Weakly-correlated nodeless superconductivity in single crystals of Ca$_3$Ir$_4$Sn$_{13}$ and Sr$_3$Ir$_4$Sn$_{13}$ revealed by critical fields, Hall effect, and magnetoresistance measurements

L M Wang, Chih-Yi Wang, Guan-Min Chen, C N Kuo and C S Lue

1 Graduate Institute of Applied Physics/Department of Physics, National Taiwan University, Taipei 106, Taiwan
2 Department of Physics, National Cheng Kung University, Tainan 70101, Taiwan
3 Taiwan Consortium of Emergent Crystalline Materials, Ministry of Science and Technology, Taipei 10601, Taiwan

E-mail: liminwang@ntu.edu.tw and cslue@mail.ncku.edu.tw

Keywords: superconductivity, electronic correlation, charge density wave

Abstract

We report a study of single crystal Ca$_3$Ir$_4$Sn$_{13}$ (CIS) and Sr$_3$Ir$_4$Sn$_{13}$ (SIS) by measuring the longitudinal and Hall resistivities, upper and lower critical fields and magnetoresistance, as well as the magnetization. The sign change in the Hall coefficient observed on both the CIS and SIS provides direct evidence for the Fermi surface reconstructing during the superlattice phase transition. Both materials are of current interest due to indications of superconductivity associated with charge-density-wave (CDW) ordering. Observations of the diamagnetic feature and the lower critical field $H_{c1}(T)$ in both CIS and SIS can be realized by means of the nodeless single-gap BCS theory. In addition, a weak electronic correlation in both systems has been revealed by the small values of the spin exchange energy, upper critical field and $\Delta(0)/k_B T_c$ ratio, derived respectively from the normal-state Hall effect, resistive transition and temperature-dependent $H_{c1}$. It is noticeable that the magnetoresistance of SIS shows a rapid increase below $T' \sim 40$ K, following Kohler’s scaling rule. The results of the magnetic susceptibility and Hall coefficient also exhibit anomalous features near $T'$. With respect to these observations, this suggests that the existence of an additional phonon mode with energy of about 4.0 meV in SIS is responsible for the presence of lattice instability toward a phase transition.

1. Introduction

The unique properties that develop in quantum critical matter have become a major focus of research over the past two decades. Within the quantum-mechanical phase transition, the singular quantum critical point (QCP) at absolute zero produces a wide region of unusual behavior at a finite temperature. Here, a QCP can be tuned by a nonthermal-control parameter, such as the magnetic field, pressure or chemical composition, and crucially influences the physical properties in correlated electronic systems. For example, it is believed that high-temperature superconducting (HTS) cuprates and a whole host of other superconductors with quasi-linearly temperature-dependent resistivity in the normal state are driven by quantum criticality. Recent investigations into (Sr, Ca)$_3$Ir$_4$Sn$_{13}$ have demonstrated the pressure- and composition-induced structure quantum phase transition in these cubic superconductors [1, 2]. Unlike the case of high-temperature superconductors, superconducting iron-based pnictides or some heavy-fermion superconductors in which superconductivity emerges as the spin-density-wave (SDW) order is suppressed [3], the superconductivity in the (Sr, Ca)$_3$Ir$_4$Sn$_{13}$ system is driven by the suppression of charge-density-wave (CDW) ordering induced in their superlattice structure. This new kind of quantum phase transition provides a new opportunity to understand the interplay between superconductivity and structural instabilities.

Sr$_3$Ir$_4$Sn$_{13}$ (SIS) has been found to be a superconductor of $T_c = 5$ K and has distinct anomalies in the electrical and thermal transport properties, magnetic susceptibility and nuclear magnetic resonance (NMR) at $T' \sim 147$ K, as characterized in previous research [4]. Applying the chemical pressure by alloying calcium in (Sr,
Ca$_3$Ir$_4$Sn$_{13}$ results in the suppression of the anomaly to $T^* \sim 33$ K in Ca$_3$Ir$_4$Sn$_{13}$ (CIS) and the enhancement of the superconducting transition to $T_c = 7$ K [1]. With various measurements, both CIS and SIS have been recognized as BCS-type superconductors with the nodeless $s$-wave superconducting gaps [5–7]. Specific heat studies have yielded $\Delta C_p/\gamma T_c$ values of 2.09 and 2.78 for SIS and CIS single crystals, respectively [5, 8]; where $C_p$ is the electronic specific heat, and $\gamma$ is the electronic specific heat coefficient (Sommerfeld constant). In addition, the specific heat and spin rotation measurements have also derived $\Delta (0)/k_B T_c$ values of 2.04 and $\sim 5$ for SIS and CIS, respectively [5, 9], where $\Delta (0)$ is the superconducting energy gap at zero temperature. Since these obtained values are relatively larger than those of $\Delta C_p/\gamma T_c = 1.43$ and $\Delta (0)/k_B T_c = 1.76$, expected from the BCS theory, both materials have been categorized as strong-coupling superconductors. However, a small ratio of the superconducting transition temperature to normalized Fermi temperature $T_c/\Delta (0) \sim 0.001$ revealed from the Seebeck coefficient measurement on CIS single crystals implies a weakly electronic correlation in CIS [10]. Also, the contradictory results have been observed through the magnetization measurements on CIS. Wang and Petrovic [10] showed weak diamagnetic behavior for CIS in the normal state, while Yang et al. [8] noticed a broad peak feature in the magnetic susceptibility and associated the observation with the coexistence of the superconductivity and ferromagnetic spin fluctuation in CIS. In addition to reexamining the magnetic properties of CIS, the inconsistency also highlights the necessity of reconfirming the gap symmetry in SIS and CIS because the ferromagnetic spin fluctuation usually results in a superconducting gap with nodes [11]. In addition, as pointed out by Gerber et al [9], so far only a few of the physical properties were reported in early studies even though the CIS compound was first synthesized more than 30 years ago, leading into many points which need to be clarified. In this study, the electronic correlation and superconducting gap symmetry in single crystals of CIS and SIS were probed by both electrical transport and magnetization measurements. A new approach to the superconducting gap energy and spin exchange energy via the upper and lower critical fields, and the normal-state Hall effect for CIS and SIS, are presented. The upper and lower critical fields, gap properties, normal-state Hall angle and magnetoresistance extracted for the first time from these experiments provide much key information on the electronic correlation in this new kind of CDW-related superconductor.

