. 1 shows the temperature variation of resistivity for MgC_xNi_3 (x = 1-1.5) samples. Superconducting transition temperature (T_c) is found to be *ca.* 6.5-7.7 K depending on the values of x. Thin films thicker than *ca.* 40 nm have a T_c *ca.* 8 K which is comparable to that of polycrystalline bulk samples. However, the T_c decreases with the decrease of film thickness[7].

T_c of MgC_xNi_3 (x = 1.0-1.5) increases with the increase of x (Fig. 1). The highest T_c corresponds to x *ca.* 1.45-1.5 and decreases with further increase of x. The T_c is found to decrease systematically with decreasing

carbon concentration from the stoichiometric value[1]. Excess of Mg and C in initial material mixture is favourable to improve the T_c and to obtain the single-phase samples[1,5]. Doping at Ni site by Co, Fe, Mn, Cu etc. also shows the decrease of T_c except an initial increase with Fe doping[9]. In addition, Das and Kremer[10] observe a rapid suppression of superconductivity (*ca.* –21 K/at% Mn) in Mn substituted $MgCNi_3$.

Yang *et al.*[6] observe the increase of T_c with pressure (P) from ac susceptibility measurement of three MgC_xNi_3 (Fig. 2) with dT_c/dP *ca.* 0.015 K/kbar. The change of T_c with the unit cell volume (V) can be given by[9] $(V/T_c)(dT_c/dV) = d\ln T_c/d\ln V = -(B/T_c)(dT_c/dP)$, where B is the bulk modulus of the superconductor. The $d\ln T_c/d\ln V$ values vary from –3.18 to –2.58 similar to MgB_2 superconductor (+ 4.16) with opposite sign. The T_c can be expressed by the McMillan formula $T_c = (\theta_D/1.45)\exp\{-1.04(1+\lambda)/[\lambda-\mu^*(1+0.62\lambda)]\}$, where, μ^* is the Coulomb pseudo potential, θ_D is the Debye temperature and λ is the electron-phonon coupling constant. The change of λ and θ_D by pressure determines[6,7] the sign of dT_c/dP. The positive dT_c/dP for MgC_xNi_3 is possibly originated from the increase of $N(E_F)$ and consequently by the enhancement of electron-phonon coupling constant λ if μ^* and $\langle I^2 \rangle$ are less pressure dependent.

2) Magnetic properties

T_c of $MgCNi_3$ decreases with the increase of magnetic field and finally becomes non-superconducting[7]. A magnetic field of 8 T leads to about 50% suppression of T_c and a complete suppression takes place at 14 T. The width $\Delta H = H_{90} - H_{10}$, with H_{90} and H_{10} being respectively, the field values where 90 and 10% of the normal state resistivity is observed, remains constant *ca.* 0.6 T down to low temperature. This indicates that $MgCNi_3$ has a small anisotropy in H_{c2} as the strongly anisotropic superconductor shows a gradual broadening of the superconducting transition with the decrease of temperature. The relation $H_{c2}(0) \approx 0.69T_c(dH_{c2}/dT)_{Tc}$ leads to the $H_{c2}(0)$ *ca.* 13.2 ± 0.7 T. It is found that the physical properties of $MgCNi_3$ are very similar to those of $Nb_{0.5}Ti_{0.5}$. Thus both the compounds may have a similar relation between $H_{c2}(0)$ and $(dH_{c2}/dT)_{Tc}$. It is contended that $MgCNi_3$ has a Werthamer-Helfand-Hohenberg (WHH) like temperature dependence of $H_{c2}(T)$ and the quadratic relationship $H_{c2}(0) = 0.0237(1+\lambda)^{2.2}T_c^2/(10^5 \times v_F^2)$, with v_F as the bare Fermi velocity which points to an effective predominant single band behaviour near the quasi clean limit. The Pauli-limiting field $H_P(0) = 1.84 \times 10^4 T_c$ is expected within the weak-coupling BCS theory. The obtained $H_{c2}(0)$ from WHH theory is higher than $H_P(0)$, suggesting that pair-breaking effects due to the Zeeman energy in $MgCNi_3$ is small[7]. For type-II superconductors, $H_p(0)$ should satisfy the

relation $H_{c2}(0) \leq H_p(0)$. The $H_p(0)$ of $MgCNi_3$ is of the order of its $H_{c2}(0)$ indicating the type-II superconductivity. Thermodynamic critical field $H_c(0)$ *ca.* 0.18-0.6 T, Ginzburg-London (GL) coherence length $\xi_{GL}(0)$ *ca.* 45-56 Å, penetration depth $\lambda_{GL}(0)$ *ca.* 1800-2480 Å, and lower critical field $H_{c1}(0)$ *ca.* 10-12.6 mT and $\kappa(0)$ [= $\lambda_{GL}(0)/\xi_{GL}(0)$] *ca.* 43.3-66 are found for this superconductor.[7] All the obtained parameters $\xi_{GL}(0)$, $\lambda_{GL}(0)$, and $\kappa(0)$ of $MgCNi_3$ also satisfy the conditions for type-II superconductivity.

