Superconducting Parameters of Spinel $CuRh_2S_4$ under Pressure

M. Ito*, A. Taira and K. Sonoda

Department of Physics and Astronomy, Graduate School of Science and Engineering, Kagoshima University, Kagoshima 890-0065, Japan

(Received February 16, 2016; revised version February 7, 2017; in final form April 14, 2017)

We investigated the magnetic properties of chalcogenide-spinel superconductor $CuRh_2S_4$ under pressure and estimated the pressure dependence of the superconducting parameters. With increasing pressure, the superconducting transition temperature (T_c), thermodynamic critical field (H_c), upper critical field (H_{c2}), penetration depth (λ), and GL parameter (κ) increase. Meanwhile, the lower critical field (H_{c1}) is unchanged and the Ginzburg–Landau coherence length (ξ_{GL}) is reduced by pressurization. The increasing value of κ indicates enhanced characteristics of the type-II superconductor $CuRh_2S_4$.

DOI: 10.12693/APhysPolA.131.1450

PACS/topics: 74.70.Dd, 74.62.Fj, 74.25.Bt

1. Introduction

Chalcogenide spinels, which have the chemical formula AB_2X_4 (A, B: transition metals, X: chalcogen), have a variety of attractive physical properties. The spinels have a cubic crystal structure with the space group $Fd\bar{3}m$. The characteristics of this structure are that A- and B-site ions are coordinated by four X-site ions to form a tetrahedron and by six X-site ions to form an octahedron, as shown in Fig. 1. Cu-based thiospinel tends to have a mixed-valence state at the B site; i.e., B^{3+} and B^{4+} coexist. $CuRh_2S_4$ is a Bardeen–Cooper–Schrieffer (BCS) superconductor with a superconducting transition temperature $T_c = 4.7$ K [1]. Hagino et al. investigated the electrical and thermodynamic properties of $CuRh_2S_4$, and estimated various superconducting parameters at ambient pressure [2]. Tachibana recently obtained a value for the zero-temperature upper critical field, $H_{c2}(0) = 33$ kOe, using low-temperature specific-heat measurements in a magnetic field [3]. The pressure dependence of T_c up to $P = 2.2$ GPa for the spinels $LiTi_2O_4$, $CuRh_2Se_4$, and $CuRh_2S_4$ was investigated by Shelton et al. [4]. They reported that T_c increases proportionally to P, because of the enhancement of the Debye temperature, θ.

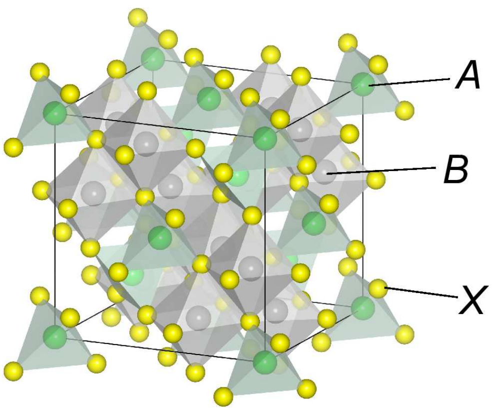

Fig. 1. Crystal structure of the spinel with the chemical formula AB_2X_4. The space group is $Fd\bar{3}m$.

Previously, one of the authors (M.I.) measured electric resistivity under pressure and reported the phenomenon of the pressure-induced transition of $CuRh_2S_4$ from a superconductor to an insulator [5]. With increasing pressure, T_c initially increases to a maximum value of 6.4 K at 4.0 GPa and then slightly decreases. With further compression, superconductivity in $CuRh_2S_4$ disappears abruptly at a critical pressure between 5.0 and 5.6 GPa, when it becomes an insulator. The origin of the pressure-induced transition from superconductor to insulator remains unclear. The present paper further investigates the effects of pressure on the superconducting properties of $CuRh_2S_4$, analyzes the magnetization of $CuRh_2S_4$ under pressure, and estimates the pressure dependence of superconductivity parameters.

2. Experimental details

Polycrystalline $CuRh_2S_4$ was prepared in a solid-state reaction. The temperature dependence of magnetization was measured using a Quantum Design MPMS SQUID magnetometer, in the temperature range from 2 to 10 K. The magnetization measurements were carried out after zero-field cooling to 2 K. Pressure up to 0.74 GPa was generated using a piston cylinder Be–Cu clamp cell that can be attached to the sample rod of the MPMS magnetometer [6]. The pressure in the low-temperature range was determined from the pressure dependence of the superconducting transition temperature of a small piece of Sn mounted in the pressure cell.