2. Experimental

Single crystals of CIS and SIS were grown by the Sn self-flux method. The crystals were well-formed slabs with the crystalline [110] orientation perpendicular to the plane of the crystal slabs, as described previously [4]. The magnetization $M$ was measured in a superconducting quantum interference device (SQUID) system (MPMS from Quantum Design). For in-plane transport measurements, the samples were cut into dimensions of around $2.5 \times 0.8 \times 0.08$ mm$^3$. Five leads were soldered with indium, and a Hall-measurement geometry was constructed to allow simultaneous measurements of both longitudinal ($\rho_{xx}$) and transverse (Hall) resistivities ($\rho_{xy}$) using the standard DC four-probe technique. Hall voltages were taken in opposing fields parallel to the c-axis up to 6 T and at an in-plane current density of $\sim 60$ A cm$^{-2}$.

3. Results and discussion

Figures 1(a) and (b) show the temperature dependence of effective magnetic susceptibility $\chi_{eff}(T)$ in a field of 0.5 T with $H//[110]$ and $H\perp[110]$ for CIS and SIS, respectively. Here, the demagnetization effect arisen from the geometric factor is considered, and the corrected effective magnetic susceptibility is calculated using $\chi_{eff}(T) = \chi/(1-\chi N)$, where $\chi = M/H$ and $N$ is the demagnetization factor, which can be obtained from the magnetization in the Meissner state [12]. The demagnetization factors of $N = 0.974$ and 0.972 are thus obtained for CIS and SIS, respectively. As can be seen, both CIS and SIS reveal a diamagnetic feature in the entire temperature range investigated, and the behaviors of $\chi_{eff}(T)$ in cases of out-of-plane ($H//[110]$) and in-plane ($H\perp[110]$) configurations show similar results, indicating weak anisotropy in this system. The anomalies of $\chi_{eff}(T)$ appearing around $T^* = 35$ and 147 K due to CDW transition for CIS and SIS, respectively, are consistent with previous observations [1, 10]. The insets of figures 1(a) and (b) show the zero-field–cooling magnetization in $H = 10$ Oe around superconducting transition temperatures for CIS and SIS, respectively. The observation of $T_c \sim 5$ and 7 K for CIS and SIS, respectively, are also consistent with previous reports [5, 8]. The right inset of figure 1(a) shows the field-dependent magnetization for CIS at 50 K within magnetic fields of up to 2 T and confirms the diamagnetic feature in it. Such an observation is in accordance with that reported by Wang and Petrovic [10] but is contrary to that reported by Yang et al. [8]. The observation also confirms that both SIS and CIS have a weak diamagnetic property, being consistent with the results of electronic structure calculations [2] as well as with recent muon spin rotation ($\mu$SR) measurements [9, 13]. In addition, the low-temperature $\chi_{eff}(T)$ for SIS shows an anomalous increase at temperature $T^*$ of $\sim 40$ K, as shown in the right inset of figure 1(b). This
temperature corresponds to some anomalies appearing in the Hall coefficient and magnetoresistance and will be discussed later.

Figure 2(a) shows the temperature-dependent resistivities for CIS and SIS samples. Obviously, two pronounced anomalies of resistivity appearing around \( T^* = 35 \) and 147 K due to CDW transitions for CIS and SIS, respectively, are observed, which are also consistent with previous observations on magnetization results. The inset of figure 2(a) shows resistive transition near the superconducting critical temperatures for the CIS and SIS samples. Sharp superconducting transitions with superconducting critical temperatures of 7.1 and 5.1 K for CIS and SIS samples, respectively, have been observed. Figure 2(b) illustrates the temperature dependence of the Hall coefficient \( R_H \) for both CIS and SIS measured at \( H = 3 \) T. As shown, the \( R_H \) values at temperatures above CDW transition temperature \( T^* \) are negative and signify that electron-type carriers dominate the electrical transport in both CIS and SIS single crystals. Below \( T^* \), a sharp reduction in \( |R_H| \) value accompanying a sign change at around \( T^* \) is observed on both the CIS and SIS. Such a sign change in \( R_H \) can be attributed to the sudden change in band structure accompanying the Fermi surface reconstructing during the superlattice phase transition. Recent electronic structure calculations for SIS have shown the characteristics of nesting Fermi surface sheets and illustrate a difference in the total Fermi energy between the superlattice phase and its parent phase, which causes the Fermi surface sheets to reconstruct [1, 2]. This reconstructing should lead into the change in type of the major electric carriers. The inset of figure 2(b) shows the magnetic-field dependence of the transverse Hall resistivity \( \rho_{xy} \) for the CIS sample at different temperatures. Similar to that observed on SIS crystal [4], the straight dashed lines correspond to a linear dependence, revealing an ordinary Hall effect. As seen, the slope of the \( \rho_{xy}-H \) curve changes signs from negative to positive upon cooling from 30 to 20 K, carefully confirming the observation shown in figure 2(b). One may notice that this sign change in \( R_H \) for CIS was not observed by Wang and Petrovic [10], and their Hall measurement showed the Hall coefficients of CIS only in the low-temperature region. The sign change in \( R_H \) observed on both CIS and SIS provides direct evidence for the Fermi surface reconstructing during the superlattice phase transition. Also, note that a downturn in \( R_H \) of the
The basic superconducting transport properties presented in figures 3(a) and (b) show resistivity as a function of temperature in magnetic fields parallel to the crystalline [110] orientation for CIS and SIS samples, respectively. As seen, the resistivity under a magnetic field shows a broadening behavior due to thermally activated flux motion, which has been proposed by Anderson and Kim [14, 15] and can be described by

