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Pressure effects on the transition temperature of superconducting MgC_xNi_3

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The effect of hydrostatic pressure (P) up to 17 kbar on the superconducting transition temperature (T_C) of the newly discovered intermetallic nonoxide perovskite superconductor MgC_xNi_3 has been reported. T_C is found to increase with increasing P at a rate of $dT_C/dP \sim 0.0134$ to 0.0155 K/kbar depending on the value of carbon content x. The absolute value of dT_C/dP for MgC_xNi_3 is about the same as that of intermetallic RNi_2B_2C (R denotes rare earth) and metallic superconductors but about one order of magnitude smaller than that of the most recently and intensively studied superconductor MgB_2. However, the $d \ln T_C/dP \sim 0.001\,81$ to $0.002\,24\ \text{kbar}^{-1}$ and the rate of change of T_C with unit cell volume (V), $d \ln T_C/d \ln V \sim -3.18$ to -2.58 of MgC_xNi_3 are having the comparable magnitude to that of MgB_2 with opposite sign. The increase of T_C with P in MgC_xNi_3 can be explained in the framework of density of states (DOS) effect.

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Soon after the discovery of a record high-T_C ($\sim$39 K) intermetallic noncuprate superconductor MgB_2,[1] a new intermetallic nonoxide superconductor $MgCNi_3$ was found[2] to undergo a superconducting transition at $T_C \sim 8$ K. Though the T_C of $MgCNi_3$ is much lower than that of MgB_2, it still attracts a lot of attention due to at least having the following physical significance related to the present studies. (1) It has a perovskite structure as does the 30 K oxide noncuprate superconductor $Ba_{1-x}K_xBiO_3$.[2] (2) A high proportion of Ni in this compound indicates that the magnetic interactions may play a dominant role in understanding its superconductivity. (3) Its normal state NMR properties are irregular[3] and analogous to that observed in the exotic superconductor Sr_2RuO_4. (4) A typical isotropic s-wave superconductivity[3] is displayed by the nuclear spin-lattice relaxation rate ($1/T_1$) with a coherence peak below T_C. (5) The change from grain boundary to core pinning by intragranular nanoparticles near T_C proposes that the arrangement of pinning sites in $MgCNi_3$ is unique.[4] (6) The Hall coefficient and thermoelectric power data[5,6] show that the carriers in this compound are electrons in contrast to MgB_2. (7) Energy band calculations[7–9] demonstrate that the density of states (DOS) of the Fermi level (E_F) is dominated by Ni d states and there is a von Hove singularity (vHS) of the DOS just below (<50 meV) the E_F.[8] Moreover, the photoemission and x-ray absorption studies show that the sharp vHS peak theoretically predicted near E_F is substantially suppressed which may be due to electron-electron and electron-phonon interactions.[10]

It is well known that the high pressure (P) plays an important role on the T_C of the metallic and intermetallic superconductors.[11–19] In general, P can change the electronic structure, phonon frequencies, or electron-phonon coupling that affecting the T_C. Both positive and negative pressure derivatives, dT_C/dP, are observed in the metallic and intermetallic superconductors.[11–19] For example, simple s,p,d-metal superconductors[16] such as Sn, In, Ta, or Hg, and the intermetallic superconductor such as the recently discovered MgB_2 (Refs. 11–13) have shown decreasing T_C with increasing P. However, depending on the rare earth site of the quaternary borocarbides, RNi_2B_2C (R denotes rare earths), both an increase and decrease of T_C are observed with an increase of pressure.[14,15] In addition, the pressure can basically shift the Fermi level (E_F) towards higher energies[14,15] and thereby provide a probe on the slope of the DOS near E_F. Moreover, it can also modify the magnetic pair breaking effect and tune the competitive phenomena between superconductivity and spin fluctuations. From our magnetic field dependent resistivity and specific-heat studies,[20,21] it has been suggested that the $MgCNi_3$ is basically a typical BCS-like superconductor. In this report, we further present the pressure effects on the T_C of this exotic superconductor to testify the above-mentioned unique electronic and magnetic properties.

