# Mechanical-Electric Coupling in Metals

Yuanjie Huang\*

Mianyang, Sichun province, People's Republic of China

\*Corresponding author's E-mail: <u>hyj201207@163.com</u>

## Abstract

In metal physics, the free electron model and the related Fermi-Dirac distribution were usually utilized to investigate multi-physical properties of metals. However, they neglected the important mechanical-electric coupling (MEC), and therefore some longstanding physical problems such as the positive Seebeck coefficients of some monovalent metals and the physical origin of charge density wave (CDW) gap may be difficult to solve. In the work, the MEC in metals was investigated. It was found that the MEC can not only monitor the diffusion relation of conduction electrons and the sign of Seebeck coefficients of the monovalent metals but also give the physical origin of the CDW gap. In addition, the MEC may lead to a single-electron model which could offer a simple way of interpreting the electron heat capacity, the Pauli magnetic susceptibility, the electrical conductivity and the electron thermal conductivity of the metals including the heavy fermion systems. Overall, the MEC may be important for the metals and it should be taken into account seriously for investigating the physical properties of the metals.

*keywords*: mechanical-electric coupling; metals; diffusion relation; Seebeck coefficient; charge density wave;

#### 1. Introduction

In many textbooks and literatures [1-8], the Fermi energy in the free electron model has been commonly treated as the electron chemical potential of conduction electrons in a metal. And it has been widely utilized to analyze the related physical phenomena such as thermoelectric power and electron degeneracy pressure. However, the variations of the potential energy of the conduction electrons was neglected in the free electron model, and it is difficult for the related theory to tackle some long-standing physical problems, *e.g.*, the magnitude of the charge density gap and the positive Seebeck coefficients of monovalent metals Li, Cu, Ag and Au whose charge carriers are electrons that is established by the experimentally measured Hall coefficients.

As enlightened by *Yuheng Zhang effect*, a strain can give rise to the shift of electron chemical potential and thereby can lead to a mechanical-electric coupling (MEC) in a metal [9, 10]. The MEC was found to induce some new physics such as the electric properties of dislocations and the electric force between dislocations [11]. On another hand, the MEC can also result in the new understandings of the conventional problems.

In this work, the MEC was adopted to modify the free electron model and thereby address the important problems in metal physics, for instance, the magnitude of charge density wave (CDW) gap, the sign of Seebeck coefficients opposite to Hall coefficient for some monovalent metals, the heat capacity and magnetic susceptibility of heavyfermions and the electron degeneracy pressure.

#### 2. Results and discussion

Yuheng Zhang equation should be introduced first, which may be the important

foundation in the work. For any material, there may usually exist some physical factors such as strain, temperature, doping and so on, which can give birth to alterations of the Fermi surface. Analogous to water flowing from a higher position to a lower position, the electrons also tend to flow from the regions with higher Fermi surface to regions with lower Fermi surface, thereby inducing an electric field between the regions. Reversely, the macro-electrostatic field in the metal may originate from the spatial variations of the Fermi surface. Upon equilibrium state, the physical relation between the macro-electric field and the correlated Fermi surface alterations may be described by *Yuheng Zhang equation* [12],

$$\nabla E_F(\vec{r}) = e\vec{E}(\vec{r}) \tag{1}$$

where *e* is electron (positron) charge,  $E_F(r)$  is the position-dependent electron (positron) chemical potential at the equilibrium state, E(r) is the position dependence of the macro-electric field.

*Yuheng Zhang equation* may be very important in various fields and its validity should be discussed here. This equation may rigorously hold for systems satisfying the following three conditions. Firstly, the electron (positron) system must be in an equilibrium state. Secondly, the electron systems must conform to the conservation of electron (positron) number. Thirdly, the electron (positron) must be a point particle and does not exhibit any measureable volume effects, which is an important foundation for quantum electrodynamics. *Yuheng Zhang equation* might be a fundamental physical relation, and could not be derived by quantum mechanics, because the point particle assumption for electrons may not be addressed by the quantum mechanics. In this

equation, the electron (positron) chemical potential may exhibit the statistical properties of studied electron systems and it usually depends on the quantum properties of the electron (positron) systems. As a result, *Yuheng Zhang equation* may statistically contain the quantum characteristics of electron (positron) systems no matter how complex their interaction and the experienced fields could be. The equation may be valid for the 1 dimensional, 2-dimensional and 3-dimensional electron systems and it may find important applications in different fields. For example, the unraveled existence of the electrostatic field inside metals may induce some interesting physical effects which were ever discussed [9-11, 13-15].

In many textbooks, the Fermi energy were regarded as the electron chemical potential at zero temperature [1-8]. And the Fermi energy of non-interacting conduction electrons at zero temperature is commonly written as [1-8]

$$\varepsilon_{F0} = \frac{\hbar^2}{2m_e} \left(3\pi^2 n_e\right)^{2/3}$$
(2)

where  $\varepsilon_{F0}$  the Fermi energy at zero temperature,  $\hbar$  is the reduced Plank constant,  $m_e$  the electron mass,  $n_e$  is the conduction electron density and it is  $n_e = N_e/V$ ,  $N_e$  is total number of conduction electrons, V the volume of the electron system.