\[ \rho_x(T, H) = \rho_0 \exp \left( -U/k_B T \right), \]

where \( U \) is the activation energy and is normally both field- and temperature-dependent. In addition, the upper critical field \( H_{c2}(T) \) can be determined by taking the 50% transition of resistivity in various fields. The inset of figure 3(a) shows the field-dependent activation energies extracted from Anderson and Kim’s theory via the Arrhenius plots for CIS and SIS crystals. In the Anderson–Kim model, the activation energy \( U \) is an indication of the magnitude of the effective pinning energy. As seen in the inset, the activation energies for CIS are slightly higher than those for SIS, and the values of \( U \) for CIS and SIS are approximately two orders of magnitude smaller than those of several 10^4 K for YBa_2Cu_3O_y (YBCO) [16], indicating a relatively weak vortex pinning in CIS and SIS systems. Also seen in the inset of figure 3(a) is that \( U \) can be fitted with an approximate field dependence of \( U \propto H^{-\alpha} \) with \( \alpha \approx 0.8 \) and 1.0 for CIS and SIS, respectively. The present observation of thermally activated behavior for SIS in a mixed state does scale with the predicted \( H^{-1} \) dependence of \( U \) [17]. The inset of figure 3(b) shows the temperature dependence of upper critical field \( H_{c2} \) for CIS and SIS single crystals, where a linear-like behavior for temperatures near \( T_c \) can be observed. According to these results, the upper critical field \( H_{c2}(0) \) can be estimated using the formula derived by Werthamer et al [18]

\[ H_{c2}(0) = 0.693 \ T_c \left| \frac{dH_{c2}}{dT} \right|_{T_c} \]

where \( \left| \frac{dH_{c2}}{dT} \right|_{T_c} \) can be derived from the linear fitting in the inset of figure 3(b). By using equation (1), the obtained \( H_{c2}(0) \) values are 4.9 and 1.8 T for CIS and SIS single crystals, respectively, which are slightly smaller than 5.5 T for CIS and 3.5 T for SIS, as reported in other studies [5, 7, 8]. Meanwhile, the larger values of \( H_{c2} \) below 30 K is observed. The origin of this feature is not clear at this moment and deserves further investigation. It will be further explored by magnetoresistance in the following discussion.
obtained for CIS can be attributed to the higher activation energy, as shown in the inset of figure 3(a), leading to a stronger flux pinning in CIS. The $H_{c2}(0)$ values also correspond to the Ginzburg–Landau coherence length $\xi(0)$ values of 8.2 and 13.5 nm for CIS and SIS, respectively, as calculated using the formula of $\xi^2(0) = \frac{\Phi_0}{2\pi H_{c2}(0)}$, where $\Phi_0 = \hbar/2e$ is the flux quantum. Additionally, it is known that the upper critical field $H_{c2}(0)$ is limited by $\mu_0 H_{c2}(0)$ (Tesla) = 1.86 $T_c$ (kelvin) for weak electron–phonon coupling [19], being one of the indications of electronic correlation in superconductivity. Taking into account $T_c = 7.1$ and 5.1 K for CIS and SIS, respectively, one can see that the obtained $H_{c2}(0)$ values are significantly lower than the calculated weak-coupling-limit values of 13.2 and 9.5 T for CIS and SIS single crystals, respectively. These results indicate that superconductivities of both CIS and SIS are weak-coupling and resemble that observed on the Y$_3$Pt$_4$Ge$_{13}$ compound in which an $s$-wave symmetry single-energy gap for its superconducting phase was inferred [20].