The details of MgC_xNi_3 sample preparation and characterization can be found in Refs. 2 and 22. With increasing the nominal carbon content, T_C was improved. Depending on the values of nominal carbon x, the samples with different T_C's are hereafter referred as A ($x=1.0$), B ($x=1.25$), and C ($x=1.5$). Electrical resistivity (ρ) of MgC_xNi_3 was measured by the standard four-probe method. Thermoelectric power (S) measurements were performed with steady state techniques. The hydrostatic pressure- (P) dependent ac magnetic susceptibility (χ_{ac}) data were taken by the piston cylinder self-clamped technique.[23] The hydrostatic pressure environment around the sample was generated inside a Teflon cell with 3M Fluroinert FC-77 as the pressure-transmitting medium. The pressure was determined by using a Sn manometer situated near the sample in the same Teflon cell. In each instance, the original value was reproduced within experimental error after the pressure released indicating complete reversibility of the pressure effect.

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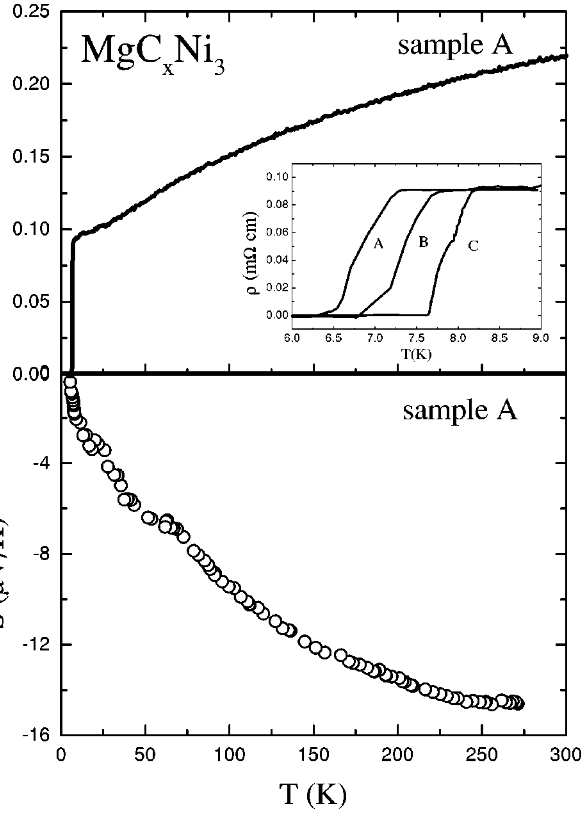

FIG. 1. Temperature (T) variation of resistivity (ρ) and thermoelectric power (S) for sample A at ambient pressure. The inset shows the resistivity (ρ) of the three samples A, B, and C near T_C.

