Superconducting Parameters of Spinel CuRh$_2$S$_4$ under Pressure

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We investigated the magnetic properties of chalcogenide-spinel superconductor CuRh$_2$S$_4$ 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 ($\lambda$), and GL parameter ($\kappa$) increase. Meanwhile, the lower critical field ($H_{c1}$) is unchanged and the Ginzburg–Landau coherence length ($\xi_{GL}$) is reduced by pressurization. The increasing value of $\kappa$ indicates enhanced characteristics of the type-II superconductor CuRh$_2$S$_4$.

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1. Introduction

Chalcogenide spinels, which have the chemical formula AB$_2$X$_4$ (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$_2$S$_4$ 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$_2$S$_4$, 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$_2$O$_4$, CuRh$_2$Se$_4$, and CuRh$_2$S$_4$ was investigated by Shelton et al. [4]. They reported that $T_c$ increases proportionally to $P$, because of the enhancement of the Debye temperature, $\theta$.

Previously, one of the authors (M.I.) measured electric resistivity under pressure and reported the phenomenon of the pressure-induced transition of CuRh$_2$S$_4$ 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$_2$S$_4$ 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$_2$S$_4$, analyzes the magnetization of CuRh$_2$S$_4$ under pressure, and estimates the pressure dependence of superconductivity parameters.

2. Experimental details

Polycrystalline CuRh$_2$S$_4$ 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.

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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$_2$S$_4$ 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, $T_c = 0$ was 4.5 K.

![Fig. 2](image)

Figure 2. Temperature dependence of magnetization divided by the applied field, $M/H$, of CuRh$_2$S$_4$ for (a) $P = 0.00$ GPa, (b) $P = 0.39$ GPa, and (c) $P = 0.74$ GPa.

As shown in Fig. 3, $M/H$ at $T = 2$ K and $H = 50$ Oe for CuRh$_2$S$_4$. The solid line is a visual aid.

![Fig. 3](image)

Fig. 3. Pressure dependence of $M/H$ at $T = 2$ K and $H = 50$ Oe for CuRh$_2$S$_4$. The solid line is a visual aid.

As shown in Fig. 3, $M/H$ at $T = 2$ K and $H = 50$ Oe does not depend on $P$ at $0 \leq P \leq 0.74$ GPa. This means that the shielding volume fraction of CuRh$_2$S$_4$ is insensitive to $P$.

![Fig. 4](image)

Fig. 4. Pressure dependence of the transition temperature normalized by the ambient pressure, $T_c/T_c|_{P=0}$, of CuRh$_2$S$_4$. The solid line shows the linear fitting result.

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 $d(T_c/T_c|_{P=0})/dP = 1.28 \times 10^{-1}$ GPa$^{-1}$. When we employ $T_c|_{P=0} = 4.5$ K, $dT_c/dP$ 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 $\theta$ as mentioned in Introduction. According to BCS theory, $T_c$ can be described using $\theta$, electron–lattice interaction $U$, and the density of states at the Fermi level $D_F$.

![Fig. 5](image)

Fig. 5. Magnetic field dependence of magnetization (i.e., $M$–$H$ curve) for CuRh$_2$S$_4$ 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 5 shows the magnetization of CuRh$_2$S$_4$, $-4\pi M$, 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 reaching 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.

3.2. Upper critical field, $H_{c2}$

Figure 5 shows the $M$ dependence of CuRh$_2$S$_4$, $-4\pi M$, 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 reaching 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.
estimated [7] using the Werthamer–Helfand–Hohenberg (WHH) formula [8], $H_{c2}(0) = 0.693T_c \left| \frac{dH}{dT} \right|_{T_c}$; the obtained $H_{c2}(0)/H_{c2}(p=0)$ 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 $\frac{d(H_{c2}(0)/H_{c2}(0)_{P=0})}{dP} = 2.73 \times 10^{-1} \text{ GPa}^{-1}$ from the solid line in Fig. 6. When we use $H_{c2}(0) = 33 \text{ kOe}$, obtained from the specific-heat measurement under a magnetic field [3], $H_{c2}(0)$ reaches $\approx 40 \text{ kOe}$ at $P = 0.74 \text{ GPa}$.

3.3. Ginzburg–Landau coherence length, $\xi_{GL}$

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

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

where $\Phi_0 = 2.07 \times 10^{-7} \text{ G cm}^2$ is the magnetic flux quantum. The pressure dependence of $\xi_{GL}$ is estimated using Eq. (1) and the $P$ dependence of $H_{c2}(0)$. Figure 7 shows $\xi_{GL}$ 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 $-1.10 \times 10^{-1} \text{ GPa}^{-1}$. When $H_{c2}(0) = 33 \text{ kOe}$ [3] is adopted, $\xi_{GL,P=0} = 93 \text{ Å}$ estimated, and $\xi_{GL}$ reduces to $85 \text{ Å}$ at $P = 0.74 \text{ GPa}$ with pressurization.