*corresponding author; e-mail: showa@sci.kagoshima-u.ac.jp

3. Results and discussion

3.1. Superconducting transition temperature, T_c

Figure 2a–c shows the temperature, T, dependence of magnetization divided by the applied field, M/H, of $CuRh_2S_4$ for various magnetic fields and pressures. At all pressures, M/H dropped greatly at T_c in the weakest magnetic field (H = 50 Oe). At P = 0.00 GPa, $T_{c\ p=0}$ was 4.5 K.

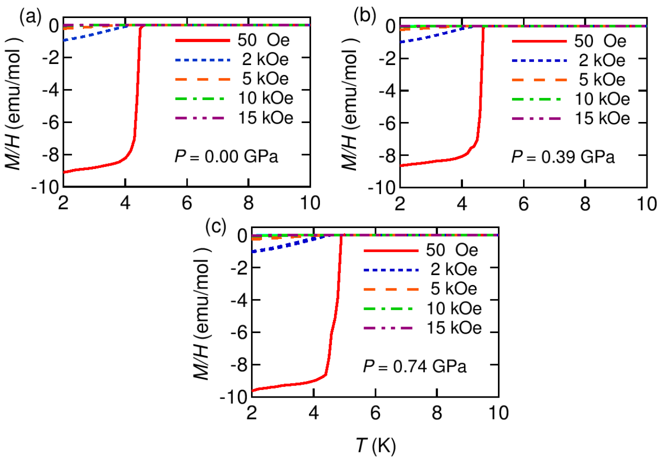

Fig. 2. Temperature dependence of magnetization divided by the applied field, M/H, of $CuRh_2S_4$ for (a) P = 0.00 GPa, (b) P = 0.39 GPa, and (c) P = 0.74 GPa.

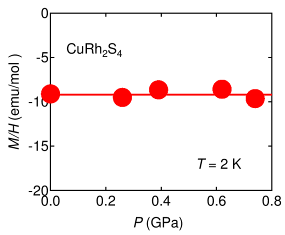

Fig. 3. Pressure dependence of M/H at T = 2 K and H = 50 Oe for $CuRh_2S_4$. The solid line is a visual aid.

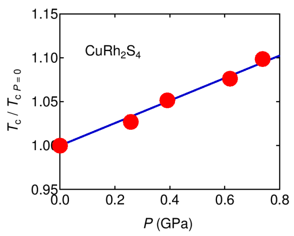

Fig. 4. Pressure dependence of the transition temperature normalized by the ambient pressure, $T_c/T_{c\ P=0}$, of $CuRh_2S_4$. The solid line shows the linear fitting result.

As shown in Fig. 3, M/H at $H = 50$ Oe and $T = 2$ K does not depend on P at $0 \leq P \leq 0.74$ GPa. This means that the shielding volume fraction of $CuRh_2S_4$ is insensitive to P.

Figure 4 shows the P dependence of T_c normalized by the value at P = 0.00 GPa, $T_c/T_{c\ p=0}$. With pressurization, $T_c/T_{c\ p=0}$ increases in proportion to P with an initial rate of $\mathrm{d}(T_c/T_{c\ p=0})/\mathrm{d}P = 1.28 \times 10^{-1}$ GPa^{-1}. When we employ $T_{c\ p=0} = 4.5$ K, $\mathrm{d}T_c/\mathrm{d}P$ is 0.57 K/GPa, which is close to the value ($\approx$ 0.5 K/GPa) reported by Shelton et al. [4]. This increase in T_c is due to increase of θ as mentioned in Introduction. According to BCS theory, T_c can be described using θ, electron–lattice interaction U, and the density of states at the Fermi energy D_{E_F} as $T_c = 1.14\theta \exp(-1/UD_{E_F})$. In general, with pressurization, θ increases and D_{E_F} decreases owing to the Pauli exclusion principle. The increase in θ and decrease in D_{E_F} increase and decrease T_c, respectively. As mentioned in Introduction, from the electrical resistivity measurement under pressure, we found that the P dependence of T_c changes from increase to decrease at P = 4.0 GPa [5]. At $P >$ 4.0 GPa, the reduction of D_{E_F} might strongly affect the P dependence of T_c for $CuRh_2S_4$.

