Anisotropy of the superconducting gap in $CeCo_2$

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(Received 26 July 1996)

We find extraordinary superconducting characteristics in the low-temperature specific heat of high quality $CeCo_2$ single crystals, suggesting that the superconducting gap is highly anisotropic. The electronic specific-heat jump at the superconducting transition temperature (T_c=1.5 K) is $\Delta C_e/\gamma T_c$=0.85, which is reduced compared to the BCS value of 1.43. At low temperatures ($0.13<T/T_c\ll1$), C_e varies approximately as T^2, indicating a possibility of lines of nodes in the gap. A possible correlation of the gap anisotropy with the ferromagnetic spin fluctuation is discussed. [S0163-1829(97)10105-9]

Among the superconductors containing valence-fluctuating Ce ions, the cubic C15 Laves-phase ($MgCu_2$-type) compound $CeCo_2$ (T_c=1.5 K) has attracted growing interest.[1] One interesting feature of $CeCo_2$ is the ferromagnetic spin fluctuation (paramagnon excitation) coexisting with the superconductivity. The ferromagnetic spin fluct--uation can be seen as the Stoner-enhanced Pauli susceptibility in the normal state. The isostructural compounds YCo_2, $ScCo_2$, and $LuCo_2$ are well known such examples. For YCo_2 and $LuCo_2$, clear metamagnetic transitions have been observed in the magnetization curves at high fields around 70 T.[2] According to the band structure calculations,[3] the sharp density-of-states peak near the Fermi energy mainly due to the Co $3d$ band plays a key role in the metamagnetic transitions. In fact, RCo$_2$ (R=magnetic rare-earth elements) are ferro or ferrimagnets depending on whether R is light (Pr, Nd, and Sm) or heavy (Gd and Tm) rare-earth elements.[4]

Recently, an anomalous peak effect has been observed in the magnetic fields just below H_{c2} in $CeCo_2$ (Refs. 1 and 5), which is similar to that reported for $CeRu_2$ (Ref. 6). This anomaly has been discussed as a possible realization of a Fulde-Ferrel-Larkin-Ovchinikov (FFLO) modulated superconducting state, where the large Pauli susceptibility was proposed to play a key role.[7]

These facts confirm that $CeCo_2$ is an ideal candidate to study the competition between the superconductivity and the ferromagnetic spin fluctuation. There have been no investigations using high quality single crystals so far, since $CeCo_2$ is an incongruent intermetallic compound. Recently, we succeeded in the preparation of $CeCo_2$ single crystals,[5] and reported the de Haas–van Alphen (dHvA) effect measurements.[8] The observed dHvA branches are well reproduced by the band structure calculation based on the itinerant $4f$ electrons of Ce. The calculation indicates that the contribution from Co $3d$, Ce $4f$, and Ce $5d$ states to the density of states at Fermi energy E_F are 45, 31, and 7%, respectively.[9] To investigate the character of the superconductivity in $CeCo_2$, we measured the low-temperature specific heat of $CeCo_2$ single crystals.

Single crystals of $CeCo_2$ were grown by the zone melting method in an induction furnace with a cold crucible under a high vacuum of 10^{-9} Torr. To check the sample dependence of the superconducting properties, we have prepared two samples, 1 and 2, with the residual resistivity ratio (RRR) of 100 and 150, respectively. The mass of the samples is 88 mg for sample 1 and 640 mg for sample 2, and the measurement accuracy is higher for sample 2 (lower than 5%). The sample 1 is the same as used for the dHvA measurements in Ref. 8. In the measurements, the quasiadiabatic heat pulse method was used using a dilution refrigerator.

The specific heat C and the electrical resistivity ρ around T_c are shown in Fig. 1 as a function of temperature. The values of T_c determined from C are 1.43 and 1.48 K for samples 1 and 2, respectively. The sample 2 with the larger RRR value has a higher T_c and a narrower transition width ΔT_c=0.03 K. For both samples, an antiferromagnetic transition anomaly at 5.9 K due to precipitated Ce_2O_3 phase, which was inevitably detected in early studies,[10] was not observed.

