Nuclear-magnetic-resonance investigation of the itinerant nearly antiferromagnetic behavior in superconducting $Zr_2(Co_{1-x}Ni_x)$

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Nuclear magnetic resonance of ^{59}Co in superconducting $Zr_2(Co_{1-x}Ni_x)$ compounds was carried out at 75 MHz in a temperature range between 1.4 and 260 K to study the properties of the low-frequency spin dynamics. A temperature-independent Knight shift and an approximate Curie Weiss behavior of the nuclear spin-lattice relaxation rate are well explained within a framework of the self-consistent renormalization theory of spin fluctuations for nearly antiferromagnetic (AF) metals. Results of the Ni substitution for Co indicate that the superconducting transition temperature relates more to the spin density fluctuations around $q=Q$ (Q being an AF wave vector) than to the density of states at the Fermi level. [S0163-1829(98)09941-X]

INTRODUCTION

The transition-metal compound Zr_2Co is known to be a superconductor with the transition temperature $T_S \simeq 5.0$ K.[1] In the $Zr_2(Co_{1-x}Ni_x)$ system of pseudo-binary-alloyed compounds, T_S rises initially, takes the highest value of $\simeq 6.0$ K around $x=0.15$ and then falls to $\simeq 1.4$ K at $x=1$ (Zr_2Ni) as is shown in Fig. 1.[2,3] The dependence of T_S on the Ni substitution for Co has been considered to be caused by changes in the density of states (DOS) at the Fermi level.

The electrical resistivity measurements by Mori and Nishimura,[3,4] however, exhibited a saturation behavior at temperatures above 50 K in all specimens with x between 0 and 1, suggesting that strong electron correlations or spin correlations play an important role in the normal state. The susceptibility measured by Yamaya, Sambongi, and Mitsui[2] in a temperature range from 300 K down to 77 K showed a Curie Weiss-type increase with decreasing temperature for specimens with x below 0.7, though this might be attributable to some possible magnetic impurities, as was noted in the paper.[2] Then, an important issue in the superconducting $Zr_2(Co_{1-x}Ni_x)$ system is to investigate the electronic and magnetic states microscopically.

In this paper, we report the results of a magnetic susceptibility measurement and a nuclear magnetic resonance (NMR) study of ^{59}Co in the normal state of $Zr_2(Co_{1-x}Ni_x)$ polycrystalline specimens with $x=0$, 0.15, and 0.4. The results indicate that the $Zr_2(Co_{1-x}Ni_x)$ system belongs to a group of nearly antiferromagnetic metals, and the values of T_S are more related to the degree of spin density fluctuations around $q=Q$ (Q being an AF wave vector) rather than to the DOS at the Fermi level.

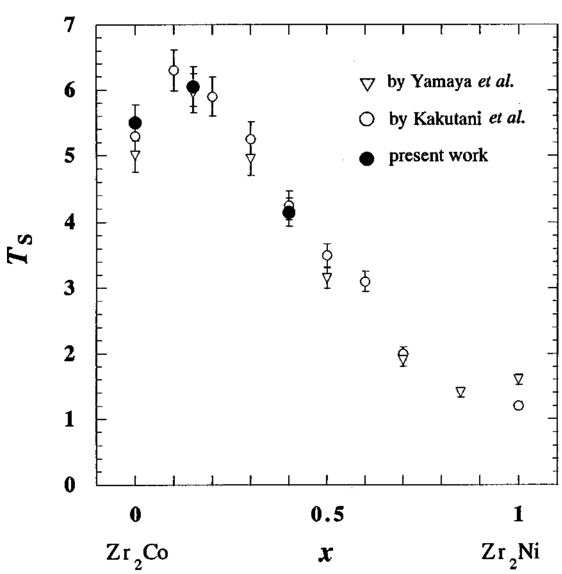

FIG. 1. Superconducting transition temperature T_s of $Zr_2(Co_{1-x}Ni_x)$ plotted against the Ni substitution x: ▽ by Yamaya, Sambongi, and Mitsui (Ref. 2); ○ by Kakutani, Nishimura, and Mori (Ref. 12); ● present work.