However, the electron chemical potential  $E_F$  refers to the energy it takes to add or remove an electron from the material and take it to vacuum infinity with zero kinetic energy [1]. The vacuum level is usually defined zero [1]. So the chemical potential is always negative. For the metals at zero temperature, it divides the empty from the occupied states and is the negative of the work function [1]. Of specially emphasized is that it may not be Fermi energy which is usually encountered in many textbooks and literatures. The Fermi energy only refers to the energy difference between the highest and lowest occupied conduction electron states in a non-interacting free electron system at zero temperature and cannot take into account the variations of potential energy of the conduction electrons. But the potential energy is important and is usually influenced by some physical factors such as strain and doping. Therefore, the electron chemical potential for a metal should include the contribution of both the Fermi energy and the potential energy of the conduction electrons. According to the theory for the electrons in a Wigner-Seitz cell, the potential energy usually includes the Coulomb attraction energy due to the positive ion core, the direct Coulomb energy among the electrons, the electron exchange energy, electron correlation energy and contributions of surface dipole layer [1, 2]. Thereby it may be written as

$$E_F = \mathcal{E}_p(r_s, \mathcal{E}_F) + \mathcal{E}_F \tag{3}$$

where  $\varepsilon_F$  stands for the Fermi energy of the conduction electrons at a finite temperature,  $\varepsilon_P(r_s, \varepsilon_F)$  denotes the potential energy of the conduction electrons and it not only depend on the electron density which is usually depicted by the dimensionless ratio  $r_s$  but also depend on the kinetic energy  $\varepsilon_k$ ,  $r_s$  is a dimensionless ratio,  $r_sa_0$  is the average radius of a sphere containing a single conduction electron in the metals,  $a_0$  is the Bohr radius, and they satisfy the following relation [2, 4, 8],

$$\frac{4}{3}\pi a_0^3 r_s^3 n_e = 1$$

In the following discussions the potential energy  $\varepsilon_p(r_s, \varepsilon_F)$  will sometimes be written as  $\varepsilon_p$  for brevity. And the MEC for an isotropic metal can be defined by

$$C_{m-e} = \frac{V dE_F}{dV} \tag{4}$$

Based on Equation (3) and the common definition of density of state [4], *i.e.*, the relation  $dN_e = Vg(\varepsilon) d\varepsilon$  where  $g(\varepsilon)$  is the density of states at the energy  $\varepsilon$ , the MEC can be expressed by

$$C_{m-e} = \frac{r_s}{3} \frac{\partial \varepsilon_p(r_s, \varepsilon_F)}{\partial r_s} - \left[1 + \frac{\partial \varepsilon_p(r_s, \varepsilon_F)}{\partial \varepsilon_F}\right] \frac{n_e}{g(\varepsilon_F)}$$
(5)

where  $g(\varepsilon_F)$  is the common density of states at Fermi energy. In the related calculations, the relation  $V\partial\varepsilon_F/\partial V = -n_e\partial\varepsilon_F/\partial n_e$  was employed.

The MEC may be of paramount importance in some physical effects and would be discussed in the followings.

## 2.1 Modified electron diffusion relation in metals

Considering the conduction electrons in a strained metal, the non-uniform volumetric strain may cause the position-dependent conduction electron density. And the spatial gradient of the conduction electron density will result in a diffusion current density according to the Fick's first law [4, 16]

$$\vec{j}_1 = -eD_e \nabla n_e(\vec{r})$$

where  $n_e(r)$  is the position dependence of the conduction electron density,  $D_e$  is the diffusion coefficient of the conduction electrons. In another respect, when the electron equilibrium state will be approached the non-uniform volumetric strain may cause an electric field in the metal based on Equation (1)

$$\frac{dE_F}{dV(\vec{r})}\nabla V(\vec{r}) = e\vec{E}$$

where V(r) is the position-dependent volume and it satisfies  $n_e(r)V(r)=1$ . The electric

field will induce a drift current density according to the Ohm's law

$$\vec{j}_2 = \frac{\sigma_e}{e} \frac{dE_F}{dV(\vec{r})} \nabla V(\vec{r})$$

where  $\sigma_e$  is the electron conductivity and it is commonly expressed as  $\sigma_e = en_e\mu_e$ ,  $\mu_e$  is the mobility of the conduction electrons. As a consequence, the total electrical current is the summation of the drift current density and the diffusion current density [16]

$$\vec{j}_t = \frac{\sigma_e}{e} \frac{dE_F}{dV(\vec{r})} \nabla V(\vec{r}) - eD_e \nabla n_e(\vec{r})$$

The total electrical current must be zero when the electron equilibrium state is reached [9, 16]. Using the definition of MEC, the diffusion relation for the conduction electrons may be obtained

$$\frac{D_e}{\mu_e} = \frac{C_{m-e}}{-e} \tag{6}$$

It indicates that the diffusion coefficient of the conduction electrons depends on the volumetric strain-involved MEC of the metal. If the MEC of the metal exhibits a large value, the diffusion coefficient will also display a huge magnitude.

In most textbooks [1-8, 16], the potential energy  $\varepsilon_p$  of the conduction electron was popularly neglected for the electron chemical potential and the Fermi energy was regarded as the electron chemical potential. Some references [1, 9] noted the difference between the electron chemical potential and the Fermi energy, but the mathematical expression of the Fermi energy instead of the electron chemical potential was still utilized to calculate the diffusion coefficient of conduction electrons [9]. Therefore, the diffusion relation obtained in terms of the Fermi energy in the related references [9, 16] may only be an approximate relation. The precise diffusion relation for the conduction electrons should be given by the MEC which adopts the electron chemical potential containing the potential energy of the conduction electrons, as is shown by Equation (6).

