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Enhancement of the Peierls-like phase transition in the Cu$_{1-x}$Li$_x$Ir$_2$S$_4$ system

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Abstract – In the spinel CuIr$_2$S$_4$ system, previous reports have shown that any chemical substitution would suppress or destroy the Peierls-like phase transition. Herein, we present our investigations on the Cu$_{1-x}$Li$_x$Ir$_2$S$_4$ system, where the Peierls-like phase transition is enhanced by the doping of Li. To our knowledge, this is the first report that the phase transition is enhanced by chemical substitution. Through low-temperature X-ray diffraction study, we find that the lattice cell is distorted by the doping of Li, which favors the tetragonal structure in the low-temperature Peierls-like phase. We suggest that the lattice distortion caused by the Li-doping is responsible for the enhancement of the phase transition.

Introduction. – The sulphospinel CuIr$_2$S$_4$ has attracted considerable attention due to the Peierls-like phase transition which rarely occurs in the three-dimensional materials [1–4]. When the first-order phase transition takes place at $T_{MI} \sim 230$K with temperature decreasing, the system changes from Normal State (NS) to Peierls-like State (PS) accompanied by the transformation of conductivity from metallic to insulating, the loss of localized magnetic moments, the lowering of the lattice symmetry from cubic to triclinic, etc. [4–7]. Studies of NMR, XPS and band structure calculations show that Cu is monovalent and Ir has mixed valence of +3.5 in NS. In PS, however, it has been determined that Ir ions are separated equally into dimerized Ir$^{4+}$ ($S = 1/2$) and non-dimerized Ir$^{3+}$ ($S = 0$) with charge ordering of isomorphic Ir$_8$S$_{24}$ bi-capped-octamers [7–10]. As for the driving force of the phase transition, an orbitally induced mechanism has been proposed to explain this three-dimensional Peierls-like phase transition, where the 5$d_{xy}$ orbits of Ir play a crucial role in the phase transition [11,12].

Although the Peierls-like phase transition and its driving force have been investigated intensively, enhancement of this transition has become a great challenge. So far, the only way to increase the phase transition temperature $T_{MI}$ is the application of hydrostatic pressure [13]. With the increase of hydrostatic pressure, $T_{MI}$ increases at a speed of 2.8 K/kbar [13,14]. However, the Peierls-like phase transition becomes less prominent, and disappears above 20Gpa [13]. From this point of view, whether the phase transition is actually enhanced by pressure or not is still unclear. On the other hand, the chemical substitution effects have also been studied extensively. However, previous experiments have found that any chemical substitution would suppress or destroy this phase transition [15–19].

In this work, we report that $T_{MI}$ can be increased by the substitution of Li for Cu in the Cu$_{1-x}$Li$_x$Ir$_2$S$_4$ system, whereas keeping the intensity of the phase transition unchanged. This means that the Peierls-like phase transition is enhanced by the doping of Li. Through low-temperature X-ray diffraction study, we notice that the lattice cell is slightly distorted by the doping of Li, which favors the tetragonal structure in PS. We suggest that this distortion of lattice caused by the doping of Li is the driving force of the enhancement of the Peierls-like phase transition.

Experiment. – Polycrystalline samples of Cu$_{1-x}$Li$_x$Ir$_2$S$_4$ ($x = 0$, 0.1, 0.2 and 0.3) were synthesized by the solid-state reaction method. The starting materials, powders of Cu (purity 99.999%), Ir (99.95%), S (99.9999%) and Li (99.9%) were mixed thoroughly.

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according to the stoichiometric ratio with 1 wt% excess S. The mixed powder samples were sealed in vacuumed quartz tubes, and heated slowly to 850 °C. After holding for 8 days, the samples were cooled down to room temperature. Then, the powder samples were pressed into pellets and sintered in vacuumed quartz tubes at 850 °C for another 2 days. The preparing process of the Li-doped samples was done in a glove-box filled of argon atmosphere ($p_{O_2}$ and $p_{H_2O} < 0.1$ ppm).