EXPERIMENT

The bulk samples were prepared by melting Zr, Co, and Ni metals of nominal purity 99.5, 99.95, and 99.9%, respectively, in appropriate proportions in an argon arc furnace. X-ray diffraction patterns at room temperature showed that the specimens formed the Al_2Cu ($I4mcm$) structure (Fig. 2) and were very close to a single phase. For NMR measurement, the ingots were crushed into powder and put through a sieve of 74 μ. ac susceptibility measurement for the samples showed a typical transition to diamagnetism of $\sim$100% Meissner shielding below $T_S \simeq 5.5$, 6.0, and 4.2 K for $x=0$,

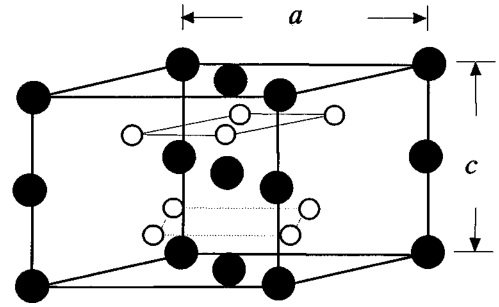

FIG. 2. The crystal structure of Zr_2Co and Zr_2Ni: ●, Co, Ni, ○, Zr.

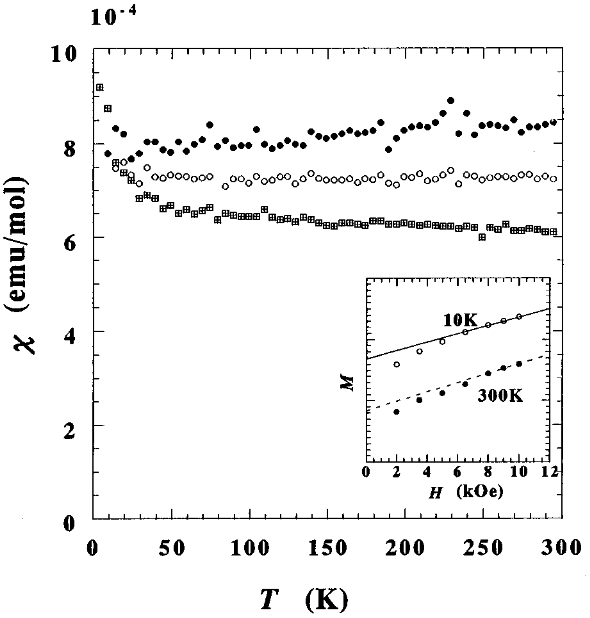

FIG. 3. Temperature dependence of the susceptibility deduced through the procedure described in the text. Inset shows typical field dependence of the magnetization at 4.2 and 300 K: ●, $x=0$; ○, $x=0.15$; ⊞, $x=0.4$.

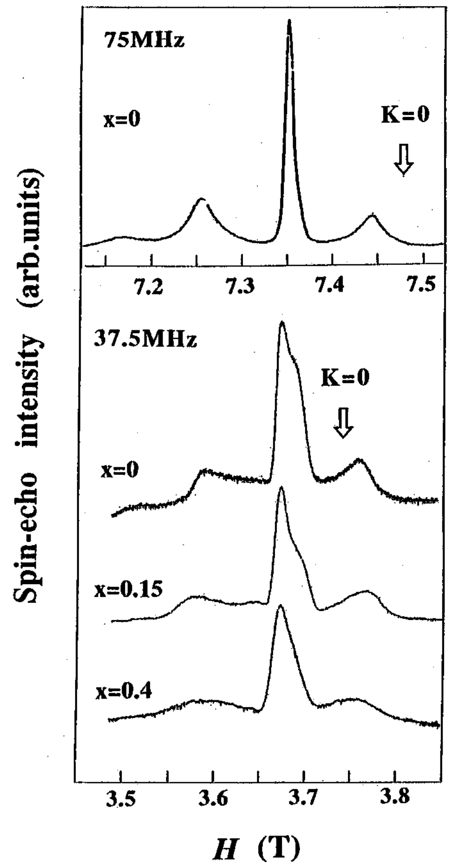

FIG. 4. A ^{59}Co spin-echo spectrum at 75 MHz in Zr_2Co and the spectra at 37.5 MHz in the samples with $x=0$, 0.15, and 0.4, observed at 4.2 K.

0.15, and 0.4, respectively, which agree with the values reported previously.[2,3] The value of the upper critical field at $T=0$, $H_{C2}(0)$, was estimated to be ~9 kOe and ~20 kOe for $x=0$ and 0.15, respectively, by extrapolating the experimental values of $H_{C2}(T)$.