3.2. Upper critical field, H_{c2}

Figure 5 shows the magnetization of $CuRh_2S_4$, $-4\pi M$, as a function of the magnetic field at 2 K for various pressures. In the range of a weak magnetic field, $-4\pi M$ increases linearly. After peaking at H of around 1200 Oe, $-4\pi M$ decreases with H and reaches zero at around 2000–2500 Oe. For $-4\pi M$ at various P, it is difficult to determine the zero-temperature upper critical field, $H_{c2}(0)$, directly from experimental results. We estimate the P dependence of $H_{c2}(0)$ from the results for the lowest temperature (T = 2 K), H_{c2}(2 K). H_{c2}(2 K) can be obtained as the magnetic field at which $-4\pi M$=0, as shown by the arrows in the main part of Fig. 5.

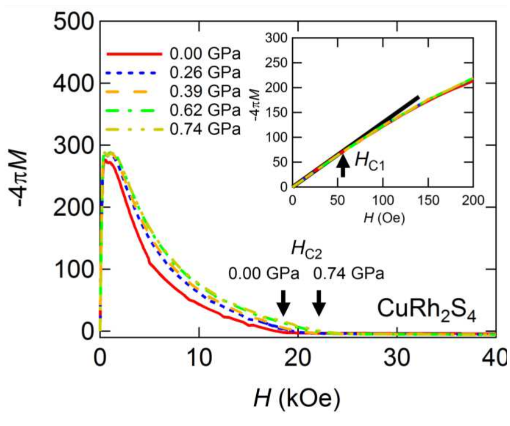

Fig. 5. Magnetic field dependence of magnetization (i.e., M–H curve) for $CuRh_2S_4$ at T = 2 K and various pressures. The arrows show the representative points of H_{c2} for P = 0 and 0.74 GPa. The inset is the expanded plot of the low-field range. The arrow shows the point of deviation of M from linear dependence.

Figure 6 shows the P dependence of H_{c2}(2 K) normalized by the value at P = 0 GPa, $H_{c2}(2\ \mathrm{K})/H_{c2}(2\ \mathrm{K})_{P=0}$. Previously, the P dependence of $H_{c2}(0)$ was indirectly estimated [7] using the Werthamer–Helfand–Hohenberg (WHH) formula [8], $H_{c2}(0) = 0.693T_c \left|\frac{dH_{c2}}{dT}\right|_{T_c}$; the obtained $H_{c2}(0)/H_{c2}(0)_{P=0}$ is also plotted in the figure. The P responses of $H_{c2}(2\text{ K})/H_{c2}(2\text{ K})_{P=0}$ and $H_{c2}(0)/H_{c2}(0)_{P=0}$ are similar and we consider $H_{c2}(2\text{ K})/H_{c2}(2\text{ K})_{P=0} = H_{c2}(0)/H_{c2}(0)_{P=0}$. We obtained the initial increasing rate of $d(H_{c2}(0)/H_{c2}(0)_{P=0})/dP = 2.73 \times 10^{-1}$ GPa^{-1} from the solid line in Fig. 6. When we use $H_{c2}(0) = 33$ kOe, obtained from the specific-heat measurement under a magnetic field [3], $H_{c2}(0)$ reaches ≈ 40 kOe at $P = 0.74$ GPa.

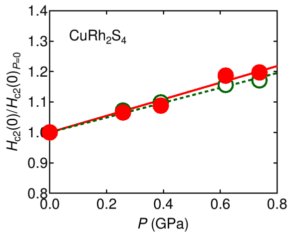

Fig. 6. Pressure dependence of the zero-T upper critical field normalized by ambient pressure, $H_{c2}(0)/H_{c2}(0)_{P=0}$, estimated from the WHH formula (open circles) and from the M–H curves at 2 K (closed circles). The solid and dotted lines show linear fitting results.

3.3. Ginzburg–Landau coherence length, ξ_{GL}

The Ginzburg–Landau (GL) coherence length, ξ_{GL}, can be obtained from the relation

$$\xi_{GL} = \left(\frac{\Phi_0}{2\pi H_{c2}(0)}\right)^{1/2}, \tag{1}$$

where Φ_0 ($= 2.07 \times 10^{-7}$ G cm^2) is the magnetic flux quantum. The pressure dependence of ξ_{GL} is estimated using Eq. (1) and the P dependence of $H_{c2}(0)$. Figure 7 shows ξ_{GL} normalized by the value of ambient pressure, $\xi_{GL}/\xi_{GL P=0}$, as a function of P. With increasing P, $\xi_{GL}/\xi_{GL P=0}$ decreases with an initial rate of -1.10×10^{-1} GPa^{-1}. When $H_{c2}(0) = 33$ kOe [3] is adopted, $\xi_{GL P=0} = 93$ Åis estimated, and ξ_{GL} reduces to 85 Åat $P = 0.74$ GPa with pressurization.