In the normal state, the temperature dependence of the specific heat can be described by $C/T=\gamma+\beta T^2$ below 4 K (see Fig. 2 in Ref. 5), from which the electronic specific heat coefficient γ and the Debye temperature Θ_D were

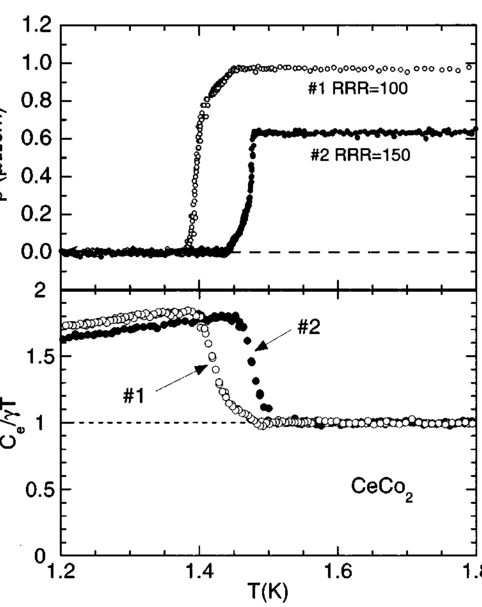

FIG. 1. Superconducting transition in the electrical resistivity and the specific heat for two samples with different residual resistivity ratio (RRR).

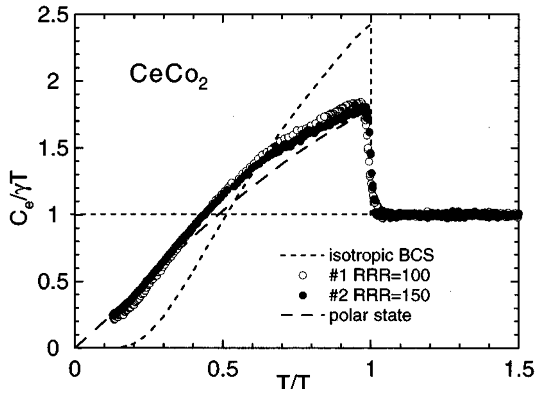

FIG. 2. T/T_c dependence of electronic specific heat C_e divided by γT. Theoretical curves for the isotropic-gap BCS and the polar state are drawn.

obtained: $\gamma = 33.5$ mJ/K^2 mol and $\Theta_D = 222$ K for sample 1, and $\gamma = 36.4$ mJ/K^2 mol and $\Theta_D = 200$ K for sample 2.

The estimated electronic specific heat C_e is shown in Fig. 2 as a function of T/T_c. Two important features are identified. First, the value of the specific heat jump at T_c ($\Delta C_e/\gamma T_c$) is 0.85 ± 0.05, which is anomalously diminished compared with 1.43 expected for the isotropic-gap BCS superconductors. Secondly, C_e at low temperatures, which gives the information on the density of states for the low-energy quasiparticle excitations in the superconducting state, shows an anomalous temperature dependence. For the isotropic-gap BCS model, C_e exponentially approaches zero with decreasing temperature due to the gap in the quasiparticle excitations. In contrast, for $CeCo_2$, $C_e/\gamma T$ decreases more slowly than that expected for the BCS model. In an Arrhenius' plot shown in Fig. 3, the data for $CeCo_2$ deviate from the exponential temperature dependence for the isotropic-gap BCS. If we compare it with the power-law variations of T, the temperature dependence of C_e is rather close to T^2 below 0.5 K as shown in the inset. These two facts indicate that the superconducting gap in $CeCo_2$ is anisotropic, i.e., the magnitude of the gap varies over the Fermi surface.

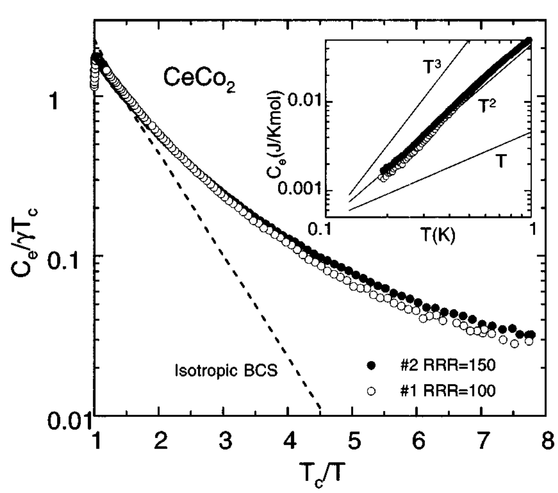

FIG. 3. Arrhenius' plot of electronic specific heat C_e. Inset shows the log-log plot of the electronic specific heat C_e as a function of temperature.