### 2.2 Modified Thomas-Fermi screening length

The MEC may have an important effect on the electron screening in the metal and it will be investigated in the section. Based on *Yuheng Zhang equation* and Maxwell equations, it follows that

$$\nabla^2 E_F(\vec{r}) = \frac{e^2}{\varepsilon_0} \left[ n_e(\vec{r}) - Z_i \delta(\vec{r}) \right]$$
(7)

where  $Z_i$  is the valence of an ion core,  $\varepsilon_0$  is the vacuum permittivity. By expanding the left-hand side of the above equation, it is

$$\frac{dE_F(\vec{r})}{dn_e(\vec{r})}\nabla^2 n_e(\vec{r}) + \frac{d^2E_F(\vec{r})}{dn_e^2(\vec{r})} \left[\nabla n_e(\vec{r})\right]^2 = \frac{e^2}{\varepsilon_0} \left[n_e(\vec{r}) - Z_i\delta(\vec{r})\right]$$

The spatial gradient of the conduction electron density  $\nabla n_e(\vec{r})$  may be a slowly varying function and thereby the nonlinear term may be too small to be considered. As a consequence, the above equation can be simplified to be a liner equation

$$\nabla^2 n_e(\vec{r}) \approx \frac{e^2}{\varepsilon_0} \left(\frac{dE_F}{dn_e}\right)^{-1} \left[n_e(\vec{r}) - Z_i \delta(\vec{r})\right]$$
(8)

So the modified Thomas-Fermi screening wave vector can be obtained

$$q_{TF}^2 = \frac{e^2}{\varepsilon_0} \left(\frac{dE_F}{dn_e}\right)^{-1}$$
(9)

It is identical to the formula in the textbook [2], which suggests that the derivation here may be rational. However, they are distinct from each other. The electron chemical potential used in the above equation includes both the kinetic energy and the potential energy of the conduction electrons, which is different from the Fermi energy only containing the kinetic energy in the textbooks [1, 2]. Using the MEC and the relation  $dE_F/dn_e = -C_{m-e}/n_e$ , Equation (9) changes into the form below

$$q_{TF}^2 = \frac{e^2 n_e}{-\varepsilon_0 C_{m-e}} \tag{10}$$

where  $q_{TF}$  is the modified Thomas-Fermi screening wave vector. As a result, the screening Coulomb potential in momentum space can be obtained according to the textbooks [1, 2, 4]

$$\varphi_i\left(\vec{k}\right) = \frac{-Z_i e}{\varepsilon_0} \frac{1}{k^2 + q_{TF}^2}$$

where  $\varphi_i(k)$  is the screening Coulomb potential of an ion core in the momentum space. The modified Thomas-Fermi screening length can be given by

$$\lambda_{TF}^2 = \frac{-\varepsilon_0 C_{m-e}}{e^2 n_e} \tag{11}$$

where  $\lambda_{TF}$  is the modified Thomas-Fermi screening length. It indicates that the screening length is heavily dependent on the MEC. In the case that the MEC is negative, the modified Thomas-Fermi screening length will exhibit a positive value. And a small magnitude of MEC will lead to a short screening length, suggesting that a strong electron screening may exist in the metal. On the contrary, a large magnitude of the negative MEC will result in a long screening length, presenting a weak electron screening in the metal.

In another interesting case that the MEC is positive, the related screening Coulomb potential will appear in the following form

$$\varphi_i(\vec{r}) = \frac{-Z_i e}{4\pi\varepsilon_0} \frac{e^{\pm i|q_{TF}|r}}{r}$$
(12)

where  $|q_{TF}|$  is the magnitude of the modified Thomas-Fermi screening wave vector. It reveals that the screening Coulomb potential may display the oscillating behaviors. By means of simple calculations, the screening Coulomb potential of the ion core in the momentum space will become

$$\varphi_i\left(\vec{k}\right) = \frac{-Z_i e}{\varepsilon_0} \frac{1}{k^2 - \left|q_{TF}^2\right|}$$
(13)

As is shown, if the magnitude of the wave vector is larger than that of the modified Thomas-Fermi screening wave vector, the screening Coulomb potential is still attractive. Nevertheless, the screening Coulomb potential will be repulsive in the situation that the wave vector is smaller than that of the screening wave vector, which is remarkably distinct from the common screening Coulomb potential. As the wave vector of the conduction electron approaches the modified Thomas-Fermi screening wave vector, the screening Coulomb potential may exhibit a singularity. The singularity may have a profound effect on the related physical properties and needs to be studied in the future.

### 2.3 Seebeck coefficient

Thermoelectric effect is an important physical effect and is usually described by Seebeck coefficient. According to the theoretical definition in textbooks and literatures [1, 17-21], it is written as

$$S_{th} = \frac{E}{\nabla T} \tag{14}$$

where  $S_{th}$  is Seebeck coefficient, E the temperature-gradient-induced electric field in

the metal. But experimentalists usually use the experimental definition of the Seebeck coefficient [1, 20]

$$S_{ex} = \frac{-\Delta V}{\Delta T} \tag{15}$$

where  $\Delta V$  is the voltage difference,  $\Delta T$  the temperature difference. Based on these definitions [1, 4, 8, 17-20], the sign of Seebeck coefficient should be the same as that of the Hall coefficient. In another word, both the Seebeck coefficient and Hall coefficient is negative if the carriers are electrons, but they would be positive if the carriers are holes. However, the experimental observations showed that the sign of Seebeck coefficient is opposite to that of Hall coefficient for some metals, *e.g.*, Li, Cu, Ag and Au [4, 8, 22]. It was an interesting but long-standing problem in solid state physics. It was ever studied in different aspects. In one aspect, some researchers attributed it to the energy variance of the mean free path near the Fermi energy because of the abnormal electron-phonon interaction [23, 24]. In another aspect, it was investigated and understood as a consequence of a substantial deviation from the density of states for the free electron model [25, 26]. In this work, another new route of understanding the problem would be proposed by adopting *Yuheng Zhang equation* and the MEC.

