PRESSURE-INDUCED $4p \rightarrow 4s$ ELECTRON TRANSFER AND ITS EFFECT ON ELECTRICAL TRANSPORT OF COPPER ①

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ABSTRACT

On the basis of band theories, the pressure-induced $4p \rightarrow 4s$ electron transfer of copper and its effect on the densities of states near Fermi level E_F in the $4p$ and $4s$ bands are discussed. The explanation for the pressure dependence of electrical resistance of copper under compression up to 11 GPa is offered.

Key words: high pressure copper electron transfer electrical resistance

1 INTRODUCTION

The physical properties of copper have been widely studied under the conditions of normal pressure, high temperature and low temperature. However, the research of up to several hundred thousands atmospheric pressure have not been reported widely. As for the electrical properties under static high pressure, only the data of Bridgman[1] in the range of 0～10 GPa are available. With the development of DAC[2] (diamond anvil cell) techniques, it is possible to research electrical properties of metal at higher pressure range. But the work concerning electrical transport of metal under static high-pressure has not been widely reported as a result of the reason for experimental techniques[3]. Using the experimental method[4], we have studied the pressure dependence of electrical resistance for copper, iron and nickel[5] and compared the differences in these resistance data on the basis of their atomic sturctures. However, the variations in resistance with pressure were not involved there. In accordance with band theories, we discussed the pressure dependence of nickel and successfully explained the disscontinuity of resistance at 28.8 GPa[6]. Here we intend to analyse the effect of pressure on electrical transport of copper in the light of pressure-induced electron transfer.

2 PRESSURE- INDUCED ELECTRON TRANSFER FOR COPPER

Fig. 1 shows the measured resistance data of copper. A Mao-Bell type of DAC[2] was used as pressure apparatus and the pressure was calibrated using the ruby pressure scale[7]. The fluorescence of ruby was excited by 488 nm laser beam of model 168 argon ion laser. The copper wire, with a purity of 99.99%, was used as sample. The experimental techniques have been described in detail elsewhere[4].

It can be seen from Fig. 1 that the relative resistance decreases with increasing pressure within the whole range of 2.2～11.0 GPa. For comparition we also show the data of Bridgman[1].

Why does the resistance of copper decrease with increasing pressure? This problem was not discussed before. In order to understand the effect of pressure on electrical conductivity of copper, it is necessary to discuss the problem.

At normal pressure, the $3d$ band of copper is fully filled and the whole $3d$ band is located below Fermi level E_F. But the $4s$ and $4p$ bands are partial-

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ly filled, as shown in Fig. 2. It should be explained that Fig. 2 is from ref. [8], but some modifications have been made to avoid misunderstandings. In the original figure, shown in Fig. 3, given by Albers *et al.*, the $4s$ and $4p$ bands were drawn into energy levels at normal and extremely high pressures ($V_0/V \sim 9$). According to the original variation trend of the $4s$ and $4p$ band, we extend the two bands. To distinguish the different bands, dotted line is used in the direction of $V_0/V < 1$ and solid

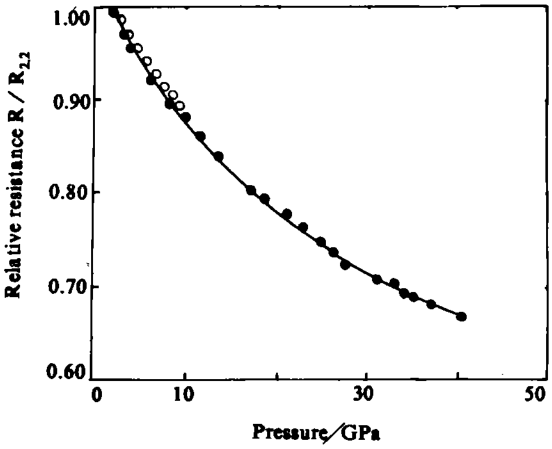

Fig. 1 Relative resistance $R/R_{2.2}$ of copper versus pressure

$R_{2.2}$ is the resistance of copper at 2.2 GPa. Open circles are the data of Bridgman[1] and full circles are the results of this paper.

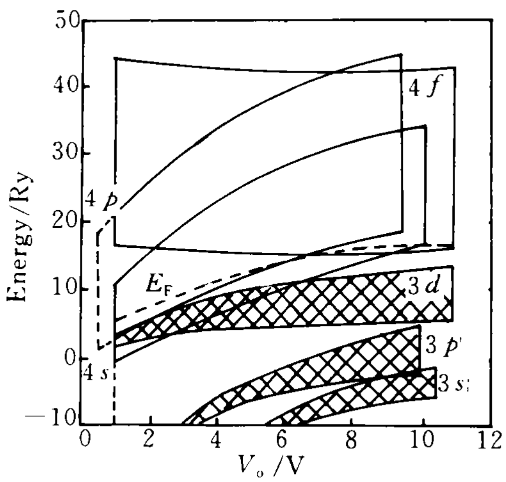

Fig. 2 Bands of copper versus pressure

This Fig. is from ref. [8] and some modifications are made.