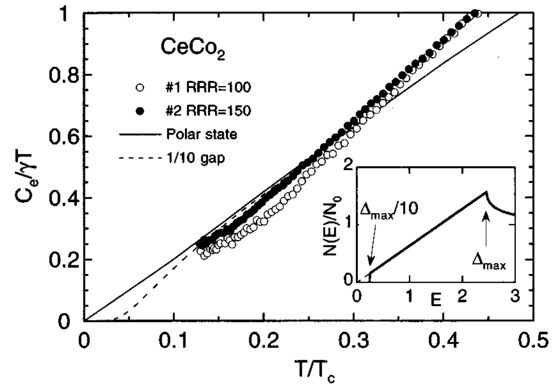

FIG. 4. Low-temperature expansion of $C_e/\gamma T$ vs T/T_c plot. Inset shows the energy dependences of the quasiparticle density of states for the polar state and that with the introduced minimum gap of $\Delta_{max}/10$.

In this temperature range, the nuclear contribution of specific heat is negligibly small; the electronic quadrupole splitting of ^{59}Co estimated by preliminary nuclear quadrupole resonance (NQR) experiments[11] gives a 0.2% correction to C_e at 0.2 K. These anomalous features in the superconducting state are reproducibly observed almost independent on the samples with different RRR as shown in Figs. 2 and 3.

To examine whether a nonzero residual $C_e/\gamma T$ would exist or not at $T=0$ K, we applied the condition of the entropy balance which helps to predict $C_e(T)$ for $T/T_c < 0.13$. The value of $\Delta S_e/\gamma T_c$, which is obtained by integrating the curve in Fig. 2 using

$$\frac{\Delta S_e}{\gamma T_c} = \int_0^{T=T_c} \frac{C_e}{\gamma T}\, d\left(\frac{T}{T_c}\right), \tag{1}$$

should be one when the entropy is balanced. We tested two different cases of the temperature dependence of C_e for $T/T_c < 0.13$. First, we assumed $C_e \propto T^2$ for $T/T_c < 0.13$; i.e., the data were extrapolated linearly to the origin in Fig. 2. The calculated value of $\Delta S_e/\gamma T_c$ was 1.03. Secondly, we assumed an extreme case where $C_e/\gamma T$ is constant for $T/T_c < 0.13$, i.e., $[C_e/\gamma T]_{T=0} = 0.2$. Then, $\Delta S_e/\gamma T_c$ becomes 1.05, which further deviates from one. Therefore, even if the residual $[C_e/\gamma T]_{T=0}$ exists, it should be much lower than 0.2.

A T^2 dependence of C_e was reported in the case of UPt_3 (Ref. 12) and URu_2Si_2 (Refs. 13 and 14). For these compounds, this is taken as an indication of non-s-wave superconductivity with gapless lines on the Fermi surface. The simplest anisotropic-gap state exhibiting the power law $C_e \sim T^2$ is the polar state, which has a line of zeros. As shown in Fig. 2, the $C_e/\gamma T$ vs T/T_c curve for the polar state shows a jump of 0.79 at T_c, and its temperature dependence agrees roughly with the experimental data of $CeCo_2$ over the entire temperature range. This indicates a possibility of lines of nodes in the gap. If we tentatively introduced a finite minimum gap $\Delta_{max}/10$ in the quasiparticle excitation of the polar state as shown in Fig. 4, where Δ_{max} represents the maximum value of the gap, a consequent decrease in C_e due to the finite gap was not detected distinguishably in the present experiment since it starts only below 0.15 K ($T/T_c \leqslant 0.1$). Although we cannot conclude whether a line of

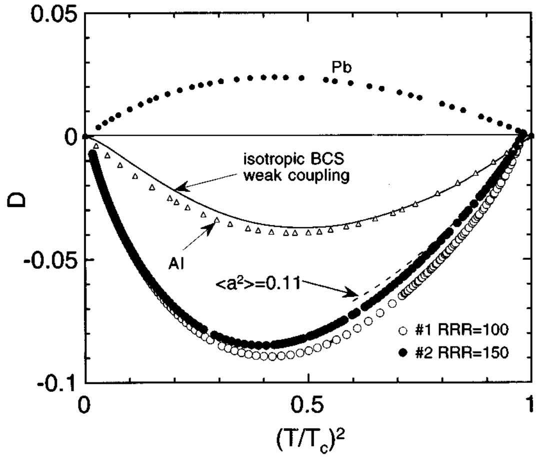

FIG. 5. Deviation function D, which represents the deviation of H_c from the parabolic temperature dependence. Isotropic gap BCS curve and the data for Al and Pb are plotted.

zeros in the gap really exists or not at the moment, however, these facts indicate that the superconducting gap is strongly anisotropic and at least $\Delta_{min}/\Delta_{max}\sim 0.1$. Such strong anisotropy has not been reported for cubic compounds before.