The structure and phase purity were checked by the Rigaku-TTR3 X-ray diffractometer using high-intensity graphite monochromatized Cu Kα radiation. The resistivity measurements were performed by the conventional four-probe method using the Quantum Design PPMS. The temperature dependence of magnetization was measured with a superconductive quantum interference device (SQUID) MPMS. The isothermal magnetization at selected temperatures was recorded by the SQUID-VSM system. The low-temperature X-ray diffraction was carried out using the X-ray diffractometer equipped with a closed-cycle helium refrigerator.

Results and discussion. – Figure 1(a) shows the powder X-ray diffraction (XRD) patterns for Cu$_{1-x}$Li$_x$Ir$_2$S$_4$ ($x = 0, 0.1, 0.2$ and $0.3$) at room temperature ($23^\circ$C). For the matrix CuIr$_2$S$_4$, all Bragg diffractions can be indexed according to the cubic symmetry (space group: $Fd-3m$), implying a single phase of normal spinel structure. As for the Li-doped samples, some tiny diffraction peaks cannot be indexed with the single cubic cell (especially for $x = 0.3$), as shown in the enlarged XRD patterns of fig. 1(b). This could be caused by two possibilities: the impurities or the appearance of another lattice symmetry. After detailed analysis, it is found that there exists very small amount of Cu$_2$S [20], indexed as triangle symbols in fig. 1(a) and (b). This demonstrates that Li has occupied Cu, leading to the precipitation of Cu$_2$S. However, there still exists some other unknown diffractions indexed as star symbols, which will be discussed later in this paper. The XRD patterns were refined by the Rietveld method, which indicates that the content of Cu$_2$S is about $\sim 6\%$. The lattice constant $a$ vs. $x$ was plotted in the inset of fig. 1(a), which shows that $a$ increases monotonously with $x$ except the sample with $x = 0.3$. As we know, Li presents the valence of +1 in the compound. The ionic radius of Li$^+$ (0.59 Å) is slightly smaller than that of Cu$^+$ (0.60 Å) [21]. However, the increase of $a$ with $x$ does not obey Vargard’s law, which implies that the rigid-band model is invalid here.

Figure 2(a) and (b) depict the temperature dependence of the resistivity ($\rho(T)$) and susceptibility ($\chi(T)$) for Cu$_{1-x}$Li$_x$Ir$_2$S$_4$, respectively. In fig. 2(a), the resistivity for $x = 0.3$ is not shown because the sample becomes loosen with the increase of Li content so that the sample with $x = 0.3$ is too fragile to measure the resistivity. As can be seen in fig. 2(a), all samples exhibit a metallic-insulating transition, and the transition temperature $T_{MI}$ increases with increasing $x$ (as given in the inset of fig. 2(a)). The shift of $T_{MI}$ towards higher temperature generally implies the enhancement of the Peierls-like phase transition. To our knowledge, the Peierls-like phase transition can be only enhanced by just one method as reported so far, i.e. the hydrostatic pressure [13]. For chemical substitutions, the metallic-insulating transition is always suppressed with chemical modifications [15–19]. In other words, the Peierls-like transition is extremely delicate and is easily destroyed by any chemical substitution in CuIr$_2$S$_4$. In this sense, the unexpected enhancement of the Peierls-like transition in Li-doped CuIr$_2$S$_4$ is remarkable and deserves further investigation.

Figure 2(b) shows $\chi(T)$ curves, which confirms the sample increase of $T_{MI}$ with the increase of $x$. The $T_{MI}$ of $x = 0.3$ reaches 255 K and 242 K for warming and cooling, respectively, which is the highest among these four samples. As
is known, the spin-dimerization phase transition accompanies with the Peierls-like phase transition, which leads to a magnetic step $\Delta \chi$ at $T_{MI}$ in the $\chi(T)$ curve. In fig. 2(b), steps with a hysteresis on warming and cooling are found in all curves. The temperature where the spin-dimerization transition happens increases with increasing Li-doping (as plotted in the inset of fig. 2(b)), in agreement with that in $\rho(T)$ curves.