The lower critical field $H_{c1}(T)$, corresponding to the field at which the presence of vortices into the superconductor and related to the magnetic penetration depth, can provide key information regarding the thermodynamic properties and superconducting energy gap. The temperature dependence of the magnetic penetration depth $\lambda(T)$ can be determined from $H_{c1}$ using the formula, $\mu_0 H_{c1} = (\Phi_0/4\pi \kappa^2) \ln \kappa$, where $\kappa = \lambda/\xi$ is the Ginzburg–Landau parameter. Meanwhile, according to the nodeless BCS superconducting band gap theory [21, 22], the term $\lambda^{-2}$ can be expressed by $\lambda^{-2}(T) = \lambda^{-2}(0) \delta(T) \tanh\left(\frac{\Delta(0)\delta(T)}{2k_B T}\right)$, with $\delta(T) = \tanh(1.82(1.018 (T_c/T−1)^{0.51})$, the Boltzmann constant $k_B$ and the residual penetration depth $\lambda(0)$. Thus, the formula for the temperature dependence of $H_{c1}$ is

$$H_{c1}(T) = \left(\frac{\Phi_0}{4\pi \mu_0}\right) \ln \kappa \lambda^{-2}(0) \delta(T) \tanh\left(\frac{\Delta(0)\delta(T)}{2k_B T}\right). \tag{2}$$

Equation (2) correlates $H_{c1}(T)$ with the parameters $\Delta(0)$ and $\lambda(0)$. $H_{c1}(T)$ can be extracted from a Meissner-like linear $M(H)$ regime to a nonlinear $M(H)$ response by tracking the $M(H)$ curves at low fields at several temperatures [23]. Figures 4(a) and (b) respectively show the measured magnetization $M(H)$ curves of CIS and SIS at various temperatures for the $H//[110]$ configuration (out-of-plane $H$). Here, the demagnetization effect is taken into account by $H = H_{app}−NM$ with the applied field $H_{app}$ and the demagnetization factor $N$. $H_{c1}$ is

Figure 3. Resistivity as a function of temperature in magnetic fields parallel to the crystalline [110] orientation for (a) CIS and (b) SIS samples. The inset of (a) shows the field-dependent activation energies extracted from Anderson and Kim’s theory with an approximate field dependence of $U \propto H^{-1}$. The inset of (b) shows the temperature dependence of upper critical field $H_{c2}$ for CIS and SIS single crystals with a linear fitting.
determined by the \( \pm 1\% \) deviation of the \( M(H) \) curve from the linear fitting in the even lower-field regime. The inset of figure 4 shows the obtained \( H_{c1} \) as a function of temperature for the CIS and SIS samples. Also shown in the inset are the fitting curves of equation (2) (solid lines) and (3) (dashed lines) for CIS and SIS.

![Figure 4](image-url)

**Figure 4.** Magnetization \( M(H) \) curves of (a) CIS and (b) SIS at various temperatures for the \( H//\{110\} \) configuration. The inset shows the obtained \( H_{c1} \) as a function of temperature for CIS and SIS samples. Also shown in the inset are the fitting curves of equation (2) (solid lines) and (3) (dashed lines) for CIS and SIS.

Furthermore, we try to fit the temperature dependence of \( H_{c1} \) for CIS and SIS using the \( d \)-wave model of the gap symmetry [24] in which the \( H_{c1}(T) \) can be denoted by

\[
H_{c1}(T) = H_{c1}(0) \left( 1 - \frac{1}{\pi} \int_{0}^{2\pi} d\phi \int_{0}^{\infty} \left( \frac{df}{dE} \right) \frac{E}{\sqrt{E^{2} - \Delta_{d}^{2}}} dE \right),
\]

with \( f = 1/\{1 + \exp(E/k_{B}T)\} \) and the \( d \)-wave gap as \( \Delta_{d} = \Delta(0)\delta(T)\cos(2\phi) \). The best fitting curves (dashed lines) of equation (3) with \( \Delta(0) = 10.5 \) and 8.5 K, respectively, for CIS and SIS are also shown in the inset of figure 4(a). However, we find that the curves obtained within the \( d \)-wave model of gap symmetry cannot be reconciled well with our experimental data at low temperatures and exclude the possibility of \( d \)-wave gap symmetry in CIS and SIS. These results again demonstrate a possibly weak-couple pairing in CIS and SIS superconductors. Additionally, the fitting of equation (2) also confirms that the gap symmetry in CIS and SIS can be described by the nodeless single-gap BCS theory and excludes the possibility of ferromagnetic spin fluctuation in these CDW-related superconductors, which are consistent with the observed results of diamagnetic magnetic susceptibility, as shown in figures 1(a) and (b). In addition, it may be worth pointing out that Biswas et al [13] recently obtained the lower and upper critical fields for SIS via magnetization and \( \mu \)SR measurements. Their value of \( H_{c2}(0) = 1.44 \) T is slightly smaller than that of 1.8 T extracted by the transport...
measurement, as presented here, whereas the value of $H_{c1}(0) = 85\, \text{Oe}$ is larger (and $\lambda(0)$ is smaller) than that of 40.5 Oe obtained here or in [5]. Their larger $H_{c1}$ values possibly result from a larger deviation criterion (>2%) of the $M(H)$ curve from the linear $M-H$ region used for determining $H_{c1}$. In spite of the inconsistent $H_{c1}$ values, Biswas et al. [13] also inferred the existence of a nodeless $s$-wave energy gap in the superconducting state of SIS according to their temperature-dependent penetration depth $\lambda$, being consistent with the argument shown here.