The temperature dependence of the thermodynamical critical field H_c of $CeCo_2$, which provides the characteristics of the superconductivity, is obtained by integrating the experimental data $C_e(T)$ in the superconducting state using

$$\Delta G=\frac{1}{2}\,\mu_0 V H_c^2(T)=\int_T^{T_c}\int_{T'}^{T_c}\frac{C_e(T'')-\gamma T''}{T''}\,dT''dT', \tag{2}$$

where V represents the volume per mole molecule. The zero temperature value $H_c(0)$ is obtained to be 340 Oe. Substituting this value of $H_c(0)$ into

$$\frac{1}{2}\,\mu_0 V H_0^2(0)=\frac{1}{2}\left(\frac{3\gamma}{2\pi^2 k_B^2}\right)\Delta(0)^2, \tag{3}$$

the energy gap $\Delta(0)$ is estimated to be $2\Delta(0)/k_BT_c=3.1$, which is smaller than the isotropic BCS value of 3.5. An additional distinctive feature of the superconductivity in $CeCo_2$ is found in the temperature dependence of H_c, which can be demonstrated using the deviation function $D(T/T_c)$ (Ref. 15) defined by

$$D(T/T_c)=H_c(T)/H_c(0)-[1-(T/T_c)^2], \tag{4}$$

as shown in Fig. 5. For comparison, two typical examples are also shown: Pb as a strong-coupling superconductor and Al as a weak-coupling superconductor which can be explained by the weak-coupling isotropic BCS curve. The D curve for $CeCo_2$ further deviates negatively from that for the weak-coupling case. This anomalous deviation of D can be attributed also to the anisotropic gap in $CeCo_2$. According to Clem's calculation[16] based on the weak-coupling BCS theory, the temperature dependence of D can be related to the square-averaged deviation of the gap parameter from its average value, defined as

$$\langle a^2\rangle=\langle(\Delta_p-\langle\Delta_p\rangle_{av})^2\rangle_{av}/\langle\Delta_p\rangle_{av}^2. \tag{5}$$

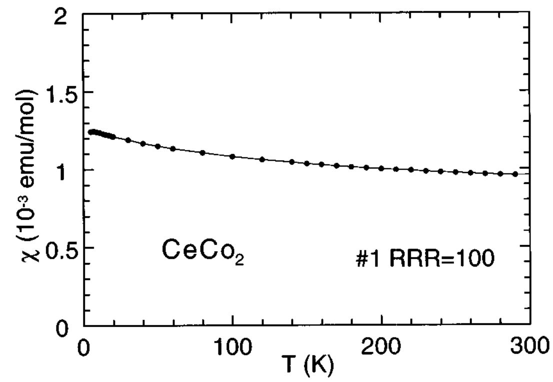

FIG. 6. Temperature dependence of the magnetic susceptibility.

Fitting the results of $D(T/T_c)$ using the Clem's theoretical curve, $\langle a^2\rangle$ is estimated to be 0.11. The fitted curve, drawn in Fig. 5, reproduces well the data below T_c. In terms of $\langle a^2\rangle$, the specific heat jump is described as

$$\Delta C_e/\gamma T_c=1.43(1-4\langle a^2\rangle). \tag{6}$$

The evaluated value of $\Delta C_e/\gamma T_c=0.8$ by substituting $\langle a^2\rangle=0.11$ into Eq. (6) is close to the measured value of 0.85.

The temperature dependence of the magnetic susceptibility $\chi(T)$ for $CeCo_2$ is shown in Fig. 6 (Ref. 17). Stoner-enhanced Pauli paramagnetism in $CeCo_2$ can be identified as a large value of χ in the normal state. The gradual decrease in χ with increasing temperature is possibly due to a strong energy dependence of the d-band density of states at E_F. The experimental value of $\chi_{exp}=(1.0\text{–}1.3)\times10^{-3}$ emu/mol is mainly ascribed to the conduction-electron Pauli susceptibility.[18]

Using $N(E_F)=154$ states/Ry cell,[8] we deduce the Stoner enhancement factor $S=\chi_{exp}/(\mu_B^2N(E_F))=5\text{–}7$, which is smaller than $S=20$ calculated by Eriksson *et al.*[19] Note that $S=6$ for Pd and $S=2-2.5$ for A-15 compounds.[18] For more detailed discussion, the separation of the orbital and spin contributions is necessary although the orbital contribution is expected to be one order of magnitude smaller than the spin contribution in a CeT_2 system.[19]

For a system with an enhanced χ_{Pauli}, the upper critical field H_{c2} could be suppressed by the strong Pauli limiting effect.[20] The Pauli limiting field H_p including the effect of the Stoner enhancement can be described by $H_p=\Delta_0/\mu_B(2S)^{1/2}$. Using the experimental data, H_p is estimated to be 0.9 T. This value of H_p is, however, still larger than the experimental value of $H_{c2}=0.2$ T indicating that H_{c2} is not limited by the Pauli limiting effect.