The thermoelectric effect is a non-equilibrium phenomena and the measured voltage difference arises from electrochemical potential difference [20]. So it was noted and revealed that the theoretical definition of Seebeck coefficient is different from the experimental definition [20]. However, only the temperature-induced lift of chemical potential was considered [20], but another important contribution was neglected, *i.e.*,

the thermal expansion-induced lift of chemical potential [9]. When an end of a metal would be heated, the related electron chemical potential would be altered. The electrons would flow from the region with high chemical potential to the region with low chemical potential. And the drift of electrons would cause an electric field and a related electric potential within the metal. As a result, the measured potential difference between the hot and cool ends is

$$-\frac{V_{ex}(T+\Delta T)-V_{ex}(T)}{\Delta T} = \frac{\left[E_F(T+\Delta T)+e\phi(T+\Delta T)\right]-\left[E_F(T)+e\phi(T)\right]}{e\Delta T} (16)$$

where  $V_{ex}(T+\Delta T)$ ,  $V_{ex}(T)$  is the experimentally measured voltage at the hot end and cool end, respectively,  $\phi(T+\Delta T)$ ,  $\phi(T)$  signifies the respective internal potential at the hot end and cool end. Based on Equations (15) and (16), the experimental Seebeck coefficient can be simplified to be

$$S_{ex} = \frac{\vec{E}_c - \vec{E}_r}{\nabla T} \tag{17}$$

where  $E_c$  is the critical electric field at equilibrium state for the electrons in the metal and it is  $\vec{E}_c = \nabla E_F / e$  according to Equation (1),  $E_r$  the real electric field between the hot and cool ends of the metal  $\vec{E}_r = -\nabla \phi$ . Of emphasized is that the thermoelectric effect is a steady state but non-equilibrium phenomena. So the direction of the critical electric field  $E_c$  is the same as that of the real electric field  $E_r$ , but the magnitude of  $E_c$ is always larger than that of  $E_r$ , making the sign of experimental Seebeck coefficient determined by the critical electric field  $E_c$ . Their magnitude difference may depend on the electrical conductivity heavily, and a larger electrical conductivity may lead to a steady state closer to equilibrium, *i.e.*,  $E_r$  approaching  $E_c$  more closely, thereby yielding a smaller Seebeck efficient. This point is in agreement with experimental observations that the magnitude of Seebeck efficient of most metals decreases with the temperature dropping [4, 27] and the metals such as Ag, Cu and Au with the high electrical conductivity usually exhibit a small Seebeck coefficient [4, 27]. Further, to be anticipated, an ideal metal with infinite electrical conductivity may display a zero Seebeck efficient and cannot exhibit the thermoelectric effect.

To investigate the sign of experimental Seebeck coefficient, Equation (17) can be expressed in another manner,

$$S_{ex} = \frac{dE_F}{edT} - \frac{\dot{E}_r}{\nabla T}$$
(18)

Seen from Equations (16) (17) and (18), the sign of the experimental Seebeck coefficient is monitored by the temperature dependence of electron chemical potential. The sign of the experimental Seebeck coefficient is positive if the electron chemical potential decreases with temperature increasing, but the sign would be negative if the electron chemical potential increases as the temperature increases. More specifically, the dominant term on the right-hand side of Equation (18) can be written as

$$\frac{dE_F}{edT} = \left(\frac{\partial E_F}{e\partial T}\right)_V + \frac{\alpha_V(T)C_{m-e}}{e}$$
(19)

where  $\alpha_V(T)$  is the temperature-dependent volume expansion coefficient of the metal and it is  $\alpha_V(T) = \frac{\partial V}{\partial T} = 3\alpha_I(T)$  for the isotropic metals,  $\alpha_I(T)$  stands for the temperaturedependent linear expansion coefficient. Based on Equation (3), the first term in the above equation can be written as

$$\left(\frac{\partial E_F}{e\partial T}\right)_V = \left(\frac{\partial \varepsilon_p}{e\partial T}\right)_V + \left(\frac{\partial \varepsilon_F}{e\partial T}\right)_V$$
(20)

For the alkali metals and monovalent noble metals, the interaction among conduction electrons may be weak and the non-interacting conduction electron model could be valid. So the potential energy of the conduction electrons  $\varepsilon_p$  may not depend on the temperature directly, leading to the relation  $(\partial \varepsilon_p / \partial T) v=0$ . According to the Sommerfeld expansion in textbooks [2-4, 6, 7, 21], the temperature-dependent Fermi energy  $\varepsilon_F$  is

$$\varepsilon_F \approx \varepsilon_{F0} - \frac{\pi^2}{6} \frac{g'(\varepsilon_{F0})}{g(\varepsilon_{F0})} (k_B T)^2$$
(21)

where  $k_B$  the Boltzmann constant,  $g(\varepsilon_{F0})$  is the density of states at the zero-temperature Fermi energy,  $g'(\varepsilon_{F0})$  the derivative of the density of states with respect to the energy  $g'(\varepsilon_{F0}) = \partial g(\varepsilon_{F0})/\partial \varepsilon_{F0}$ . Thus, the second term in Equation (21) could be obtained

$$\frac{\partial \varepsilon_F}{e\partial T} = -\frac{\pi^2}{3e} \frac{g'(\varepsilon_{F0})}{g(\varepsilon_{F0})} k_B^2 T$$
(22)