The magnetization M was measured as a function of the external field up to $H=10$ kOe in a temperature range between $T=4.2$ and 300 K, with a torsion-type magnetic balance. As is typically shown in the inset of Fig. 3, M was not proportional to H up to ~6 kOe over the present experimental temperature range due to the spurious contribution from an extremely small amount of contaminated ferromagnetic Co metal ($T_C=1404$ K). Similar M dependence on H in $Zr_2(Co_{1-x}Ni_x)$ was pointed out in the previous paper.[2] Then we tentatively deduced the value of the susceptibility χ from the slope dM/dH in a field range between ~8 and 10 kOe. In the specimens with $x=0$ and 0.15, as is shown in Fig. 3, χ deduced through this procedure hardly has little dependence on the temperature, which disagrees with the large Curie Weiss-type behavior reported previously.[2] On the other hand, χ of the specimen with $x=0.4$ exhibited a small Curie-tail with lowering temperature.

KNIGHT SHIFT

The ^{59}Co NMR in high magnetic fields was carried out in a temperature range between 4.2 and 260 K with a phase-coherent spin-echo spectrometer. ^{59}Co ($I=7/2$) spin-echo spectrum was observed at constant resonance frequencies of 75.0 and 37.5 MHz in a field sweeping procedure. The ^{59}Co spectra obtained for all the samples exhibited a typical equally separated quadrupole powder pattern as is displayed in Fig. 4. From the splitting of the first satellites, we obtained a value of the quadrupole frequency $\nu_Q=e^2qQ/14\hbar=1.83$, 2.03, and 1.97 MHz for $x=0$, 0.15 and 0.4, respectively. The central line of the NMR spectra was anisotropic in shape and the full linewidth was inversely proportional to the resonance field, as can be seen in the spectra at 75 and 37.5 MHz for $x=0$. The anisotropic shape is then due mainly to the second-order quadrupole splitting $\delta\nu=\nu_I-\nu_{II}$ of the central line, where the frequencies ν_I and ν_{II} correspond to θ such that $\mu=\cos\theta=0$ and $\sqrt{5/9}$, respectively.[5] The frequency difference between the peak and the shoulder in the central line agrees satisfactorily with a calculated value $\delta\nu=(25\nu_Q^2/144\nu_0)[(I(I+1)-3/4]$ using the experimental value of ν_Q.

The Ni substitution for Co hardly changed the ν_Q value but, as can be seen in Fig. 4, resulted in a small increase in the satellite linewidth.

Figure 5 shows a pure quadrupole resonance (PQR) spectrum observed at 5.5 K under a zero field. The frequencies of 3.7 and 5.6 MHz at the resonance peaks agree satisfactorily with the values of $2\nu_Q$ and $3\nu_Q$, respectively.

The Knight shift determined from the second-order quadrupole-splitting central line, plotted in Fig. 6, exhibits near temperature independence, and increasing value with increasing Ni substitution. The large and positive Knight shift is indicative of the dominant orbital contribution. The lack of any significant increase in K for $x=0.4$ at low temperatures indicates that the small Curie tail in χ observed in the specimen is not intrinsic, and may be attributed to possible magnetic impurities.

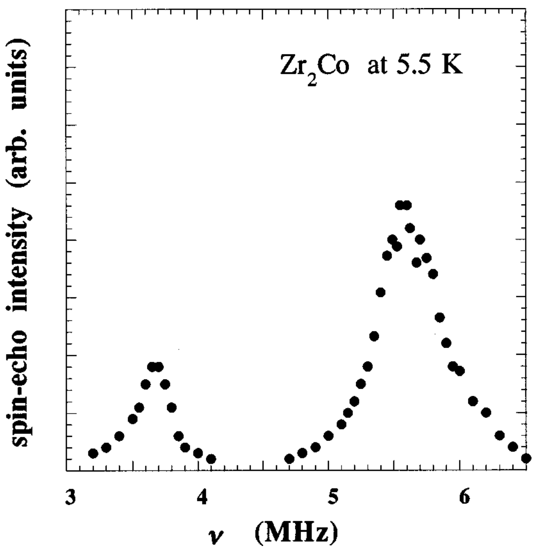

FIG. 5. A pure quadrupole resonance spectrum of ^{59}Co observed at 5.5 K under a zero field.