3.4. Penetration depth, $\lambda$, GL parameter, $\kappa$, lower critical field, $H_{c1}$, and thermodynamic critical field, $H_c$

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

$$H_c(0) = \frac{\Phi_0}{2\sqrt{2\pi\lambda_{GL}}},$$

where the GL parameter $\kappa$ is

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

We get $H_{c1}(0) = 47 \text{ Oe}$ using $\lambda_{P=0} = 3558 \text{ Å}$ and $\xi_{GL,P=0} = 93 \text{ Å}$ from 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 $T = 2 \text{ K}$, $H_{c1}(2 \text{ K}) = 55 \text{ Oe}$, as the point at which $\lambda$ 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 $H_{c1}(0) (\approx 47 \text{ Oe})$ 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 $\xi_{GL}$ (Fig. 7), the $P$ dependence of $\lambda$ can be obtained.

Figure 8 shows the $P$ dependence of the penetration depth normalized by ambient pressure, $\lambda/\lambda_{P=0}$, of CuRh$_2$S$_4$.

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 $2.04 \times 10^{-2} \text{ GPa}^{-1}$. $\kappa$ at $P = 0 \text{ GPa}$, $\kappa_{P=0}$, has a value of 38 according to Eq. (4). The $P$ dependence of $\kappa$ 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 $1.33 \times 10^{-1} \text{ GPa}^{-1}$. 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$_2$S$_4$ is a typical type-II superconductor with $\kappa_{P=0} = 21 \Rightarrow 38$ [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 $H_e(0)$ using Eq. (2), as shown in Fig. 10. $H_e(0)/H_e(0)_{P=0}$ increases with pressurization at an initial rate of $9.62 \times 10^{-2} \text{ GPa}^{-1}$. 

![Fig. 6. Pressure dependence of the zero-T upper critical field normalized by ambient pressure, $H_{c2}(0)/H_{c2}(0)_{P=0}$, estimated using 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.](image)

![Fig. 7. Pressure dependence of the GL coherence length normalized by ambient pressure, $\xi_{GL}/\xi_{GL,P=0}$, of CuRh$_2$S$_4$. The solid line shows the linear fitting result.](image)

![Fig. 8. Pressure dependence of the penetration depth normalized by ambient pressure, $\lambda/\lambda_{P=0}$, of CuRh$_2$S$_4$.](image)
4. Conclusion

We investigated the magnetization of spinel superconductor CuRh$_2$S$_4$ under pressure and obtained the pressure dependence of superconducting parameters. $T_c$ increases at the rate $d(T_c/T_{c\ P=0})/dP = 0.128$ GPa$^{-1}$. We also obtained the initial rates of change with pressure $d(H_c(0)/H_{c\ P=0})/dP = 0.0962$, $d(H_{c1}(0)/H_{c1\ P=0})/dP = 0.273$, $d(H_{c2}(0)/H_{c2\ P=0})/dP = 0.0204$, $d(\kappa/\kappa_{P=0})/dP = 0.133$, and $d(\xi_{GL}/\xi_{GL\ P=0})/dP = -0.11$. Meanwhile, $H_{c1}(0)$ does not change with pressurization. The pressure dependence of superconducting parameters of CuRh$_2$S$_4$ is summarized in Table I. Because $(\kappa/\kappa_{P=0})$ increases with pressurization, the superconducting state of CuRh$_2$S$_4$ 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>
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<th>Parameter</th>
<th>Initial change rate with pressure [GPa$^{-1}$]</th>
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<tr>
<td>$T_c/T_{c\ P=0}$</td>
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<tr>
<td>$(M/H)/(M/H)_{P=0}$</td>
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<tr>
<td>$H_c(0)/H_{c\ P=0}$</td>
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<tr>
<td>$H_{c1}(0)/H_{c1\ P=0}$</td>
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<tr>
<td>$H_{c2}(0)/H_{c2\ P=0}$</td>
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</tr>
<tr>
<td>$\xi_{GL}/\xi_{GL\ P=0}$</td>
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<tr>
<td>$\lambda/\lambda_{P=0}$</td>
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<tr>
<td>$\kappa/\kappa_{P=0}$</td>
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Acknowledgments

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

References