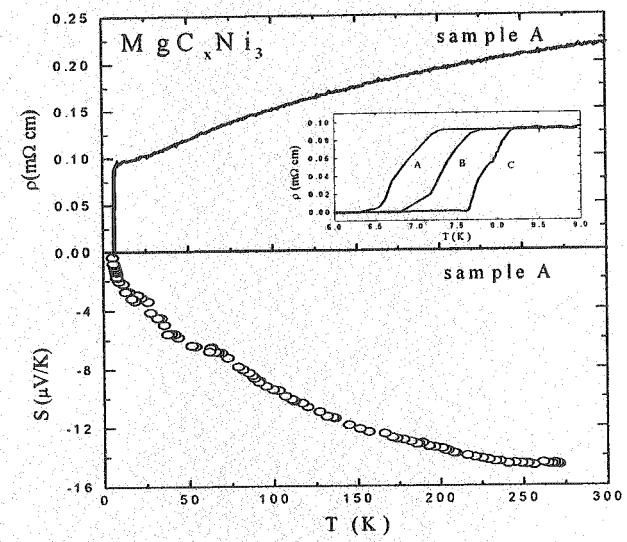

Fig. 1. Temperature (T) variation of resistivity (ρ) and ac magnetic susceptibility (χ_{ac}) thermoelectric power (S) for sample A ($MgCNi_3$) at samples6, 7 with x = 1.0 (A), 1.25 (B) ambient pressure. The inset shows the resistivity (ρ) of at various pressures (P). the three MgC_xNi_3 samples[6,7] with x = 1.0 (A), x = 1.25 (B) and x= 1.5 (C) near T_c

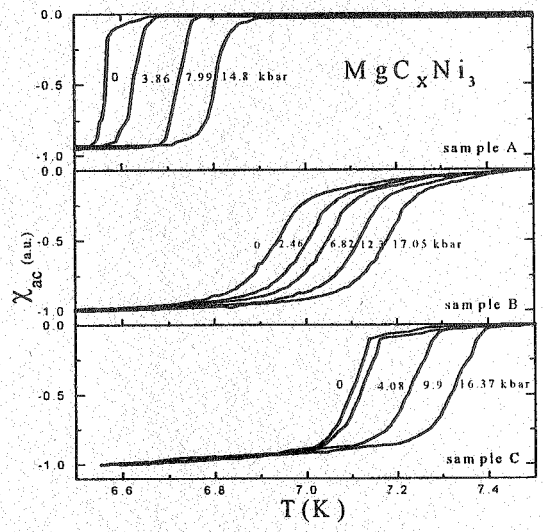

Fig. 2. Variation of of MgC_xNi_3 and 1.5 (C) near T_c

The critical current density (J_c) of $MgC_{1.5}Ni_3 \sim 10^3$-10^4 A/cm^2 at 4.2 K. Normal state magnetoresistance (MR) is given by $\Delta\rho/\rho_0 = [\rho(H)$-

$\rho_0]/\rho_0$ where $\rho(H)$ and ρ_0 are respectively the resistivities with or without a magnetic field H. The resistance of $MgCNi_3$ increases with magnetic filed showing a positive magnetoresistance. However, the MR of $MgCNi_3$ is much smaller than the borocarbide superconductors. The Hall coefficient (R_H) of $MgCNi_3$ at a magnetic filed of 10 T is almost constant up to a temperature of 140 K and beyond that the magnitude of it decreases with the increase of temperature. R_H of $MgCNi_3$ is negative for the whole temperature range that definitely indicates that the carrier in $MgCNi_3$ is electron type and is supported by its thermoelectric power data. At T = 100 K, $R_H = -6.1 \times 10^{-10}$ m^3/C and the carrier density (n) is *ca.* $1.0 \times 10^{22}/cm^3$, which is comparable with that of the theoretically calculated value ($1.3 \times 10^{22}/cm^3$) and that in perovskite $(Ba,K)BiO_3$, but less than that of the metallic binary MgB_2.

3) Thermal properties

Thermal conductivity (k) of $MgCNi_3$ is nearly constant[7] above 210 K. It is of the order of intermetallics, larger than that of borocarbides and smaller than MgB_2. It has been observed that the electronic contribution is slightly higher than the lattice contribution in the normal state. It has been also found from thermal conductivity that the scattering of electrons with static imperfections of the crystal becomes dominant near T_c. Lower part of Fig. 1 shows the thermoelectric power (S) of MgC_xNi_3 sample with x = 1.0 (sample A). The temperature dependence of S is negative confirming the carriers to be electron type, which is consistent with other published results and inconsistent with the theoretical predictions[7]. The absolute value of S(275 K) *ca.* 9.5-14 μV/K of this sample decreases with decreasing temperature and is a characteristic of metallic transport in normal state[6,7]. The magnetic field dependence of specific heat (C) suggests that $MgCNi_3$ is an s-wave superconductor in nature[7].

4) Energy gap

The superconducting energy gap Δ is found[7] to be *ca.* 1.1-1.15 meV from different measurements. These values of Δ are consistent with the calculated one from the specific heat and other data. The tunneling spectroscopy as well as the specific heat studies show that $2\Delta/k_BT_c$ of $MgCNi_3$ varies from 3.75 to 5 which is higher than the typical weak coupling BCS value (*ca.* 3.52). The electron-phonon coupling constant λ = 0.66-0.84 indicates the moderate coupling superconductivity in $MgCNi_3$. Therefore, it can be concluded that $MgCNi_3$ is a BCS s-wave, moderate coupling, type-II and single gap superconductor.

Conclusions

The synthesis, structure and properties of $MgCNi_3$ superconductor are discussed. It has a perovskite structure. T_c of MgC_xNi_3 is sensitive to carbon content increasing with x. However, the doping on Mg and Ni site decreases the T_c. External pressure increases the T_c of MgC_xNi_3. Hall coefficient and thermoelectric power data of $MgCNi_3$ show that the carriers in this compound are electrons. The density of states (DOS) of the Fermi level (E_F) is dominated by Ni 3d-states and there is a von Hove singularity of the DOS just below the E_F. This is a single gap superconductor in contrast to MgB_2. The field dependent specific heat and resistivity results imply that it is a moderate coupling, type-II and s-wave BCS superconductor.

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