From the $\chi(T)$ curves shown in fig. 2(b), we can deduce quantitatively other parameters which reflect the difference among these samples. The parameters obtained from $\chi(T)$ are listed in table 1. In the CuIr$_2$S$_4$ system, the conductivity changes from metallic state to insulating state, accompanied with the disappearance of Pauli paramagnetism and Landau diamagnetism. Therefore, the magnetic step has the relationship of $\Delta \chi = \chi_{Pauli} + \chi_{Landau}$ with $\chi_{Pauli} = -3\chi_{Landau}$. Thus, $\Delta \chi$ can be described as [6]

$$
\Delta \chi = \frac{2}{3} \chi_{Pauli} = \frac{2}{3} \mu_0 \mu_B^2 N(E_F),
$$

where $\mu_0$ and $\mu_B$ represent the vacuum magnetococonductivity and Bohr magneton, respectively; and $N(E_F)$ is the density of state at the Fermi level. According to eq. (1), the magnetic step $\Delta \chi$ is in proportion to the $N(E_F)$. It can be obtained $N(E_F) = 0.70$ states/eV·atom here, which approaches 0.67 states/eV·atom in ref. [6]. From results listed in table 1, it is found that $\Delta \chi$ is hardly affected in the Li-doped samples, which implies that $N(E_F)$ is rarely influenced by the Li-doping. This indicates that the intensity of the phase transition is hardly affected by the Li-doping. On the other hand, the width of the Peierls-like phase transition $\Delta T$, defined as the width of the hysteresis of the magnetic step on cooling and warming, reflects the intensity of this phase transition in another aspect. The more narrow $\Delta T$ is, the more prominent the phase transition is [22]. It is found from table 1 that $\Delta T$ changes hardly with $x$, indicating that the intensity is rarely influenced by Li-doping. This is different from that under the hydrostatic pressures. In that case, with the application of hydrostatic pressure, the phase transition broadens and disappears gradually. The fact that the intensity is nearly unaltered indicates that the Peierls-like phase transition is substantially enhanced in the Li-doped CuIr$_2$S$_4$ system.

In order to study the effect of Li-doping on the magnetic behaviors, the magnetization needs to be analyzed in detail. In view of the Curie tail at low temperatures, $\chi(T)$ below $T_{MI}$ can be fitted using the following equation [23]

$$
\chi = \chi_0 + \frac{C}{T}, \quad \text{(2)}
$$

where $\chi_0$ is the temperature-independent susceptibility, $C$ is the Curie constant. The fitting results of $\chi_0$ and $C$ are listed in table 1. As can be seen, $\chi(T)$ deviates the Curie-Weiss law at $\sim$120 K for the Li-doped samples. As mentioned, some impurity of CuS$_2$ exists in the Li-doped sample. However, there is no trace of magnetic transition for CuS$_2$ at $\sim$120 K [24]. Thus, this deviation of susceptibility may result from the scattering of spins

**Table 1: Fitting results of the magnetization for Cu$_{1-x}$Li$_x$Ir$_2$S$_4$.**

<table>
<thead>
<tr>
<th>Sample(x)</th>
<th>$\Delta \chi$(emu/mol)</th>
<th>$\Delta T$(K)</th>
<th>$C$(emuK/mol)</th>
<th>$\chi_0$(emu/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$1.7 \times 10^{-4}$</td>
<td>10.9</td>
<td>0.0013</td>
<td>-0.00014</td>
</tr>
<tr>
<td>0.1</td>
<td>$1.9 \times 10^{-4}$</td>
<td>13.1</td>
<td>0.0039</td>
<td>-0.00008</td>
</tr>
<tr>
<td>0.2</td>
<td>$1.5 \times 10^{-4}$</td>
<td>10.1</td>
<td>0.0061</td>
<td>-0.00006</td>
</tr>
<tr>
<td>0.3</td>
<td>$0.9 \times 10^{-4}$</td>
<td>12.6</td>
<td>0.0056</td>
<td>0.00013</td>
</tr>
</tbody>
</table>