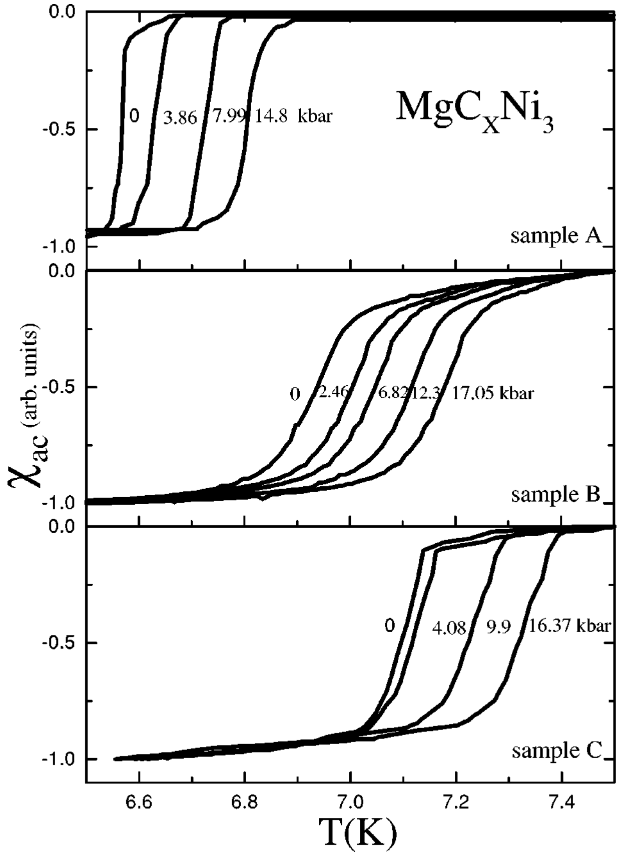

FIG. 2. Variation of ac magnetic susceptibility (χ_{ac}) of samples A, B, and C near T_C at various pressures (P).

Figure 1 shows the temperature dependence of resistivity (ρ) and thermoelectric power (S) for sample A. The inset of Fig. 1 displays the ρ of samples A, B, and C near T_C. The variation of ρ with temperature shows the same trend as reported in the literature[2,5,6,24,25] with $T_C \sim 7-8$ K, $\rho_{300\ K}/\rho_{10\ K} \sim 2.3$ and 90%-10% transition width ~ 0.2 K. The different values of T_C for three studied MgC$_x$Ni$_3$ samples are mainly due to the carbon stoichiometry.[2,24] The temperature dependence of S is negative, confirming the carriers to be electron type, which is consistent with the published results.[5,6] The nonlinear temperature dependence of S seems to suggest that the enhancement of electron-phonon interaction plays an important role in the superconductivity of MgC$_x$Ni$_3$ as in chevrel-phase compounds[26] Cu$_{1.8}$Mo$_6$S$_{8-y}$Se$_y$ and Cu$_{1.8}$Mo$_6$S$_{8-y}$Te$_y$.

Temperature variation of ac magnetic susceptibility (χ_{ac}) of samples A, B, and C under pressure (0–17 kbar) is shown in Fig. 2. At ambient pressure, T_C (~ 6.5 K) of sample A is the same as that obtained from specific heat[21] but a little lower than that from the resistivity data (Fig. 1). The T_C (midpoint) for sample A increases from 6.56 to 6.79 K with an increase of pressure from ambient to 14.80 kbar as shown in Fig. 3, having the rate of $dT_C/dP \sim 0.015$ K/kbar and $d\ln T_C/dP$ $[=(1/T_C)(dT_C/dP)] \sim 0.002\ \mathrm{kbar}^{-1}$. The similar trend of pressure effect on T_C for samples B and C is also shown in Figs. 2 and 3. The positive values of dT_C/dP and $d\ln T_C/dP$ for these three samples are listed in Table I. It is noted that these values of $d\ln T_C/dP$ (Table I) for MgC$_x$Ni$_3$ lie in the range of $\sim 0.001-0.008\ \mathrm{kbar}^{-1}$ of conventional superconductors.[27]

For a clear and detailed idea of the pressure effect on the T_C of other metallic and intermetallic superconductors, some of them are also listed in Table I for comparison. The decrease and increase of T_C are observed, respectively, in metallic superconductors Ta and V with an analogous magnitude of dT_C/dP and $d\ln T_C/dP$ as MgC$_x$Ni$_3$ (Table I). It is explained by the decrease of the electron-phonon coupling constant in Ta and by the suppression of spin fluctuations as well as the increase of electron-phonon coupling in V.[16–18] The magnitude of positive dT_C/dP for electron-carrier MgC$_x$Ni$_3$ is about the same as that of its three-dimensional analog LuNi$_2$B$_2$C superconductor, and the latter has been interpreted by an increase of the DOS with P.[14] However, the negative dT_C/dP and $d\ln T_C/dP$ for hole-carrier MgB$_2$ may be either from a decrease of the DOS (Ref. 12) or by a lattice stiffening.[13]