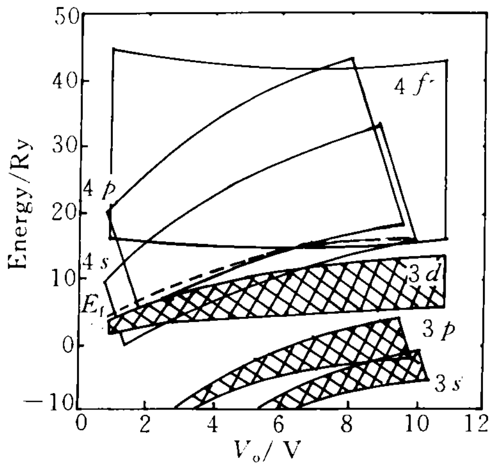

Fig. 3 Bands of copper versus pressure

This is the original figure from ref. [8]

lines parallel to energy axis are employed in extremely high pressure area, as shown in Fig. 2.

Because of the decreasing of distance among atoms under compression, the atomic interaction and overlap of outer electrons of atoms will increase, which will lead to relative shift of bands and make the bands become extensive. It can be seen from Fig. 2 that the whole $3d$ band of copper keeps being fully filled in extremely wide range of pressure ($V_0/V \approx 1 \sim 10$). Therefore we can ignore the $3d$ band just as we do for $3s$ and $3p$ bands wihch are also fully filled, only consider the $4s$ and $4p$ bands which are partially filled. Because $4s$ electron is closer to nucleus than $4p$ electron, the effect of pressure on $4p$ electron is larger than $4s$ electron. This means that the speed of shift for $4p$ band along increasing energy is faster than $4s$ band, which will result in transfer of electron near the Fermi level E_F from the $4p$ band to $4s$ band. This pressure-induced $4p \to 4s$ electron transfer can also be seen from Fig. 2. With increasing pressure, the number of electrons in the $4p$ band becomes smaller and smaller, and finally the $4p$ band becomes vacant at higher range of pressure (corresponding to the compression V_0/V of above 6.5). The decreasing of electron number in $4p$ band means that some of the $4p$ electrons transfer to other bands under high pressure. Because there are only $4s$, $4p$ bands near E_F, the $4p$ electrons can only transfer to $4s$ band. The pressure-induced electron transfer varies the occupations of the $4s$, $4p$ bands and make the Fermi level E_F change. The electrical resistance of copper results mainly from the scattering of electrons near the E_F from the $4s$ band to the vacant states near the same level in the $4p$ band. The scattering probability is proportional to the densities of the vacant states in the $4p$ band. Because the pressure-induced $4p$ to $4s$ electron transfer alters the densities of vacant state in $4p$ band, the probability of scattering from $4s \rightarrow 4p$ will be affected. The variation in scattering probability will directly lead to the change in electrical resistance. In order to understand the pressure dependence of resistance of copper, we have to know how the densities of states near E_F in $4s$, $4p$ bands vary with the increasing pressure.

3 EFFECT OF PRESSURE-INDUCED $4p \rightarrow 4s$ ELECTRON TRANSFER ON THE DENSITIES OF STATE IN THE $4p$ BAND

Albers *et al.* [8] calculated the densites of states of copper at the Fermi energy $D(E_F)$ as a function of compression V_0/V, as shown in Table 1.

Table 1 Fermi energy E_F (in Ry) and density of states of copper at the Fermi energy $D(E_F)$ (in states/atom Ry) as a function of compression V_0/V

V_0/V	E_F	$D(E_F)$
1	0.58	4.0
1.3	0.85	3.4
2	1.54	2.4
3	2.62	1.6
5	5.03	1.0
7	7.48	0.85
10	10.75	0.74

From ref. [8] (only parts of the data are quoted.)