The MEC term on the right-hand side of Equation (19) was ever neglected [20], but it is important for understanding the experimental Seebeck coefficient [9]. Substituting Equations (5) and (22) into Equation (19) may yield

$$\frac{dE_F}{edT} = -\frac{\pi^2}{3e} \frac{g'(\varepsilon_{F0})}{g(\varepsilon_{F0})} \frac{k_B^2 T}{\varepsilon_{F0}} + \frac{\alpha_V(T)}{e} \left[ \frac{r_s}{3} \frac{\partial \varepsilon_p}{\partial r_s} - \left( 1 + \frac{\partial \varepsilon_p}{\partial \varepsilon_F} \right) \frac{n_e}{g(\varepsilon_F)} \right]$$
(23)

As is shown, of great importance is the density of states and the potential energy  $\varepsilon_p$  whose accurate expressions may be difficult to obtain. Nevertheless, for alkali metals and some monovalent noble metals, the free electron density of state at Fermi surface could be employed approximately [2, 4, 8, 21]

$$g(\varepsilon_{F0}) = \frac{(2m_e)^{3/2} \varepsilon_{F0}^{1/2}}{2\pi^2 \hbar^3}$$

and the potential energy  $\varepsilon_p$  may be estimated simply in terms of a central potential [2]

$$\varepsilon_p \approx \frac{-3Ry}{r_s} \left( 1 - \frac{1}{r_s^2} \right) \tag{24}$$

where Ry is Rydberg,  $Ry=e^2/8\pi\varepsilon_0a_0=13.6 \ eV$ ,  $\varepsilon_0$  the vacuum permittivity. The above estimation of  $\varepsilon_p$  was built on the assumption of non-interacting conduction electrons and did not consider the exchange energy, correlation energy and the surface contribution of the surface dipole layer. It may be a reasonable approximation for the alkali metals and some monovalent noble metals and can be utilized to investigate the related phenomena. Thus, the MEC is

$$C_{m-e} = \left[\frac{Ry}{r_s} \left(1 - \frac{3}{r_s^2}\right) - \frac{2}{3}\varepsilon_{F0}\right]$$
(25)

The approximation for the density of states  $g(\varepsilon_F) \approx g(\varepsilon_{F0})$  was used for the calculations of the MEC and the temperature effect was not into account, because the relation  $k_BT << \varepsilon_{F0}$  may be valid in the concerned temperature range. So the Equation (23) becomes

$$\frac{dE_F}{edT} = -\frac{\pi^2}{6} \frac{k_B T}{\varepsilon_{F0}} \frac{k_B}{e} + \frac{\alpha_V(T)}{e} \left[ \frac{Ry}{r_s} \left( 1 - \frac{3}{r_s^2} \right) - \frac{2}{3} \varepsilon_{F0} \right]$$
(26)

To examine whether Equation (26) can give the right sign of the experimental Seebeck coefficient successfully or not, the sign of the values  $dE_F/edT$  for the alkali metals and some monovalent noble metals was calculated based on the related parameters [27-33] and the results were shown in Table 1. It could be seen that the sign of calculated values  $dE_F/edT$  and the MEC  $C_{m-e}$  can agree well with that of the experimental Seebeck coefficient, suggesting that the total derivative of electron chemical potential with respect to the temperature  $dE_F/edT$  can give the right sign of the experimental Seebeck coefficient. Inversely speaking, the sign of the experimental Seebeck coefficient is

Table 1 The calculated mechanical-electric coupling  $C_{m-e}=VdE_F/dV$  and the sign of  $dE_F/edT$  for the alkali metals and some monovalent noble metals. The related parameters are experimental Seebeck coefficient  $S_{ex}$  at room temperature, Fermi energy  $\varepsilon_{F0}$  at zero temperature, linear expansion coefficient  $\alpha_l$  at room temperature, the dimensionless ratio  $r_s$  for which  $r_s a_0$  is the average radius of a sphere containing a single conduction electron in the metal and  $a_0$  is the Bohr radius.

metals	Li	Na	K	Rb	Cs	Cu	Ag	Au
Ст-е	-0.158	0.617	1.03	1.10	1.15	-1.72	-0.638	-0.664
( <i>eV</i> )								
dE <sub>F</sub> /edT	+	_	_	_	_	+	+	+
(µV/K)								
Sex	10.6	-5.8	-12.9	-9.5	-0.9	1.83	1.51	1.94
(µV/K)	[28]	[28]	[28]	[28]	[28]	[27,	[27,	[27,
						29]	29]	29]
$\varepsilon_{F0} (eV)$	4.72	3.23	2.12	1.85	1.58	7.00	5.48	5.51
[8]								
αι	46	71	79.64	66	72	16.5	18.9	14.2
(10 <sup>-6</sup> /K)	[30]	[30]	[31]	[32]	[33]	[30]	[30]	[30]
$r_s[8]$	3.25	3.93	4.86	5.20	5.63	2.67	3.02	3.01

controlled by  $dE_F/edT$  and especially the MEC  $C_{m-e}$ . A positive MEC  $C_{m-e}$  generally gives birth to a negative Seebeck coefficient and a negative value of  $C_{m-e}$  usually leads to a positive Seebeck coefficient. Therefore, the sign of the experimental Seebeck

coefficient does not depend on the type of carriers. A negative experimental Seebeck coefficient of a metal cannot conclude that the carriers are the electrons, and the positive experimental Seebeck coefficient can also not conclude that the carriers are the holes in the metal. In most cases, what the sign of experimental Seebeck coefficient can indicate may be the sign of MEC  $C_{m-e}$ . In a word, for the types of carriers, what Hall coefficient predicts may be more accurate than that predicted by Seebeck coefficient.