Fig. 2: (Color online) The temperature dependence of (a) resistivity ($\rho(T)$) and (b) susceptibility ($\chi(T)$) for Cu$_{1-x}$Li$_x$Ir$_2$S$_4$; the insets of (a) and (b) depict $T_{MI}$ vs. Li-content ($x$) obtained from $\rho(T)$ and $\chi(T)$, respectively.
caused by Cu$_2$S impurities and lattice defects. One can see that both $C$ and $\chi_0$ increase with the increase of $x$. The Curie constant $C$ correlates to the paramagnetism produced by defects. The defects increase with the doping of Li, which gives the explanation to the increase of $C$. However, the mechanism of the increase of $C$ still needs to be confirmed. The isothermal magnetization ($M(H)$) for Cu$_{1-x}$Li$_x$Ir$_2$S$_4$ ($x = 0$ and 0.3) at 4 K are given in fig. 3. In fact, the $M(H)$ at 4 K can be fitted according to (CGS) [25]

\[
M = N\mu \left( \coth \frac{\alpha}{\alpha} - 1 \right) + \chi_0 H, \tag{3}
\]

\[
\alpha = \frac{\mu H}{k_B T}. \tag{4}
\]

The first item on the right of the equation represents the Langevin paramagnetism, and the second one is the magnetisms which exhibit linear temperature-dependence, i.e., Pauli paramagnetism, Landau and Larmor diamagnetism. The experimental data is fitted very well according to eq. (3). In CuIr$_2$S$_4$ system, only Ir$^{4+}$ possesses the moment of $\mu_{eff} = 2\sqrt{S(S+1)} \mu_B = 2\sqrt{\frac{1}{2}(1+\frac{1}{2})} \mu_B \approx 1.73 \mu_B$. However, the fitting results suggest that the experimental moment $\mu$ is substantially larger than $\mu_{eff}$. On the other hand, $N/N_A < 1\%$ ($N_A$ is the Avogadro constant). The fitting results of large $\mu$ and small $N$ indicate the existence of paramagnetic clusters in this system [26]. In a word, the increase of $C$ is increased by the paramagnetic clusters.

From above experimental results, it can be seen that the Peierls-like phase transition is enhanced by the Li-doping undoubtedly, which was failed in previous chemical substitution experiments. As is known, 5$d_{xy}$ orbits of Ir$^{4+}$ ions play a crucial role in this phase transition, which is delicate to the chemical substitution. Previous chemical doping experiments have failed in the enhancement of the phase transition because doped ions either have the wrong charge or have magnetic moments. The Cu$_{1-x}$Ag$_{x}$Ir$_2$S$_4$ system has also been investigated [27]. However, the phase transition was suppressed due to the expansion of the lattice. Li$^+$ presents the same valence as Cu$^+$ which will not destroy the proportion of Ir$^{3+}$/Ir$^{4+}$. Besides, Li$^+$ has a full outer shell electron configuration of 2$s^2$, which has no magnetic moment. However, the increase of $\alpha$ with Li-content in Cu$_{2-x}$Li$_x$Ir$_2$S$_4$ would disfavor the phase transition according to the lattice effect. Thus, the enhancement of phase transition in Cu$_{2-x}$Li$_x$Ir$_2$S$_4$ system may originate from an absolute different mechanism.