It can be seen from the table that the densities of states $D(E_F)$ will decrease with pressure-increasing. According to Fig. 2, we know that $D(E_F)$ should consist of the densities of states at E_F in the $4s$ and $4p$ bands. Therefore we can express $D(E_F)$ as follows:

$$D(E_F) = {}^{4s}D(E_F) + {}^{4p}D(E_F) \qquad (1)$$

where the ${}^{4s}D(E_F)$ and ${}^{4p}D(E_F)$ are the densities of states at E_F in the $4s$ and $4p$ bands, respectively. Let pressure increase from normal pressure to P (GPa), and the variation in densities of states at E_F is $\triangle D(E_F)$. From equation (1) we can obatin

$$\triangle D(E_F) = \triangle {}^{4s}D(E_F) + \triangle {}^{4p}D(E_F) \qquad (2)$$

Since $D(E_F)$ decreases with pressure, we can have

$$\triangle D(E_F) < 0 \qquad (3)$$

There are three possible situations to satisfy equation (3):

$$\text{a)} \begin{cases} \triangle {}^{4s}D(E_F) < 0 \\ \triangle {}^{4p}D(E_F) < 0 \end{cases} \qquad (4)$$

$$b) \begin{cases} \triangle {}^{4s}D(E_F) > 0 \\ \triangle {}^{4p}D(E_F) < 0 \\ |\triangle {}^{4s}D(E_F)| < |\triangle {}^{4p}D(E_F)| \end{cases} \qquad (5)$$

$$c) \begin{cases} \triangle {}^{4s}D(E_F) < 0 \\ \triangle {}^{4p}D(E_F) > 0 \\ |\triangle {}^{4s}D(E_F)| > |\triangle {}^{4p}D(E_F)| \end{cases} \qquad (6)$$

We now analyse which one among the above three situations can truly stand. We first discuss the third situation which requires $\triangle {}^{4s}D(E_F) < 0$. As a matter of fact, this situation will not happen, as we can see from the following discussion. Slater[9] calculated the densities of states of the $3d$ and $4s$ bands of copper at normal pressure, as shown in Fig. 4. As we can see from the Fig. 4, the densities of states near Fermi level E_F in $4s$ band will gradually increase in the direction of energy-increasing, and start to decrease only near the top of $4s$ band. Although pressure will cause the $4s$ band to broaden and shift, the basic features of the density-states curve will not be changed below 100 GPa. Zhou and co-workers[10] calculated the density-of-states of copper at pressures of 0 GPa, 100 GPa and 410 GPa, respectively. Their calculation results showed that the essential features of the density-of-states curve will not be destroyed at 100 GPa except for the extension and shift. We can reasonably think that the density-of-states curve of the $4s$ band will keep its essential features shown in Fig. 4 at the pressures below 50 GPa. As discussed above, pressure will cause the transfer of electrons near E_F in the $4p$ band to the vacant states at the same level in $4s$ band. According to Fig. 4, we know that the $4p \rightarrow 4s$ electron transfer will make the densities of vacant states increase near E_F in $4s$ band, i. e. $\triangle {}^{4s}D(E_F) > 0$. Therefore we think that the equation (6), which requires $\triangle {}^{4s}D(E_F) < 0$, is practically impossible. For the same rea-

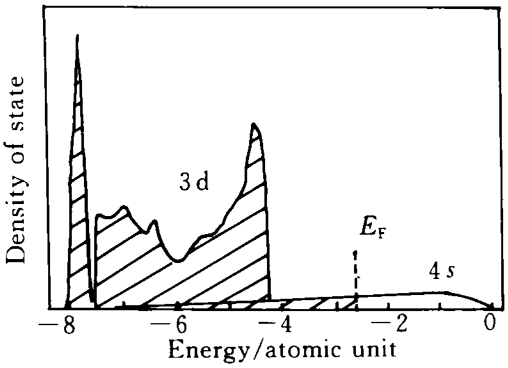

Fig. 4 Energy versus density of state

son the first situation (4) is also impossible. The only possible situation left is equation (5) which meet the requirement of $\triangle^{4s}D(E_F) > 0$, i. e. the pressure-induced decreasing of the general state-density results from the decreasing of state-density in the 4 p band under compression. According to equation (5), we know that the pressue-induced 4 p → 4 s electron transfer results in the decreasing of the densities of states near E_F in the 4 p band. The decreasing-densities near E_F in 4 p band will make the 4 s → 4 p scattering of electrons near E_F more difficult, and thus make the elctrical resistance decrease. We suggest that this is the reason why the resistance of copper decreases with increasing pressure in the range of 2. 2～41. 0 GPa.

4 CONCLUSIONS

(1) With increasing pressure, the electrons near E_F will transfer from the 4 p band to the 4 s band. The pressure-induced 4 p → 4 s electron transfer will result in the increasing of the densities of unoccupied states near E_F in the 4 s band and make the densities of unoccupied states decrease near E_F in the 4 p band.

(2) Because of the pressure-induced 4 p → 4 s electron transfer and the decreasing of the densities of unoccupied states near E_F in the 4 p band, the scattering of electrons near E_F from the 4 s band to 4 p band will become more diffcult, and thus make the resistance decrease.

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