A normal-state Hall measurement can provide further insight into the spin exchange energies in superconductors. Figures 5(a) and (b) plot cot $\theta_H$ as defined by $\cot \theta_H = \rho_{xx}/\rho_{xy}$ versus $T^2$ for CIS and SIS measured in the fields of 3 and 6 T, respectively. As can be seen, the data almost fall on a straight line in the temperature range below $T^*$ and can be fitted to the equation of $\cot \theta_H = \Lambda T^2 + C$ with the parameters $\Lambda$ of 1.063 (0.023) K$^{-2}$ and $C$ of 182.6 (5.7) for CIS (SIS) in an applied field of 6 T, where $C$ corresponds to the impurity contribution. Also shown in the inset of figure 5(b) is the $T^2$ behavior of $\cot \theta_H$ for CIS and SIS at temperatures above $T^*$ with the parameters $\Lambda$ and $C$ of 32.34 (34.20) K$^{-2}$ and 475.2 (946.6) for CIS (SIS) in an applied field of 3 T. The $\Lambda$ value for CIS is almost two orders of magnitude larger than those observed in HTS cuprates, MgB$_2$ or superconducting pnictides ($10^{-3} - 10^{-2}$ K$^{-2}$) [25–28]. It has been pointed out that the temperature dependence of $\cot \theta_H$ for many superconductors with a wide range of doping retains its simple $\Lambda T^2 + C$ form at temperatures above $T_c$ even though the temperature dependence of $\rho_{xx}$ changes considerably [29]. The $T^2$ behavior of $\cot \theta_H$ for CIS and SIS seemingly conforms to this contention because of the nonlinear-$T$ resistivity observed in CIS at temperatures below $T^*$, as seen in figure 2(a), unlike HTS cuprates in which a linear-$T$ resistivity is commonly observed. So far, the $T^2$ dependence of $\cot \theta_H$ has been observed in HTS cuprates, MgB$_2$, superconducting pnictides and CDW-related superconductors, as shown here, regardless of their temperature dependence of $\rho_{xx}$. In fact, $R_{H}$ or $\rho_{xy}$ itself is complex, and many different explanations have been proposed for the anomalous normal-state Hall effect. A widely known approach proposed by Anderson [30] argues that the system has non-Fermi liquid (Luttinger liquid) properties, and the temperature dependence of $R_{H}(T)$ could be better understood in terms of two apparently decoupled scattering rates with the spin-charge separation scenario. Following Anderson’s theory, Chien et al. analyzed the normal-state Hall angle in single-crystal YBa$_2$Cu$_{3-x}$Zn$_x$O$_y$ [31] and derived a correlation between parameter $\Lambda$ and the spin exchange energy as

![Figure 5](image-url)
where \( J \) is the bandwidth of spin excitations (or the spin exchange energy in Anderson’s theory), and \( n \) is the planar carrier density. The spin exchange energy \( J \) for \( \text{YBa}_2\text{Cu}_3\text{O}_y \) was determined by the experimental value of \( \Lambda \) to be \( \sim 830 \) K. A similar estimation for \( \text{Tl}_2\text{Ba}_2\text{CuO}_y \) has recently shown \( J \approx 800 \) K [32]. By substituting the experimental values of \( \Lambda \) and the carrier concentration derived from the Hall coefficient into equation (4), the analog exchange energy \( J \) for the superconducting CDW system of CIS and SIS can be determined to be 88 and 464 K, respectively. The obtained spin exchange energy for CIS is much smaller than those of HTS cuprates and is in accordance with the extremely small \( T_c/J_T \) value of \( \sim 0.001 \) derived from the Seebeck coefficient measurement [10]. Surprisingly, both the Hall and thermo-electric measurements agree with the aspect of a weak electronic correlation in CIS. On the other hand, the obtained spin exchange energy for SIS is larger than that of CIS but is still much smaller than those of HTS cuprates, again implying that the mediate couplings for forming superconducting pairs in CIS are relatively weak in comparison with HTS cuprates. Recently, the \( T^2 \) behavior of \( \text{cot}\theta_{\phi} \) has also been observed in many heavy-fermion superconductors. For example, compounds of \( \text{CeIrIn}_5 \) and \( \text{CeCoIn}_5 \) exhibit \( \text{cot}\theta_{\phi} = AT^2 + C \) with the parameters \( A \) of \( \sim 1.1 \) and 0.254 \( \text{K}^{-2} \) [33, 34], respectively, which are comparable to that of 1.063 for CIS but are much larger than those for HTS cuprates or superconducting pnictides. Both \( \text{CeIrIn}_5 \) and \( \text{CeCoIn}_5 \) are suggested to be \( d \)-wave-symmetry superconductors in which the microscopic coexistence of superconductivity and antiferromagnetic fluctuation (AF) near a QCP has been reported [33, 34]. Interestingly, the larger \( A \) values imply that the spin exchange energies in these AF-related heavy-fermion superconductors would not be large.

In addition to the anomalous normal-state Hall effect for the general understanding of superconductivity in CDW-related superconductors, it is of crucial importance to clarify the normal-state charge transport in fields. In particular, the classical orbital magnetoresistance (MR) offers the key to an understanding of the electron transport on the Fermi surface since it involves the same scattering processes as the Hall current. Harris et al [35] have shown that the classical orbital MR can measure the variance of a local Hall angle around the Fermi surface and is closely related to the temperature dependence of the measured Hall angle. The relationship between MR and the Hall angle can be expressed as

\[
\text{MR}_{\text{orb}} \equiv \text{MR}_{\perp} - \text{MR}_{/} = \left\{ \theta(s)^2 \right\} - \left\{ \theta(s) \right\}^2,
\]

