Study of lattice dynamics in the CuIr$_2$S$_4$ system

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Abstract. The lattice dynamics in the CuIr$_2$S$_4$ system have been investigated through Raman spectroscopy and the induced-pressure effect. Four Raman active modes are observed experimentally. Upon cooling, these Raman spectra undergo changes due to the Peierls-like phase transition. In addition, the substitution of Ag for Cu affects the amplitude of the Raman spectra while keeping their wave number unchanged. Furthermore, the positive and negative pressure effects are induced by shrinking and expanding the lattice. It is suggested that the pressure effect is an effective proof of the orbital-induced Peierls state mechanism.

1 Introduction

The spinel sulphide CuIr$_2$S$_4$ has attracted considerable attention for the orbital-induced Peierls state [1–9]. With decreasing temperature, this three-dimensional compound experiences a rare Peierls-like phase transition at $T_M \approx 230$ K, accompanied by a change of conductivity from a metallic state to an insulating state, and the evolution of its structure from cubic ($Fd\bar{3}m$) to triclinic ($P\bar{T}$) [1,10,11]. In this compound, the Ir ions display an average valence of +3.5 in the metallic state, and are separated equally into Ir$^{3+}$ and Ir$^{4+}$ in the insulating phase [12–14]. After the phase transition, these Ir$^{3+}$ ($S = 0$) and Ir$^{4+}$ ($S = 1/2$) ions form bi-capped hexagonal rings, and chemical-dimerization as well as spin-dimerization happens only to Ir$^{4+}$ ions along the (110) direction [2]. The orbital configuration of the Ir ion plays an important role in this phase transition. It is suggested that the orbits of the Ir ions induce the quasi-one-dimensional Peierls state in the low temperature insulating phase, the so called orbital-induced Peierls state. This mechanism provides a perfect explanation for the complicated charge ordered structure at low temperatures [3,15,16].

Although the orbital-induced Peierls state in CuIr$_2$S$_4$ has been studied in detail, the lattice dynamics for this system are rarely investigated. In addition, some problems involving the lattice still remain open, such as the pressure effect [17–19]. The transition temperature $T_{MI}$ in this system increases with the increase of hydrostatic pressure, which is in contrast to that in the common Mott insulator (i.e., it is an inverse Mott insulator) [20]. That is to say, the orbital-induced Peierls state is enhanced by the hydrostatic pressure [17]. However, the relationship between the orbital-induced mechanism and the pressure effect has not been clarified yet.

In this paper, the lattice dynamics in the CuIr$_2$S$_4$ system have been investigated by Raman spectroscopy and the induced-pressure effect. The vibration modes for the Raman spectra have been determined. Moreover, changes occurred to the Raman spectra due to the Peierls-like phase transition at $T_M$. On the other hand, the negative and positive pressure effect is induced in order to study the influence of the lattice variation on the phase transition. It is found that the lattice variation has a linear effect on the phase transition temperature, which suggests that the pressure effect provides a strong evidence for the orbital overlap of Ir 5$d$ electrons proposed in the orbital-induced Peierls state model.

2 Experiment

Polycrystalline samples of Cu$_{1-x}$Ag$_x$Ir$_2$S$_4$ ($x = 0, 0.05, 0.1$ and $0.15$) were prepared by the solid-state reaction method described previously [21]. The XRD patterns at room temperature confirm single phase with cubic structure belonging to the space group Fd$ar{3}m$ It is found using the Rietveld method that the lattice constant $a$ increases with the increase of $x$ for the Ag-doped samples [21]. Raman scattering spectra at selected temperatures were obtained on a Spex-1403 Raman spectrophotometer using a back-scattering technique. The magnetic properties were measured using a commercial SQUID magnetometer (quantum design MPMS). An Easylab Mccell 10 pressure cell was used to generate hydrostatic pressures.
3 Result and discussion

3.1 Raman spectra analysis

Figure 1 shows Raman spectra at selected temperatures for Cu\textsubscript{1-x}Ag\textsubscript{x}Ir\textsubscript{2}S\textsubscript{4} (x = 0 and 0.15). At 300 K, there are four peaks on the spectrum of CuIr\textsubscript{2}S\textsubscript{4} (Fig. 1a), indicating four Raman active modes. In order to determine these Raman active modes, the structure of CuIr\textsubscript{2}S\textsubscript{4} is analyzed. At room temperature, CuIr\textsubscript{2}S\textsubscript{4} possesses a cubic normal spinel type structure with the space group Fd\overline{3}m, and the point group belonging to O\textsubscript{h}. The spinel type structure gives the total vibration modes:

\[ \Gamma = 1A_{1g} + 2A_{2u} + 1E_{g} + 2E_{u} + 1F_{1g} + 4F_{1u} + 3F_{2g} + 2F_{2u} \]  

with only five Raman active modes:

\[ 1A_{1g} + 1E_{g} + 3F_{2g}. \]  

The corresponding force constants and internal coordinates of the Raman active modes are listed in Table 1; the schema of the force constants are shown in Figure 2.