# 2.4 Electron degeneracy pressure in metals

The non-interacting conduction electrons in a metal can exert an electron degeneracy pressure upon external compression. Based on the free electron model, the ground-state electron degeneracy pressure and the related bulk modulus was given [21] by

$$P_e = \frac{2}{5} n_e \varepsilon_{F0}$$

where  $P_e$  is the electron degeneracy pressure. Nevertheless, the potential energy of the conduction electrons was neglected in the theory. According to Equation (3), the total energy of ground-state conduction electrons in a metal should be expressed as

$$U_e = N_e E_{F0} - \frac{2}{5} N_e \varepsilon_{F0}$$
<sup>(27)</sup>

The corresponding electron degeneracy pressure may be corrected by the MEC  $C_{m-e}$ 

$$\overline{P}_{e} = -n_{e} \left( C_{m-e} + \frac{4}{15} \varepsilon_{F0} \right)$$
(28)

where  $\overline{P}_e$  is the corrected electron degeneracy pressure by considering the potential energy of the electrons. As is shown, the corrected electron degeneracy pressure sensitively depends on the MEC and will be negative if the MEC satisfies  $C_{m-e} > -4\varepsilon_{F0}/15$ , which is very different from the classical theory. The negative electron degeneracy pressure means that the conduction electrons would facilitate the compression but resist the stretching. On the contrary, if the MEC fulfills  $C_{m-e} < -4\varepsilon_{F0}/15$  the corrected electron degeneracy pressure would present a positive pressure, which can inhibit the compression of the metal. Utilizing the relatively simple estimation of the potential energy of conduction electrons and the related MEC for the alkali metals [2], *i.e.*, Equations (25) and (26), the electron degeneracy pressure could be estimated and is shown in Table 2.

Table 2 The corrected electron degeneracy pressure of alkali metals and the related physical parameters.

Metals	Li	Na	K	Rb	Cs
С <sub>т-е</sub> (еV)	-0.158	0.617	1.03	1.10	1.15
$n_e (\times 10^{28}/m^3) [8]$	4.70	2.65	1.40	1.15	0.91
ε <sub>F0</sub> (eV) [8]	4.72	3.23	2.12	1.85	1.58
$\bar{P}_e$ (GPa)	-8.33	-6.29	-3.58	-2.94	-2.29

### 2.5 Heat capacity of conduction electrons

In common textbooks and literatures [2-8], the total energy of conduction electrons in a metal only take into account the kinetic energy and it is given by

$$U_k = 2\sum_{\vec{k}} \varepsilon_k f(\varepsilon_k)$$

where  $U_k$  is the total kinetic energy of conduction electrons in a metal, the number 2 due to the spin degeneracy,  $f(\varepsilon_k)$  the kinetic energy dependence of the Fermi-Dirac distribution function. However, it neglects the contribution of the potential energy of conduction electrons. In reality, the potential energy  $\varepsilon_p$  must include the contributions of Coulomb energy, exchange energy and correlation energy. The calculation of the real potential energy  $\varepsilon_p$  at finite temperatures may be very complex and difficult. But all the necessarily calculated terms for the potential energy  $\varepsilon_p$  may be in the form  $\int_0^\infty \varepsilon_p(\varepsilon) f(\varepsilon) d\varepsilon$  (where  $\varepsilon_p(\varepsilon)$  is any continuous function and  $f(\varepsilon)$  is Fermi-Dirac function) [1], so the potential energy  $\varepsilon_p$  could be calculated formally according to the Sommerfeld expansion [2-4, 6, 7].

Considering the potential energy  $\varepsilon_p$  of the conduction electrons, the total energy of the conduction electrons in metals at finite temperature should be written as

$$U = 2\sum_{\vec{k}} \left[ \varepsilon_p \left( r_s, \varepsilon_k \right) + \varepsilon_k \right] f \left( \varepsilon_k + \varepsilon_p \left( r_s, \varepsilon_k \right) \right)$$
(29)

The kinetic energy dependence of the potential energy may arise from the exchangecorrelation energy of conduction electrons, as revealed in textbooks [1, 2, 4]. The kinetic energy dependence may be important for electron heat capacity, electron magnetic susceptibility, electrical conductivity and electron thermal conductivity which would be discussed in the following sections. Consequently, the total energy could be written in the integral form

$$U = V \int_{x_0}^{\infty} xg(x) f(x) dx$$

where the variables x,  $x_0$  and  $x_F$  are the single-electron energies  $x = \varepsilon_k + \varepsilon_p(r_s, \varepsilon_k)$ ,  $x_0 = \varepsilon_p(r_s, 0)$ and  $x_F = \varepsilon_F + \varepsilon_p(r_s, \varepsilon_F)$ . The function g(x) is the electron density of states  $g(x) = dN_e/Vdx$  and it fulfills the relation

$$g(\varepsilon_k) = g(x) \frac{dx}{d\varepsilon_k}$$
(30)

Since the electron density of states  $g(\varepsilon_k)$ , g(x) are always positive, the value of the

derivative  $dx/d\varepsilon_k$  is surely positive. Therefore the single-electron energy *x* must be a monotonically increasing function with the kinetic energy  $\varepsilon_k$ , giving the one-to-one mapping relationship between the single-electron energy *x* and the kinetic energy  $\varepsilon_k$ , which is consistent with the calculations under the Hartree-Fock approximation [1, 2, 4]. In terms of the Sommerfeld expansion [2-4, 6, 7], the total energy of the conduction electrons accurate to the second order of (*k*<sub>B</sub>*T*) could be evaluated

$$U = V \left[ \int_{x_0}^{x_F} xg(x) dx + \frac{\pi^2 (k_B T)^2}{6} \frac{\partial x_F g(x_F)}{\partial x_F} \right]$$