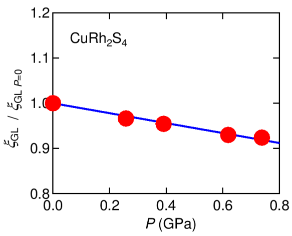

Fig. 7. Pressure dependence of the GL coherence length normalized by ambient pressure, $\xi_{GL}/\xi_{GL\ P=0}$, of $CuRh_2S_4$. The solid line shows the linear fitting result.

3.4. Penetration depth, λ, GL parameter, κ, lower critical field, H_{c1}, and thermodynamic critical field, H_c

Penetration depth, λ, is related to the zero-temperature thermodynamic critical field, $H_c(0)$, by

$$H_c(0) = \frac{\Phi_0}{2\sqrt{2}\pi\lambda\xi_{GL}}. \tag{2}$$

λ at $P = 0$ GPa, $\lambda_{P=0}$, is 3558 Å, when using $H_c(0)_{P=0} = 704$ Oe reported by Hagino et al. [2]. Meanwhile, the zero-temperature lower critical field, $H_{c1}(0)$, is expressed as

$$H_{c1}(0) = \frac{\Phi_0}{4\pi\lambda^2(0)} \ln\kappa, \tag{3}$$

where the GL parameter κ is

$$\kappa = \frac{\lambda}{\xi_{GL}}. \tag{4}$$

We get $H_{c1}(0) = 47$ Oe using $\lambda_{P=0} = 3558$ Åand $\xi_{GL P=0} = 93$ Åfrom Eqs. (3) and (4). It is difficult to measure $H_{c1}(0)$ accurately from M–H curves obtained in experiments. We estimated the lower critical field at $T = 2$ K, $H_{c1}(2\text{ K}) = 55$ Oe, as the point at which $-4\pi M$ deviates from having a linear dependence on H as shown by an arrow in the inset of Fig. 5. This value of $H_{c1}(2\text{ K})$ is close to $H_{c1}(0)$ (≈ 47 Oe) obtained above. Because $H_{c1}(2\text{ K})$ is insensitive to P up to 0.74 GPa, we consider that $H_{c1}(0)$ is also constant for varying P. From numerical calculations using Eq. (3), (4) and the P dependence of ξ_{GL} (Fig. 7), the P dependence of λ can be obtained.

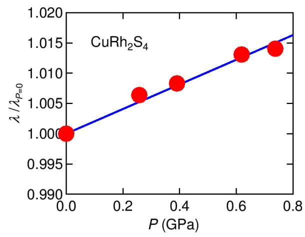

Fig. 8. Pressure dependence of the penetration depth normalized by ambient pressure, $\lambda/\lambda_{P=0}$, of $CuRh_2S_4$.

Figure 8 shows the P dependence of $\lambda/\lambda_{P=0}$. With increase of P, $\lambda/\lambda_{P=0}$ increases with an initial rate of 2.04×10^{-2} GPa^{-1}. κ at $P = 0$ GPa, $\kappa_{P=0}$, has a value of 38 according to Eq. (4). The P dependence of κ is obtained from the results presented in Figs. 7 and 8. Figure 9 shows that $\kappa/\kappa_{P=0}$ increases monotonically against P with an initial rate of 1.33×10^{-1} GPa^{-1}. It is well known that superconductors are classified as type-I superconductors for $\kappa < 1/\sqrt{2}$ and type-II superconductors for $\kappa > 1/\sqrt{2}$. $CuRh_2S_4$ is a typical type-II superconductor with $\kappa_{P=0} = 21 \div 38$ [2]. The increasing value of $\kappa/\kappa_{P=0}$ means that the characteristics of the type-II superconductor of this system are further enhanced by pressurization. We finally estimated the P dependence of $H_c(0)$ using Eq. (2), as shown in Fig. 10. $H_c(0)/H_c(0)_{P=0}$ increases with pressurization at an initial rate of 9.62×10^{-2} GPa^{-1}.

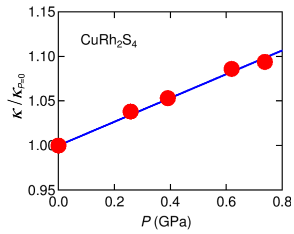

Fig. 9. Pressure dependence of the GL parameter normalized by ambient pressure, $\kappa/\kappa_{P=0}$, of $CuRh_2S_4$. The solid line shows the linear fitting result.