Table 1. The Raman-active modes for the spinel structure compound Cu(Ag)Ir\textsubscript{2}S\textsubscript{4}.

<table>
<thead>
<tr>
<th>Sample (species)</th>
<th>Force constant</th>
<th>Internal coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsubscript{1g}</td>
<td>K\textsubscript{2}</td>
<td>Ir-S</td>
</tr>
<tr>
<td>K\textsubscript{1}</td>
<td>Cu(Ag)-S</td>
<td></td>
</tr>
<tr>
<td>F\textsubscript{2}</td>
<td>S-S(1)</td>
<td></td>
</tr>
<tr>
<td>F\textsubscript{1}</td>
<td>Ir-Ir</td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>S-Ir-S</td>
<td></td>
</tr>
<tr>
<td>E\textsubscript{g}</td>
<td>K\textsubscript{2}</td>
<td>Ir-S</td>
</tr>
<tr>
<td>F\textsubscript{3}</td>
<td>S-S(2)</td>
<td></td>
</tr>
<tr>
<td>F\textsubscript{2}</td>
<td>S-S(1)</td>
<td></td>
</tr>
<tr>
<td>F\textsubscript{1}</td>
<td>S-S(3)</td>
<td></td>
</tr>
<tr>
<td>F\textsubscript{2}(1)</td>
<td>K\textsubscript{2}</td>
<td>Ir-S</td>
</tr>
<tr>
<td>K\textsubscript{1}</td>
<td>Cu(Ag)-S</td>
<td></td>
</tr>
<tr>
<td>F\textsubscript{1}</td>
<td>S-S(1)</td>
<td></td>
</tr>
<tr>
<td>F\textsubscript{2}</td>
<td>S-S(2)</td>
<td></td>
</tr>
<tr>
<td>F\textsubscript{3}</td>
<td>S-S(3)</td>
<td></td>
</tr>
<tr>
<td>F\textsubscript{2}(2)</td>
<td>K\textsubscript{1}</td>
<td>Cu(Ag)-S</td>
</tr>
<tr>
<td>K\textsubscript{2}</td>
<td>Ir-S</td>
<td></td>
</tr>
<tr>
<td>F\textsubscript{3}</td>
<td>S-S(2)</td>
<td></td>
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<tr>
<td>F\textsubscript{2}</td>
<td>S-S(1)</td>
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<tr>
<td>F\textsubscript{1}</td>
<td>S-S(3)</td>
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<tr>
<td>F\textsubscript{2}(3)</td>
<td>K\textsubscript{1}</td>
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<tr>
<td>K\textsubscript{2}</td>
<td>Ir-S</td>
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<td>F\textsubscript{1}</td>
<td>S-S(1)</td>
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<td>F\textsubscript{2}</td>
<td>S-S(2)</td>
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</tr>
<tr>
<td>F\textsubscript{3}</td>
<td>S-S(3)</td>
<td></td>
</tr>
</tbody>
</table>

In fact, the wave number of the five Raman active vibration modes in the spinel structure have the relationship:

\[ A_{1g} > F_{2g}(1) > F_{2g}(2) > E_{g} > F_{2g}(3) \]