In the calculations, it was assumed that the distinction between the top single-electron energy  $x_F$  and bottom single-electron energy  $x_0$  is much larger than the thermal energy, *i.e.*,  $x_F - x_0 >> k_B T$ . Using the relation between the Fermi energies at zero temperature and finite temperature, *i.e.*, Equation (21), the total energy can be simplified to be

$$U = U_0 + V \frac{\pi^2 \left(k_B T\right)^2}{6} g\left(x_F\right)$$

where  $U_0$  is the total energy of conduction electrons at zero temperature. The definition of the electron heat capacity at constant volume will be given [3, 4, 6, 7] by

$$c_e = \left(\frac{\partial U}{\partial T}\right)_V$$

Using Equation (30), the heat capacity of conduction electrons per unit volume could be expressed in the form  $c_e=\gamma T$  where the parameter  $\gamma$  is

$$\gamma = \frac{\pi^2 k_B^2}{3} \frac{g(\varepsilon_{F0})}{1 + \frac{\partial \varepsilon_p(r_s, \varepsilon_{F0})}{\partial \varepsilon_{F0}}}$$
(31)

As shown in Equation (31), the consideration of potential energy  $\varepsilon_p(r_s, \varepsilon_{F0})$  can modify

the heat capacity of conduction electrons in a metal. If the derivative of potential energy with respect to the Fermi energy approaches zero, *i.e.*,  $\partial \varepsilon_p(r_s, \varepsilon_{F0})/\partial \varepsilon_{F0}=0$ , the electron heat capacity becomes the common result in textbook and literatures [4, 8]. Interestingly, if the value of  $\partial \varepsilon_p(r_s, \varepsilon_{F0})/\partial \varepsilon_{F0}$  is close to -1, as shown by Equation (31), the electron heat capacity would be very large, exhibiting a heavy mass of the conduction electrons. It could be the physical interpretation of heavy-fermion systems based on the simple single-electron model. Furthermore, for isotropic metals it is

$$\frac{dE_F}{dT} = \alpha_V C_{m-e} + \left[1 + \frac{\partial \varepsilon_p(r_s, \varepsilon_F)}{\partial \varepsilon_F}\right] \left(\frac{\partial \varepsilon_F}{\partial T}\right)_V$$

For heavy fermions, the chemical potential versus the temperature could be approximated as the followings due to the term  $\partial \varepsilon_p(r_s, \varepsilon_{F0})/\partial \varepsilon_{F0}$  close to -1

$$\frac{dE_F}{dT} \approx \alpha_V C_{m-e} \tag{32}$$

The heavy-fermion systems usually exhibits the thermal expansion coefficient several orders of magnitude larger than that of normal metals at low temperatures [34-41]. Hence, according to Equation (32) the temperature dependence of the electron chemical potential for the heavy-fermion systems may be much more conspicuous than that of normal metals, which agrees with the experimental observations that the Fermi surface of the heavy- fermion system varies remarkably in a wide temperature range [42].

## 2.6 Magnetic susceptibility of conduction electrons in a metal

Upon application of a magnetic field, the total energy of conduction electrons in a metal at zero temperature could be written as

$$U = V \left[ \int_{x_0}^{x_{F\uparrow}} x \frac{g(x)}{2} dx + \int_{x_0}^{x_{F\downarrow}} x \frac{g(x)}{2} dx - n_{\uparrow} \mu_B B + n_{\downarrow} \mu_B B \right]$$

where  $n_{\uparrow}$  is the number density of up-spin conduction electrons,  $n_{\downarrow}$  the number density of down-spin electrons,  $\varepsilon_{F\uparrow}$ ,  $\varepsilon_{F\downarrow}$  are the Fermi energies of up-spin electrons and downspin electrons, respectively, the single-electron energies are  $x_{F\uparrow}=\varepsilon_{F\uparrow}+\varepsilon_p(r_s,\varepsilon_{F\uparrow})$ ,  $x_{F\downarrow}=\varepsilon_{F\downarrow}+\varepsilon_p(r_s,\varepsilon_{F\downarrow})$ ,  $\mu_B$  denotes the Bohr magneton, *B* is the externally applied magnetic field, g(x)/2 is the density of states for the up-spin conduction electrons and down-spin conduction electrons. When the conduction electrons reaches the equilibrium state, they would arrange themselves so that the total energy must be the smallest at zero temperature. So the derivative of the total energy with respect to the up-spin electron density should be zero and it is

$$x_{F\uparrow} \frac{g(x_{F\uparrow})}{2} \frac{\partial x_{F\uparrow}}{\partial n_{\uparrow}} - x_{F\downarrow} \frac{g(x_{F\downarrow})}{2} \frac{\partial x_{F\downarrow}}{\partial n_{\downarrow}} - 2\mu_{B}B = 0$$
(33)

For the up-spin electron density and the down-spin electron density, they certainly satisfy the following relations due to the conservation of electron number,

$$n_{\uparrow} = \int_{x_0}^{x_{F\uparrow}} \frac{g(x)}{2} dx$$
$$n_{\downarrow} = \int_{x_0}^{x_{F\downarrow}} \frac{g(x)}{2} dx$$
$$n_e = n_{\uparrow} + n_{\downarrow}$$