NUCLEAR SPIN-LATTICE RELAXATION

The ^{59}Co spin-lattice relaxation times T_1's were measured at the peak intensity point, ν_I, of the central line at 75.0 MHz, utilizing a single-rf-pulse-saturation method. The width of the ν_I line, $\simeq$100 Oe, hardly depends on the the temperature and the Ni substitution, and we applied the saturation rf field, H_1, of about 100 Oe.

All the experimental magnetization $M(t)$ at t after the saturation pulse showed a multi-exponential recovery, as is shown typically in Figs. 7(a) and 7(b). The value of T_1 was obtained by the parameter fitting of the theoretical recovery curve given by[6]

$$\frac{M(\infty)-M(t)}{M(\infty)}=0.013e^{-t/T_1}+0.068e^{-6t/T_1}+0.206e^{-15t/T_1}+0.714e^{-28t/T_1} \quad (1)$$

with the experimental data, as is drawn in the figures by solid curves. To check the effect of the second-order quadrupole

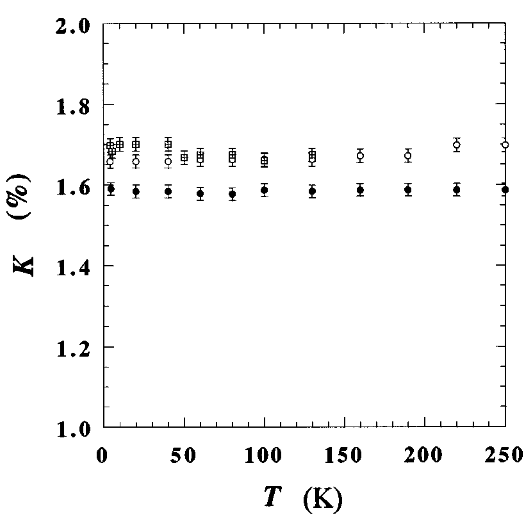

FIG. 6. Temperature dependence of the Knight shift: ●, $x=0$; ○, $x=0.15$; ⊞, $x=0.4$.

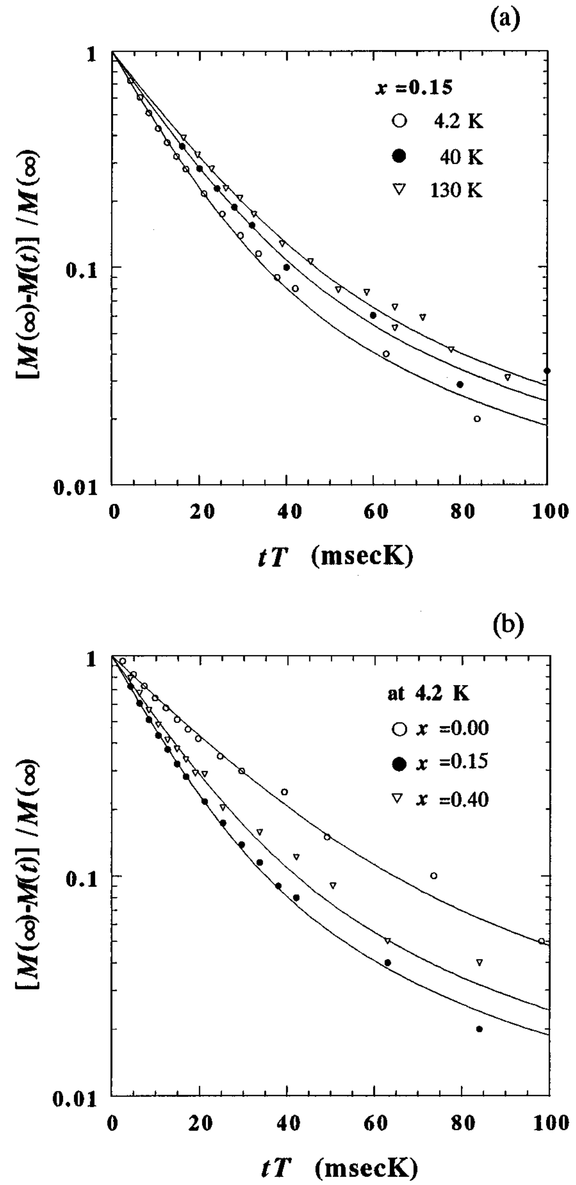

FIG. 7. Typical magnetization recovery behaviors $[M(\infty)-M(t)]/M(\infty)$; (a) for $x=0$ at 4.2, 40, and 130 K; (b) at 4.2 K for $x=0$, 0.15, and 0.4. Solid curves are the best fit with the data drawn using Eq. (1) in the text.

broadening on the experimental recovery behavior, T_1 was also measured at 37.5 MHz using the ν_I peak of the central line at 4.2 K. The decay curve and T_1 value obtained at 37.5 MHz were in good agreement with those at 75.0 MHz.