The change of T_C with the unit cell volume (V) can be given by[11,14]

$$(V/T_C)(dT_C/dV) = d\ln T_C/d\ln V = -(B/T_C)(dT_C/dP), \tag{1}$$

where B is the bulk modulus of the superconductor. Using the calculated value of B for MgC$_x$Ni$_3$ as 1510 kbar (Ref. 25) and taking the obtained dT_C/dP and T_C from Table I, the $d\ln T_C/d\ln V$ values are found from Eq. (1), respec-

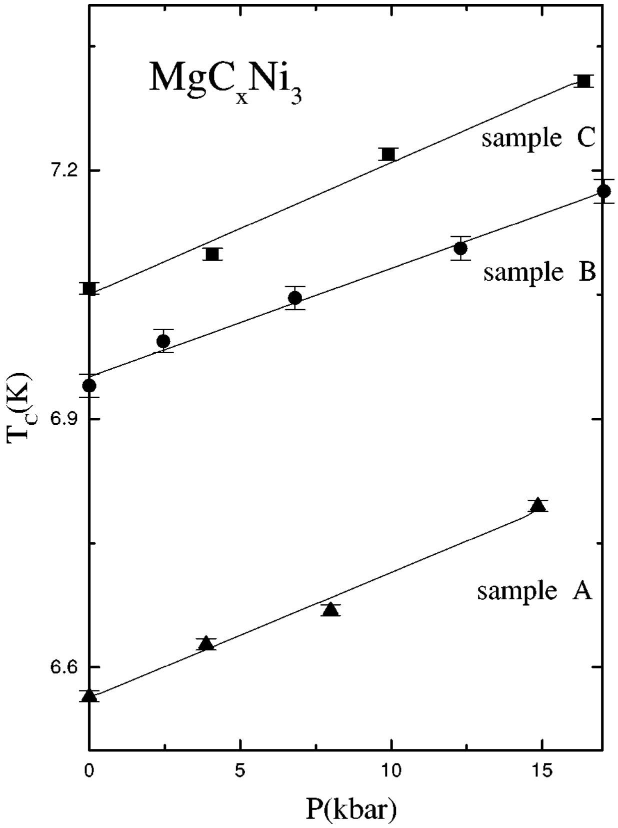

FIG. 3. Pressure (P) dependence of superconducting transition temperature (T_C) of samples A, B, and C.

tively, for samples A, B, and C as -3.18, -2.58, and -2.76. These values are of the same order of magnitude in the MgB_2 superconductor ($+4.16$) with opposite sign.[11]

Since the DOS is sufficiently large in MgC_xNi_3, produces strong electron-phonon coupling[9] and is supported by its S data, the T_C can be expressed by the McMillan formula[28] as

$$T_C=(\theta_D/1.45)\exp\{-1.04(1+\lambda)/[l-\mu^*(1+0.62\lambda)]\}, \tag{2}$$

where, μ^* is the Coulomb pseudopotential and θ_D is the Debye temperature. λ is the electron-phonon coupling constant and is given by

$$\lambda=N(E_F)\langle I^2\rangle/M\langle\omega^2\rangle, \tag{3}$$

where $N(E_F)$ is the DOS at the Fermi level, $\langle I^2\rangle$ is the square averaged electronic matrix element for electron-phonon interaction, M is the ionic mass, and $\langle\omega^2\rangle$ is the square averaged phonon frequency. It appears from Eq. (2) that the change of λ and θ_D by pressure will determine the sign of dT_C/dP. It is well established that the pressure induces the lattice stiffening and generally reduces the T_C.[14–17] However, the DOS effect can either enhance or reduce the T_C correspondingly by the increase or decrease of $N(E_F)$ due to applied pressure.[14,15] The dependence of T_C on θ_D is complicated as it appears both in the linear and exponent [being connected with $\langle\omega^2\rangle$ in Eq. (3)] terms of Eq. (2). Again, the change of exponent λ in Eq. (2) will be more effective than that of the linear term θ_D in determining T_C. θ_D generally increases by P amplifying the phonon frequency[19] as $\langle\omega^2\rangle=0.5\theta_D{}^2$ and thus may decrease λ [Eq. (3)], which in turn may reduce T_C [Eq. (2)]. Therefore, the positive dT_C/dP for MgC_xNi_3 possibly originates from the increase of $N(E_F)$ and consequently by the enhancement of electron-phonon coupling constant λ [Eqs. (3)] if μ^* and $\langle I^2\rangle$ are less pressure dependent. In addition, P causes not only a shifting of the E_F but also a broadening of the energy bands. This broadening of energy bands may also increase $N(E_F)$. Most recently, Louis and Iyakutti[19] have successfully calculated the pressure effects on T_C of vanadium (V). Similarly, the computation of some important parameters such as $d\ln N(E_F)/dP$ and $d\ln\omega/dP$ of MgC_xNi_3 may be useful for quantitative analysis of our data.