where \( \text{MR}_{\text{orb}} \) is the in-plane orbital MR, \( \text{MR}_{\perp} \equiv \Delta \rho(H)_{\perp}/\rho_{\text{xx}}(0) = [\rho_{\text{xx}}(H) - \rho_{\text{xx}}(0)]_{\perp}/\rho_{\text{xx}}(0) \) is the transverse MR with the field perpendicular to current \( I \), \( \text{MR}_{/} \equiv \Delta \rho(H)_{/}/\rho_{\text{xx}}(0) = [\rho_{\text{xx}}(H) - \rho_{\text{xx}}(0)]_{/}/\rho_{\text{xx}}(0) \) denotes the MR with the field parallel to current \( I \) (longitudinal MR, where the Lorentz force is absent in this geometry) and \( \theta(s) \) is the local Hall angle with an arc-length \( s \) along the Fermi surface. Equation (5) also involves the elementary case of zero orbital MR for a circular Fermi surface of an isotropic metal [35]. Figure 6(a) shows the temperature dependence of \( \text{MR}_{\text{orb}} \) measured with the resistivity changes between \( H = 0 \) and 3 T for CIS and SIS, respectively. As can be seen, the \( \text{MR}_{\text{orb}} \) values of CIS are much larger than those of HTS cuprates at temperatures below 30 K and increase quickly at temperatures below 40 K, while there is no significant change in the \( \text{MR}_{\text{orb}} \) of CIS. This MR behavior corresponds seemingly to the \( R_H \) behavior, as shown in figure 2(b), in which the SIS sample shows a downturn in \( R_H \) around 30 K, while the \( R_H \) of CIS shows a monotonous increase when the temperature is decreased to be below 35 K. Also seen in figure 6(a) is a fitting curve which shows a roughly \( T^{-2} \)-dependent \( \text{MR}_{\text{orb}} \), for SIS at temperatures below 40 K. The inset of figure 6(a) shows the temperature dependences of \( \text{MR}_{\perp} \) and \( \text{MR}_{/} \) for CIS. Both \( \text{MR}_{\perp} \) and \( \text{MR}_{/} \) also show rapid increases at temperatures below 40 K, implying that the MR is affected by a strong spin–flip scattering in the low-temperature region. It is worthy to note that the temperature of \( \sim 40 \) K corresponds to the temperature \( T' \), where an anomalous increase in effective magnetic susceptibility \( \chi_{\text{eff}}(T) \) is observed, as previously shown in figure 1(b). Figure 6(b) plots \( \text{MR}_{\text{orb}} \) vs. \( H \) for SIS in the low-temperature normal-state regime. Also shown in the inset of figure 6(b) is the plot of \( \text{MR}_{\text{orb}} \) vs. \( H^2 \) corresponding to the data in figure 6(b). Clearly, a nearly \( H^2 \) dependence of \( \text{MR}_{\text{orb}} \) is observed for the SIS single crystal at temperatures below 50 K. As a result, SIS indeed exhibits the typical \( H^2 \)-dependent MR character at the low-temperature region. In conventional metals, the magnetoresistance \( \text{MR}_{\text{orb}} \) due to an orbital motion of carriers can be scaled as a function of the term \( H/\rho_{\text{xx}}(0) \), which is regarded as following the Kohler’s scaling rule [36]. To examine this relation, figure 7(a) plots the \( \text{MR}_{\text{orb}} \), as a function of \( [H/\rho_{\text{xx}}(0)]^2 \) for SIS at temperatures ranging from 8 to 50 K, a temperature region which is far below the Debye temperature \( \sim 184 \) K [5] but well above \( T_c \), where the resistances due to the electron–phonon–dominated interaction, superconducting fluctuation and flux motion can be neglected. As seen, the \( \text{MR}_{\text{orb}} \) can be fitted to be proportional to the term \( [H/\rho_{\text{xx}}(0)]^2 \) with a merged temperature-independent slope; that is a scaling of Kohler’s rule. Another pronounced MR characteristic is the modified Kohler’s scaling, which relates the magnetoresistance with the resistivity and Hall angle [35, 36].
Figure 7(b) shows the corresponding data of MRorb against tan²θH for the SIS sample. As can be seen, the data at different temperatures show distinctly different curves, indicating that the MRorb of SIS does not obey the modified Kohler’s rule. Contrary to this result of SIS, it has been demonstrated that the scaling of Kohler’s rule breaks down in cases of optimum-doped YBCO, La2−xSrxCuO4, NaFe1−xCoxAs and BaFe2(As1−xP)2 [28, 35, 37] in which the MR violates the Kohler’s scaling and can be scaled by the square of the Hall angle (modified Kohler’s rule) in these optimally doped systems. The scenario of SDW QCP has recently been proposed to describe the normal-state transport properties [38, 39]. It has even been proposed that the SDW QCP is a central organizing principle of organic, iron-pnictide, heavy-fermion and HTS cuprates [36, 40]. Recently, heavy-fermion superconductors, such as CeIrIn3 and CeCoIr5 compounds, continue to be a central focus of investigation, as mentioned previously. Most of them belong to the class of field-tuned or pressure-tuned heavy-fermion systems near a QCP in which the electrical transport properties have been suggested to be governed by the AF spin fluctuation. It has been reported that the MR in CeIrIn3 and CeCoIr5 does not obey Kohler’s rule but can be scaled by tan²θH (modified Kohler’s rule) [34, 41, 42]. Apparently, the normal-state MR effect in the SIS superconductor, which has superconductivity that is driven by the suppression of CDW ordering accompanying a pressure-induced structure quantum phase transition, reveals a significantly different property from those of SDW-suppressed or AF-related heavy-fermion superconductors. In addition, an interesting compound, MgCNi3, having a perovskite structure without any oxygen, exhibits a Tc of ~8 K even though it contains a high proportion of Ni [43, 44]. The MR behavior in MgCNi3 shows that the classical Kohler’s rule is valid [43]; meanwhile, the estimated Hc2(0) satisfies the value expected within the same weak-coupling BCS theory [44]. This situation in MgCNi3 is analogous to that observed here in SIS and implies that the normal-state MR behaviors in weakly-correlated superconductors tend to follow the scaling of the classical Kohler’s rule.