Therefore, the four vibration modes in the spectrum of CuIr\textsubscript{2}S\textsubscript{4} are A\textsubscript{1g} (403 cm\textsuperscript{-1}), F\textsubscript{2g}(1) (375 cm\textsuperscript{-1}), F\textsubscript{2g}(2) (327 cm\textsuperscript{-1}) and E\textsubscript{g} (302 cm\textsuperscript{-1}), respectively. The F\textsubscript{2g}(3) mode is not observed. When above T\textsubscript{MI} \approx 230 K, the Raman modes for CuIr\textsubscript{2}S\textsubscript{4} remain unchanged with cooling. When below T\textsubscript{MI}, all Raman modes move towards higher wave numbers, in addition to the abrupt weakening of the intensities of these modes. Even the F\textsubscript{2g}(1) and F\textsubscript{2g}(2) modes become too weak to be observed. In fact, all these changes can be related to the chemical-dimerization of the Ir-Ir bonds below T\textsubscript{MI}. When the Peierls-like phase transition takes place, the chemical-dimerization of Ir\textsuperscript{4+}-Ir\textsuperscript{4+} bonds along the (110) direction occurs simultaneously. This makes the vibration of the bonds difficult. Thus, the vibration frequencies move towards higher values with higher energy. At the same time, some vibration modes become weaker due to the dimerization of Ir-Ir bonds, leading to the weakening of the intensities of the Raman modes.
For a further understanding of the Raman modes, Raman spectra of the Ag-doped sample Cu$_{0.85}$Ag$_{0.15}$Ir$_2$S$_4$ were measured for comparison, as shown in Figure 1b. With the substitution of Ag for Cu, the wave number of the Raman modes is not changed, but the intensities of $A_{1g}$, $F_{2g}(1)$ and $F_{2g}(2)$ become weaker compared with the $E_g$ mode. This indicates that the Ag doping only affects the vibration amplitudes, but does not influence the vibration frequencies. In fact, the Ag doping only affects the internal coordinate of Cu(Ag)-S, i.e., the $K_1$ force constant (see Tab. 1 and Fig. 2). The $A_{1g}$, $F_{2g}(1)$ and $F_{2g}(2)$ modes contain the $K_1$ force constant, while $E_g$ is unrelated to $K_1$. So, the intensities of the $A_{1g}$, $F_{2g}(1)$ and $F_{2g}(2)$ modes become weaker in the Ag-doped system. From Table 1, one can see that the $E_g$ mode contains $H_1$ involving S-Cu(Ag)-S. Actually, $H_1$ is a bending force which contributes little to the vibration mode [25]. This is the reason why the $E_g$ mode is hardly influenced by the Ag doping. With decreasing temperature, similar changes occur to the Raman spectra of Cu$_{0.85}$Ag$_{0.15}$Ir$_2$S$_4$ except that its transition temperature becomes lower than that of CuIr$_2$S$_4$.

### 3.2 Positive and negative pressure effect

As discussed above, the doping with Ag has changed the vibration modes of the lattice, which results in changes to the Raman modes. In fact, the doping with Ag not only affects the vibration of the bonds, but also causes a negative pressure in this system. As reported previously, the Ag doping expands the lattice (negative pressure), which weakens the Peierls-like phase transition [21]. Based on this point, the Peierls-like phase transition will be enhanced by shrinking the lattice (positive pressure). So, the hydrostatic pressure is used to achieve a lattice shrinking effect. The temperature dependences of the magnetization for CuIr$_2$S$_4$ under (a) positive and (b) negative pressures are shown in Figure 3. As expected, $T_{MI}$ moves towards higher temperatures with the increase of hydrostatic pressure, while moving towards lower temperatures with Ag doping under negative pressures. Figure 4 plots the transition temperature $T_{MI}$ as a function of Ag content or pressure, which demonstrates that $T_{MI}$ changes linearly with lattice variation. It can be shown that $T_{MI}$ increases with the pressure as $dT_{MI}/dp = 2.7$ K/kbar, while decreasing with the lattice constant as $dT_{MI}/da = 1061$ K/˚A [21]. One can see that the change of lattice constant has a significant effect on $T_{MI}$.

In fact, the positive and negative pressure effect can be understood according to the orbit-induced Peierls state model. In this model, the overlap of the Ir $d_{xy}$ orbit plays a dominant role after the phase transition. As illustrated in Figure 5, the chemical-dimerized Ir$^{4+}$-Ir$^{4+}$ bond is along the (110) direction, and the $d_{xy}$ orbits of dimerized Ir$^{4+}$ overlap with each other. When the lattice expands, the Ir-Ir distance increases, leading to the weakening of the orbit-induced Peierls state. Inversely, when the lattice shrinks, the Ir-Ir distance becomes shorter, causing the enhancement of the orbit-induced Peierls state. Thus, the positive and negative pressure effect in the CuIr$_2$S$_4$ system is a manifestation of the orbit-induced Peierls state mechanism.

### 4 Conclusion

In summary, the lattice dynamics of the CuIr$_2$S$_4$ system have been investigated by means of Raman spectra and the induced-pressure effect. The four Raman active
modes have been determined. Moreover, the Peierls-like phase transition is observed in the Raman spectra with decreasing temperature. Furthermore, doping with Ag only changes the vibration amplitude but does not affect the frequencies of the Raman modes since the Ag doping only changes the $K_1$ force constant. In addition, the positive and negative pressure effects have also been used for studying the pressure effect, which gives an effective proof supporting the orbit-induced Peierls state model.

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