Even though it is unfavorable that strong spin fluctuations exist in MgC_xNi_3,[21] the marginal or unstable spin fluctuations suppressing T_C have not been totally ruled out.[8] In general, pressure reduces the spin fluctuations and increases T_C because the spin fluctuations and superconductivity are mutually competitive phenomena. This may also be one of the reasons for the positive pressure effect on T_C of MgC_xNi_3. Another considerable factor showing a positive dT_C/dP is the carbon stoichiometry in the sample. Generally, the deficiency of carbon from the optimum value decreases the T_C.[2,24] The nonstoichiometry of carbon (if any) may also affect the energy bands of the sample and alter the

TABLE I. The superconducting transition temperature T_C (determined from the midpoint of resistive transition for MgC_xNi_3) at ambient pressure, dT_C/dP, and $d\ln T_C/dP$ for some metallic as well as intermetallic superconductors.

Sample composition	T_C (K)	dT_C/dP (10^{-2} K/kbar)	$d\ln T_C/dP$ (10^{-3}/kbar)	Reference
MgB_2	38.6	-8.0	-2.07	12
MgB_2	37.5	-16.0	-4.26	13
$LuNi_2B_2C$	15.9	$+1.88$	$+1.18$	14
Ta	4.3	-0.26	-0.60	16
V	5.3	$+1.0$	$+1.88$	18, 19
$MgC_xNi_3(A)$	6.9	$+1.55$	$+2.24$	This work
MgC_xNi_3(B)	7.4	$+1.34$	$+1.81$	This work
$MgC_xNi_3(C)$	7.9	$+1.52$	$+1.92$	This work

position of E_F compared to that expected from theoretical energy band calculations[7–9] for stoichiometric $MgCNi_3$. The present investigations for three samples with different carbon content and T_C show almost the same positive value of dT_C/dP suggesting that the carbon deficiency does not significantly affect the pressure effect of MgC_xNi_3 on T_C. However, it is noted that Kumary *et al.*[25] recently found a decrease of T_C up to a pressure of 17 kbar and an increase of T_C beyond this pressure using resistivity measurements. It may be possible to briefly explain these controversial results as followings. (1) The T_C determined from the resistivity (transport property) is always higher than that from susceptibility and specific heat (bulk property) measurements.[2,20,21,25] This may suggest that a small amount of higher T_C phase existing in the grain boundaries[4] superconducts through percolation effects. (2) The negative dT_C/dP observed in Ref. 25 using resistivity measurements at low pressures may be due to the reduction of grain boundary effects by pressure. Once the pressure is applied high enough (~17 kbar) to overcome the grain boundary effect, the bulk superconductivity dominates and the positive dT_C/dP is found to be the same with our results using susceptibility measurements.

In summary, pressure increases T_C of three intermetallic, nonoxide, and perovskite electron-type superconductors MgC_xNi_3. The magnitude of change rate $d\ln T_C/dP$ in MgC_xNi_3 is about the same order as that in MgB_2 and RNi_2B_2C (R denotes rare earths), which lies in the range of that of conventional superconductors. The positive value of dT_C/dP for three MgC_xNi_3 samples are almost the same and independent of various T_C resulting from different carbon stoichiometry. The present results of positive dT_C/dP of MgC_xNi_3 can be explained mainly by the increase of density of states by pressure.

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