It is noteworthy that MgB2 reveals the T⁴ dependence of cotθH with a small A value of 0.005 K⁻², as mentioned previously [27], but shows a large normal-state MR in which Kohler’s rule is not obeyed [45]. Meanwhile, the breakdown of Kohler’s rule in MgB2 has been attributed to the multiband effect [45]. Being different from CIS and SIS, MgB2 reveals the paramagnetic feature with small magnetic moments in the normal state [46]. According to equation (4), a small A value should correspond to a larger exchange energy J in MgB2.
Compared with the cases of CIS and SIS in which a diamagnetic feature accompanying a larger $\Lambda$ value has been observed, as presented previously, the spin exchange in MgB$_2$ seemingly can be enhanced in a paramagnetic environment even though the spins in MgB$_2$ are not active [27]. It is well known that the diamagnetic properties of CIS and SIS, as demonstrated by our magnetization measurement or the $\mu$SR studies [9, 13], should originate from the so-called Larmor diamagnetism, which is probably sufficient to exceed the paramagnetic Pauli spin susceptibility of the conduction carriers in CIS and SIS [6]. This is consistent with the smaller spin exchange energy obtained for CIS or SIS. Kohler’s scaling of MR behavior for SIS at low temperatures also implies that the conduction carriers in CIS should be dominated by a single electronic band. So far, we have seen that these QCP systems indeed behave in unconventional normal-state transport properties (the unusual Hall effect or MR following the modified Kohler’s rule) as indicated by Naira et al [36], regardless of the CDW- or SDW-related superconductors they belong to. Furthermore, in this study, we also find that the MR behavior, which obeys the conventional Kohler’s rule or the modified Kohler’s rule, is influenced by the magnitude of spin exchange.

Looking deeper into the MR behavior in SIS via equation (5), one can see that the MR$_{orb}$ varies as $\sim T^{-2}$ (figure 6(a)), while the Hall measurement shows a roughly $T^{-4}$ dependence of $(\theta_H)^2$ due to the $T^2$-dependent $\cot \theta_H$ (here, $\theta_H = \tan \theta_H \propto T^{-2}$). This observation indicates that the MR$_{orb}$ in SIS is dominated by the first term, $(\theta(s)^2)$ (corresponding to $-\Delta \sigma_{xx}/\sigma_{xx}$), not the second term, $(\theta(s)^2)$ (corresponding to $(\theta_H)^2$). As a result, the MR$_{orb}$ of SIS certainly does not obey the modified Kohler’s rule, as seen in figure 7(b). Moreover, it has been pointed out that the numerical value of the ratio $\text{MR}_{orb}/(\theta_H)^2$ can provide further information about the sign changing of the local Hall angle, i.e. the reconstruction of the Fermi surface [35]. This idea can be understood by looking closely at equation (5). The second term $(\theta(s)^2)$ in equation (5) corresponding to the observed $(\theta_H)^2$ will be of an extremely small value in comparison with the first term $(\theta_H)^2$, as the local Hall angle is changing in sign over some segments of the Fermi surface due to band reconstruction, resulting in a larger ratio $\text{MR}_{orb}/(\theta_H)^2$. The inset of figure 7 plots the temperature dependence of $\text{MR}_{orb}/\tan^2 \theta_H$ for CIS and SIS samples. As can be seen, the value of $\text{MR}_{orb}/\tan^2 \theta_H$ for CIS is much larger than that for SIS due to an extremely small Hall angle in CIS even though a small MR$_{orb}$ value is observed in CIS, as shown in figure 6(a). The MR$_{orb}/\tan^2 \theta_H$ for CIS increases gradually with the rising temperature and shows a rapid increase at temperatures approaching the CDW transition temperature $T^*$ of $\sim 35$ K. The MR$_{orb}/\tan^2 \theta_H$ for SIS shows another upturn with lowering the temperature below $T$ of $\sim 40$ K. The MR$_{orb}/\tan^2 \theta_H$ for SIS also exhibits a rapid increase at the temperature $T^*$ of $\sim 147$ K (not shown) because of the sign change in $R_H$ and $\theta_H \approx 0$ at $T^*$. Following the argument previously stated, these observed rapid increases in $\text{MR}_{orb}/\tan^2 \theta_H$ can denote the occurrence of band structure.