Shown in Fig. 8 are data for the relaxation rate $(T_1T)^{-1}$ plotted against the temperature. $(T_1T)^{-1}$ in Zr_2Co did not follow the Korringa-type relation ($T_1T=$const.) and was enhanced with decreasing temperature, in contrast to the temperature-independent behavior of the Knight shift. With the Ni substitution, the $(T_1T)^{-1}$ enhancement at low temperatures became pronounced at $x=0.15$ and then largely diminished at $x=0.4$. The small amount of possible paramagnetic impurities is not responsible for the upturns of $(T_1T)^{-1}$, because the Curie tail in χ was observed explicitly only for $x=0.4$ with the smallest $(T_1T)^{-1}$ enhancement among all. The relaxation process to the paramagnetic impu-

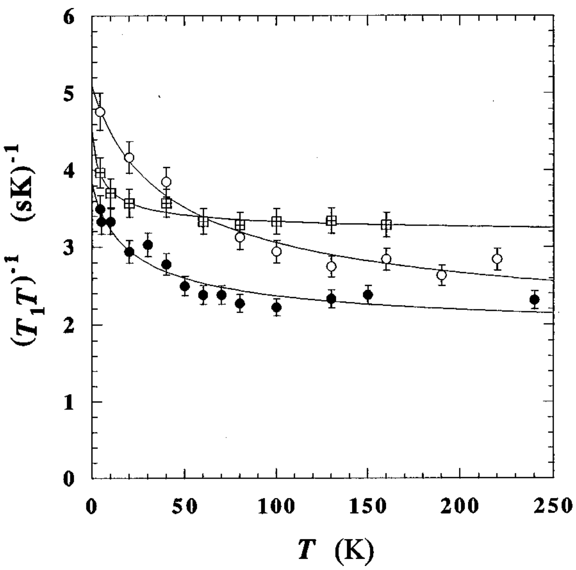

FIG. 8. Temperature dependence of the nuclear spin-lattice relaxation rate: ●, $x=0$; ○, $x=0.15$; ⊞, $x=0.4$.

rities is, in addition, ineffective at low temperatures under the present experimental high field of ~73.5 kOe. Thus, on reference to Fig. 1, the $(T_1T)^{-1}$ enhancement tends to be more pronounced in the specimen with higher T_S.

As the upper critical field of $Zr_2(Co_{1-x}Ni_x)$ is very small, we have tried to examine the temperature dependence of T_1 in the superconducting state utilizing the zero field ^{59}Co PQR at 5.6 MHz (Fig. 5). However, the PQR signal intensity decreased rapidly just below T_S and disappeared probably due to the extremely small penetration depth. Then we measured T_1 under a weak external field of ≃5.7 kOe, though the signal intensity in the superconducting state was not sufficient yet for an accurate T_1 measurement. A preliminary result in the vortex state of the specimen with $x=0.15$ clearly showed a large increase in T_1 with lowering temperature below $T_S(H)$, indicating that a superconducting energy gap is formed at the Fermi level of the Co d band.

DISCUSSION

The different behavior of the temperature-dependent $(T_1T)^{-1}$ from the temperature-independent Knight shift in the normal state is explained by the fact that the former provides information on the q sum of the dynamical susceptibility $\chi_q(\omega)$, while the latter is proportional to the uniform susceptibility $\chi_0(0)$. In transition-metal compounds and alloys, the effect of the electron correlations originated from a narrow d band on the dynamical susceptibility should be taken into account. The self-consistent renormalization (SCR) theory by Moriya and co-workers[7,8] indicates that local spin fluctuation components in q space and their mutually interacting modes play an important role in itinerant weakly and nearly antiferromagnetic metals, where the spin density fluctuations around $q=Q$ play a predominant role. The SCR theory predicts for the three-dimensional system a characteristic temperature dependence of $(T_1T)^{-1}$ given by[9]

$$\frac{1}{T_1T}=\frac{\alpha}{\sqrt{T-T_N}}. \tag{2}$$

for $T>T_N$, where α is a proportionality constant related to the details of the band structure at the Fermi level E_F and T_N is the Néel temperature.