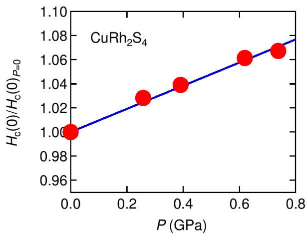

Fig. 10. Pressure dependence of the zero-T thermodynamic critical field normalized by ambient pressure, $H_c(0)/H_c(0)_{P=0}$, of $CuRh_2S_4$. The solid line shows the linear fitting result.

4. Conclusion

We investigated the magnetization of spinel superconductor $CuRh_2S_4$ under pressure and obtained the pressure dependence of superconducting parameters. T_c increases at the rate $\mathrm{d}(T_c/T_{c\ p=0})/\mathrm{d}P = 1.28 \times 10^{-1}$ GPa^{-1}. We also obtained the initial rates of change with pressure $\mathrm{d}(H_c(0)/H_c(0)_{P=0})/\mathrm{d}P = 9.62 \times 10^{-2}$ GPa^{-1}, $\mathrm{d}(H_{c2}(0)/H_{c2}(0)_{P=0})/\mathrm{d}P = 2.73 \times 10^{-1}$ GPa^{-1}, $\mathrm{d}(\lambda/\lambda_{P=0})/\mathrm{d}P = 2.04 \times 10^{-2}$ GPa^{-1}, $\mathrm{d}(\kappa/\kappa_{P=0})/\mathrm{d}P = 1.33 \times 10^{-1}$ GPa^{-1}, and $\mathrm{d}(\xi_{\mathrm{GL}}/\xi_{\mathrm{GL}P=0})/\mathrm{d}P = -1.10 \times 10^{-1}$ GPa^{-1}. Meanwhile, $H_{c1}(0)$ does not change with pressurization. The pressure dependence of superconducting parameters of $CuRh_2S_4$ is summarized in Table I. Because $(\kappa/\kappa_{P=0})$ increases with pressurization, the superconducting state of $CuRh_2S_4$ enhances the features of a type-II superconductor with pressurization. More detailed pressure studies in a higher pressure range are needed to clarify the origin of the pressure-induced transition of this system from superconductor to insulator.

TABLE I

Superconducting parameters of $CuRh_2S_4$ under pressure.

Parameter	Initial change rate with pressure [GPa^{-1}]
$T_c/T_{c\ P=0}$	0.128
$(M/H)/(M/H)_{P=0}$	no change
$H_c(0)/H_c(0)_{P=0}$	0.0962
$H_{c1}(0)/H_{c1}(0)_{P=0}$	no change
$H_{c2}(0)/H_{c2}(0)_{P=0}$	0.273
$\xi_{\mathrm{GL}}/\xi_{\mathrm{GL}P=0}$	–0.11
$\lambda/\lambda_{P=0}$	0.0204
$\kappa/\kappa_{P=0}$	0.133

Acknowledgments

The figure of the crystal structure was drawn with VESTA [9].

References

[1] N.H. Van Maaren, G.M. Schaeffer, F.K. Lotgering, *Phys. Lett. A* **25**, 238 (1967).

[2] T. Hagino, Y. Seki, N. Wada, S. Tsuji, T. Shirane, K. Kumagai, S. Nagata, *Phys. Rev. B* **51**, 12673 (1995).

[3] M. Tachibana, *Solid State Commun.* **152**, 849 (2012).

[4] R.N. Shelton, D.C. Johnston, H. Adrian, *Solid State Commun.* **20**, 1077 (1976).

[5] M. Ito, J. Hori, H. Kurisaki, H. Okada, A.J. Perez Kuroki, N. Ogita, M. Udagawa, H. Fujii, F. Nakamura, T. Fujita, T. Suzuki, *Phys. Rev. Lett.* **91**, 077001 (2003).

[6] Y. Uwatoko, T. Hotta, E. Matsumoto, H. Mori, T. Ohki, J.L. Sarrao, J.D. Thompson, N. Mori, G. Oomi, *Rev. High Pressure Sci. Technol.* **7**, 1508 (1998).

[7] M. Ito, K. Ishii, F. Nakamura, T. Suzuki, *AIP Conf. Proc.* **850**, 627 (2006).

[8] N.R. Werthamer, E. Helfand, P.C. Hohenberg, *Phys. Rev.* **147**, 295 (1966).

[9] K. Momma, F. Izumi, *J. Appl. Crystallogr.* **44**, 1272 (2011).