Figure 7. (a) MR$_{orb}$ as a function of $[H/\rho_{xx}(0)]^2$ (Kohler’s plot) for SIS at temperatures ranging from 8 to 50 K. (b) The corresponding data of MR$_{orb}$ against $\tan^2 \theta_H$ for the SIS sample. The inset: temperature dependence of $\text{MR}_{orb}/\tan^2 \theta_H$ for CIS and SIS samples.
reconstructing during the superlattice phase transition. The resistivities show magnetic
activated behavior with a power-law magnetic
which is deduced from the nodeless BCS superconducting band gap theory. These results con
ferromagnetic spin
leading to the presence of lattice instability toward a phase transition at this temperature.

An interesting subject is the origin of anomalies at $T^*$ for SIS. A recent electronic structure calculation has shown
an additional soft phonon mode (relative to the absence in CIS) of energy of 4.0 meV at the $R$ point for SIS [2].
This energy corresponds to $\sim 46$ K and indicates the presence of lattice instability toward a phase transition at
that temperature. This is seemingly consistent with the observed temperature $T^*$ of 40 K in SIS. Certainly, more
theoretical or experimental studies on the anomalous properties of SIS at low temperatures are necessary.

4. Conclusions and outlook

In summary, the longitudinal and Hall resistivities, upper and lower critical fields, magnetoresistance and
magnetizations of superconducting CIS and SIS were investigated to clarify both magnetic and transport
properties of these CDW-related superconductors. Both CIS and SIS show basic features with the CDW
transition temperature $T^*$ of 35 and 147 K, respectively, and the superconducting critical temperature $T_c$ of 7.1
and 5.1 K, respectively. The Hall coefficient $R_H$ values for CIS and SIS at temperatures above $T^*$ are negative and
change sign at around $T^*$, implying a sudden change in band structure accompanying the Fermi surface
reconstructing during the superlattice phase transition. The resistivities under magnetic fields show thermally
activated behavior with a power-law magnetic-field dependence of activation energy $U \propto H^{-\alpha}$ observed.
The values of $U$ for CIS and SIS are approximately two orders of magnitude smaller than those of several $10^4$ K
for HTS cuprates, indicating a relatively weak vortex pinning in CIS and SIS systems. Meanwhile, the upper critical
field $H_{c2}(0)$ values obtained are significantly lower than the calculated weak-coupling-limit values for both CIS
and SIS, indicating that the superconductivities of CIS and SIS are weak-coupling. As to magnetic properties,
both CIS and SIS reveal a diamagnetic feature in the entire investigated temperature range. The lower critical
$H_{c1}(T)$ extracted by the deviation from the Meissner-state linear $M(H)$ curve can be described by equation (2),
which is deduced from the nodeless BCS superconducting band gap theory. These results confirm that the gap
symmetry in CIS and SIS can be described by the nodeless single-gap BCS theory and excludes the possibility of
ferromagnetic spin fluctuation in CDW-related superconductors. The obtained ratios of $\Delta(0)/k_B T_c \approx 1.36$ and
1.49 for CIS and SIS, respectively, are slightly smaller than that of 1.76, predicted by the traditional BCS theory,
and again demonstrate a possibly weak-couple pairing in CIS and SIS superconductors. Moreover, the normal-
state Hall angle is observed to follow $\cot \theta_H = AT^2 + C$ in both CIS and SIS crystals. According to equation (4),
the spin exchange energy $J$ for CIS and SIS can be determined to be 88 and 464 K, respectively. Smaller values of spin
exchange energy, the upper critical field and the $\Delta(0)/k_B T_c$ ratio agree with the thought of a relatively weak
electronic correlation in CIS and SIS.

In MR measurements, the MR$_{orb}$ values of SIS are much larger than those of CIS at temperatures below 30 K
and increase quickly at temperatures below 40 K. The MR$_{orb}$ of SIS is found to follow a scaling of Kohler’s rule
but does not obey the modified Kohler’s rule, revealing a significantly different property from those of SDW-
suppressed superconductors. It is found that the MR behavior, which obeys the conventional Kohler’s rule or
the modified Kohler’s rule, is influenced by the magnitude of spin exchange. The MR effect in SIS shows a rapid
increase with decreasing temperature below the temperature $T^*$ of $\sim 40$ K, which is consistent with the
temperature of anomalies observed in the magnetic susceptibility and the Hall coefficient, implying the
reconstructions of band structure occurring around $T^*$. The anomalies at $T^*$ for SIS originate seemingly from an
additional soft phonon mode (relative to the absence in CIS) of energy of 4.0 meV, which corresponds to $\sim 46$ K,
leading to the presence of lattice instability toward a phase transition at this temperature.

Acknowledgments

The authors thank the Ministry of Science and Technology of Taiwan for financial support under Grant Nos.
MOST-101-2112-M-002-020-MY2 and MOST-103-2112-M-002-011 (LMW), MOST-103-2112-M-006-014-
MY3 and MOST-103-2119-M-006-014-MY3 (CSL).

References

[1] Klintberg L E, Goh S K, Alireza P L, Saines P J, Tompsett D A, Logg P W, Yang J, Chen B, Yoshimura K and Grosche F M 2012 Phys. Rev. Lett. 109 237008

[2] Tompsett D A 2014 Phys. Rev. B 89 075117

[3] Jin K, Butch N P, Kirshenbaum K, Paglione J and Greene R L 2011 Nature 476 73

[4] Kuo C N, Liu H F, Lue C S, Wang L M, Chen C C and Kuo Y K 2014 Phys. Rev. B 89 094520

[5] Kase N, Hayamizu H and Akimitsu J 2011 Phys. Rev. B 83 184509