The data of $(T_1T)^{-1}$ can be fitted by the following formulas,

$$\frac{1}{T_1T}=1.73+\frac{6.74}{\sqrt{T+10}}\,(sK)^{-1}\quad \text{for } x=0, \tag{3}$$

$$\frac{1}{T_1T}=1.55+\frac{16.6}{\sqrt{T+22}}\,(sK)^{-1}\quad \text{for } x=0.15, \tag{4}$$

and

$$\frac{1}{T_1T}=3.12+\frac{2.16}{\sqrt{T+2.5}}\,(sK)^{-1}\quad \text{for } x=0.4, \tag{5}$$

as is drawn in Fig. 8 by the dotted curves. The second term with negative value of T_N in the formulas corresponds to the relaxation rate predominated by the staggered susceptibility χ_Q that follows an approximate Curie Weiss law. Thus, from the combination of the temperature-independent Knight shift and the Curie Weiss-type behavior of the relaxation rate, we concluded that the specimens with $x=0$, 0.15, and 0.4 belong to a group of the nearly antiferromagnetic metals with $T_N \simeq -10$, $\simeq -22$, and $\simeq -2.5$ K, respectively. The large increase in T_1 observed in the superconducting vortex state indicates that the electrons in the Co d band with spin density fluctuations around $q=Q$ are also responsible for the superconductivity formation.

The temperature-independent contribution coming from the first term in Eqs. (3), (4), and (5) originates mainly from the orbital relaxation given by[10]

$$\frac{1}{(T_1T)_{\text{orb}}}=4\pi\gamma_N^2\hbar k_B A_{\text{orb}}^2 N(E_F)^2 p, \tag{6}$$

where A_{orb} is the orbital hyperfine coupling constant, $N(E_F)$ the DOS at E_F, and p the reduction factor that depends on the relative weight at E_F of the irreducible representation of the atomic d functions. For the cubic point group,

$$p=\tfrac{2}{3}f(\Gamma_5)[2-\tfrac{5}{3}f(\Gamma_5)], \tag{7}$$

where $f(F_5)$ is the relative weight of the Γ_5 representation. Using a value of the orbital hyperfine coupling constant $A_{\text{orb}} \simeq 530$ kOe/μ_B,[11] Eq. (6) yields experimental values of DOS at E_F for the d electrons as $N(E_F) \simeq 0.75$, ≃0.7, and ≃1.0 states (eV Co-atom spin)$^{-1}$ for $x=0$, 0.15, and 0.4, respectively. Here the value of the reduction factor p was taken to be close to 2/5, assuming that Γ_3 and Γ_5 representations carry equal weight at E_F. In spite of our crude approximation, the values of $N(E_F)$ for $x=0$ and 0.15 are reasonably compared with the values $N(E_F)(1+\lambda) \simeq 1.8$ and ≃2.0 states (eV f.u. spin)$^{-1}$ for $x=0$ and 0.2, respectively, obtained by electronic specific heat measurement,[12] where $(1+\lambda)$ is the phonon enhancement factor.

Within the framework of the BCS theory, the changes in T_S have been discussed in terms of electron-phonon coupling $\lambda = N(E_F)V_{\text{ph}}$ and electron-electron coupling $\mu = N(E_F)V_C$ parameters,[13]

$$k_B T_S = 1.13\hbar\omega_D \exp\left(-\frac{1}{\lambda-\mu}\right), \tag{8}$$

where ω_D is the Debye frequency. The present experimental result of the remarkable increase in $N(E_F)$ with the large drop of T_S, typically observed in the specimen with $x = 0.4$, conflicts with the BCS prediction. Thus, as the $(T_1T)^{-1}$ enhancement at low temperatures is largely pronounced in $Zr_2(Co_{1-x}Ni_x)$ with higher T_S, we may conclude that, the superconducting transition temperature relates more to the spin density fluctuations around $q=Q$ rather than to the density of states at the Fermi level. Further experimental study on the T_1 behavior of ^{59}Co in the superconducting state and ^{91}Zr NMR study are in progress.

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