The γ value is generally expressed by $\gamma_{exp}=(1+\lambda_{e\text{-ph}}+\lambda_{spin})\gamma_{band}$ assuming no Kondo mass enhancement, where $\lambda_{e\text{-ph}}$ and λ_{spin} are the electron-mass renormalization factor due to the electron-phonon interaction and paramagnon spin fluctuations, respectively. Using the value of $\gamma_{band}=13.3$ mJ/K^2 mol from the band-structure calculation,[8] $(1+\lambda_{e\text{-ph}}+\lambda_{spin})$ is estimated to be 2.63. Assuming the electron-phonon interaction as the origin of the superconductivity in $CeCo_2$, a rough extimation based on the McMillan equation including λ_{spin} [Eq. (6) in Ref. 21] yields $\lambda_{e\text{-ph}}=1.2$ and $\lambda_{spin}=0.43$. If we substitute $\lambda_{spin}=0$ into the McMillan equation to examine the effect of the spin fluctuation, the value of T_c becomes 15 K, which is one order of magnitude larger than the experimental T_c. This indicates that T_c is largely suppressed by the strong spin fluctuations.

We discuss two possible origins for the anisotropic gap in $CeCo_2$: (1) the Ce Kondo-lattice effect and (2) the Stoner-enhanced Pauli paramagnetism. For the Kondo lattice system, Miyake *et al.*[22] and Ohkawa *et al.*[23] discussed the possibility of an anisotropic-gap singlet-pairing superconductivity, and pointed out that the low-lying excitations can be gapless for appropriate values of parameters characterizing the model. In $CeCo_2$, the Ce ions are in a strong mixed-valence state judging from no clear Kondo mass enhancement in γ value and the itineracy of the $4f$ electron confirmed by the dHvA measurements. Therefore, it is expected that the Stoner-enhanced Pauli paramagnetism plays a more important role in the anisotropic gap in $CeCo_2$ than the Kondo-lattice effect. The paramagnon excitation may cause strong pair breaking effect around $\mathbf{q}=0$ and, as a result, leads to a $\mathbf{q}$-dependent superconducting gap.

As another possibility for an anisotropic-gap superconductivity in the case of strong Stoner enhancement, a triplet-pairing superconductivity based on the paramagnon exchange mechanism can be possible as theoretically proposed by Appel and Fay[24] and Anderson.[25] Experiments to determine the superconducting symmetry in $CeCo_2$ is desired.

In summary, we have measured the low-temperature specific heat of high-quality $CeCo_2$ single crystals and found clear evidence of the anisotropic superconducting gap; the electronic specific-heat jump at T_c is reduced ($\Delta C_e/\gamma T_c=0.85$) and C_e varies approximately as T^2 at low temperatures of $0.13<T/T_c\ll 1$. We propose that the paramagnon excitation, which is related to the Stoner-enhanced Pauli susceptibility, is possibly the origin for the gap anisotropy in $CeCo_2$.

The authors would like to acknowledge Professor K. Miyake, Professor Y. Kitaoka, Dr. K. Ishida, and Dr. M. Higuchi for helpful discussions. They also thank O. Inoue for his technical support. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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[17] The values of χ were obtained using $[M(5\ \mathrm{T})-M(2.5\ \mathrm{T})]/(2.5\ \mathrm{T})$ to exclude the contribution of a small amount of magnetic impurity. If $\chi=M(0.1\ \mathrm{T})/(0.1\ \mathrm{T})$ was used, then it shows an upturn below 10 K, which is probably due to a precipitated Ce^{3+} magnetic impurity (estimated to be 0.04% using Curie law), which could consistently explain the excess entropy of $(\Delta S_e/\gamma T_c-1)\sim 0.03$. A preliminary NQR measurement [K. Ishida *et al.* (private communication)] shows that the spin-lattice relaxation rate T_1 obeys a Korringa law above T_c indicating the almost temperature independence of the intrinsic χ.

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