On the other hand, we notice that some unknown diffractions appear for the Li-doped samples besides that of Cu$_2$S (see fig. 1(a) and (b)). In order to clarify these unknown diffractions, we performed the low-temperature XRD experiment for Cu$_{0.7}$Li$_0.3$Ir$_2$S$_4$, which is shown in fig. 4(a). As is well known, the phase transition occurs accompanied by the change of lattice symmetry from cubic ($Fd\bar{3}m$) in NS to triclinic (PT) in PS [5,7]. However, for simplicity and directview, the structure can be approximately expressed by the tetragonal structure (I4$_1$/amd) obtained by expanding the lattice along the (001) direction and shortening along the (100) and (010) directions of the cubic unit cell [6,28]. Here, we choose the tetragonal (I4$_1$/amd) structure to describe the lattice symmetry in PS for direct view. It is found that the XRD pattern at 300 K ($T > T_{MI}$) belongs to a cubic cell, while diffractions of XRD patterns below $T_{MI}$ can be well indexed with tetragonal structure (I4$_1$/amd). Figure 4(b) gives the evolution of lattice symmetry around $T_{MI}$. The structure changes from cubic in NS to tetragonal in PS gradually, and these two structures coexist in the phase transition areas. The structure hysteresis is apparent on cooling and warming, which is consistent with that in $\rho(T)$ and $\chi(T)$ curves.

For a further study of the structural phase transition, the XRD diffractions of (311), (222) and (400) around $T_{MI}$ are shown in fig. 5. The coordinates $\vec{R}_l (1, 0, 0)$, $\vec{B}_l (0, 1, 0)$
Enhancement of the Peierls-like phase transition in the Cu\textsubscript{1-x}Li\textsubscript{x}Ir\textsubscript{2}S\textsubscript{4} system

Fig. 4: (Color online) (a) XRD patterns recorded at selected temperatures for Cu\textsubscript{0.7}Li\textsubscript{0.3}Ir\textsubscript{2}S\textsubscript{4}; (b) the fraction of cubic and tetragonal lattice around \(T_{MI}\) (the inset shows the coordinate transformation from cubic to tetragonal).

and \(\mathbf{c}^c_1 (0, 0, 1)\) in the cubic symmetry are changed into \(\mathbf{a}^t_1 (\sqrt{\frac{1}{2}} - \sqrt{\frac{1}{2}}, 0), \mathbf{b}^t_1 (\sqrt{\frac{1}{2}}, \sqrt{\frac{1}{2}}, 0)\) and \(\mathbf{c}^t_1 (0, 0, 1)\) in tetragonal one, as shown in the inset of fig. 4(b). The lattice index obeys the relation \(h^2_c + k^2_c + l^2_c = 2(h^2_t + k^2_t) + l^2_t\), where \(h_t, k_t\) and \(l_t\) are for the lattice index in cubic cell, whereas \(h_t, k_t\) and \(l_t\) are for tetragonal symmetry. According to this relation, the (311)\(_c\) peak splits into (103)\(_t\), and (211)\(_c\), while (222)\(_c\) changes into (202)\(_t\), (400)\(_c\) splits into (004)\(_t\) and (220)\(_t\). As mentioned above, some “unknown” diffractions appear in the Li-doped samples. Here we point that these “unknown” peaks can be exactly indexed as the tetragonal diffractions. Some diffractions of the tetragonal structure in PS are persistent in the cubic phase as shown in fig. 1. These “unknown” diffractions imply that the doping of Li distorts the cubic lattice cell into the tetragonal, which is just the structure in PS. This distortion is apparent for the sample with \(x = 0.3\) even at room temperature. The enhancement of the tetragonal structure favors the Peierls-like phase transition. In this sense, the structure distortion caused by Li-doping should be responsible for the enhancement of the Peierls-like phase transition.

Fig. 5: (Color online) XRD patterns of \(2\theta = 28^\circ - 38^\circ\) registered at intervals of 2 K around \(T_{MI}\) for Cu\textsubscript{0.7}Li\textsubscript{0.3}Ir\textsubscript{2}S\textsubscript{4}.

Conclusion. – In summary, the Peierls-like phase transition in the Cu\textsubscript{1-x}Li\textsubscript{x}Ir\textsubscript{2}S\textsubscript{4} system was investigated. It was found the Peierls-like phase transition was enhanced by the substitution of Li for Cu. Through low-temperature XRD study, we found that the structure was slightly distorted by the doping of Li. It was suggested that this small distortion of lattice should be responsible for the Peierls-like phase transition in the Cu\textsubscript{1-x}Li\textsubscript{x}Ir\textsubscript{2}S\textsubscript{4} system.

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