Thereby the corresponding differential equations could be valid at zero temperature,

$$\frac{\partial x_{F\uparrow}}{\partial n_{\uparrow}} = \frac{2}{g(x_{F\uparrow})}$$

$$\frac{\partial x_{F\downarrow}}{\partial n_{\downarrow}} = \frac{2}{g(x_{F\downarrow})}$$

Substituting these equations into the Equation (33), it is

$$\varepsilon_{F\uparrow} + \varepsilon_p \left( r_s, \varepsilon_{F\uparrow} \right) - \mu_B B = \varepsilon_{F\downarrow} + \varepsilon_p \left( r_s, \varepsilon_{F\downarrow} \right) + \mu_B B \tag{34}$$

This equation actually indicates that the chemical potential of up-spin conduction electrons equals to that of down-spin conduction electrons. Since the magnetic field induced Zeeman spitting energy of a conduction electron is much smaller than its kinetic energy, the Fermi energies and potential energies in Equation (34) could be expanded into Taylor's series to first order,

$$\varepsilon_{F\uparrow} \approx \varepsilon_{F0} + \frac{\partial \varepsilon_{F\uparrow}}{\partial n_{\uparrow}} \bigg|_{\varepsilon_{F\uparrow} = \varepsilon_{F0}} \frac{\partial n_{\uparrow}}{\partial B} B$$

$$\varepsilon_{p}\left(\varepsilon_{F\uparrow}\right) \approx \varepsilon_{p}\left(r_{s},\varepsilon_{F0}\right) + \frac{\partial \varepsilon_{p}\left(r_{s},\varepsilon_{F\uparrow}\right)}{\partial \varepsilon_{F\uparrow}} \frac{\partial \varepsilon_{F\uparrow}}{\partial n_{\uparrow}} \bigg|_{\varepsilon_{F\uparrow}=\varepsilon_{F0}} \frac{\partial n_{\uparrow}}{\partial B} B$$

$$\varepsilon_{F\downarrow} \approx \varepsilon_{F0} + \frac{\partial \varepsilon_{F\downarrow}}{\partial n_{\downarrow}} \bigg|_{\varepsilon_{F\uparrow} = \varepsilon_{F0}} \frac{\partial n_{\downarrow}}{\partial B} B$$

$$\varepsilon_{p}\left(\varepsilon_{F\downarrow}\right) \approx \varepsilon_{p}\left(r_{s},\varepsilon_{F0}\right) + \frac{\partial \varepsilon_{p}\left(r_{s},\varepsilon_{F\downarrow}\right)}{\partial \varepsilon_{F\downarrow}} \frac{\partial \varepsilon_{F\downarrow}}{\partial n_{\downarrow}} \bigg|_{\varepsilon_{F\downarrow}=\varepsilon_{F0}} \frac{\partial n_{\downarrow}}{\partial B} B$$

Insertion of these expanded functions into Equation (34) will yield

$$\left(1 + \frac{\partial \varepsilon_p(r_s, \varepsilon_{F0})}{\partial \varepsilon_{F0}}\right) \frac{2}{g(\varepsilon_{F0})} \left(\frac{\partial n_{\uparrow}}{\partial B} - \frac{\partial n_{\downarrow}}{\partial B}\right) = 2\mu_B$$
(35)

On another hand, the magnetic moment created by the difference of up-spin conduction electrons and down-spin conduction electrons could be given by

$$M=\mu_B\left(n_{\uparrow}-n_{\downarrow}\right)$$

The corresponding magnetic susceptibility could be expressed in the partial derivative form

$$\chi_p = \mu_0 \frac{\partial M}{\partial B}$$

By simple calculations, it is

$$\chi_p = \mu_0 \mu_B \left( \frac{\partial n_{\uparrow}}{\partial B} - \frac{\partial n_{\downarrow}}{\partial B} \right)$$

Substituting the above equation into Equation (35), the Pauli magnetic susceptibility of the conduction electrons can be obtained

$$\chi_{p} = \frac{\mu_{0} \mu_{B}^{2} g\left(\varepsilon_{F0}\right)}{1 + \frac{\partial \varepsilon_{p}\left(r_{s}, \varepsilon_{F0}\right)}{\partial \varepsilon_{F0}}}$$
(36)

It demonstrates that compared with the common results in textbooks and literatures the potential energy of conduction electron leads to the same modification on both the magnetic susceptibility and the electron heat capacity. The conduction electrons in a metal popularly exhibit the Landau diamagnetic susceptibility  $\chi_l$  whose magnitude is one third of the Pauli magnetic susceptibility [16], *i.e.*,  $\chi_l = -\chi_p/3$ . So the experimentally measured magnetic susceptibility  $\chi_e$  would be  $\chi_e=2\chi_p/3$ . And the ratio between the experimentally magnetic susceptibility  $\chi_e$  and the parameter  $\gamma$ , named "Wilson ratio", is almost constant  $\chi_e/\gamma=2\mu_0(\mu_B/\pi k_B)^2$  on basis of Equations (31) and (36), which is in agreement with the common conclusion in literatures [43]. Analogous to the discussion for the electron heat capacity, when the value of the derivative  $\partial \varepsilon_p(\varepsilon_{F0})/\partial \varepsilon_{F0}$  approaches -1, the magnetic susceptibility  $\chi_e$  would increase dramatically, displaying the typical features of the heavy fermions. Interestingly, if the derivative  $\partial \varepsilon_p(\varepsilon_{F0})/\partial \varepsilon_{F0}$  is -1, the

magnetic susceptibility and the heat capacity of the conduction electrons would be infinite, indicating that a ferromagnetic phase transition happens. In another word, some properties of heavy-fermion system and the ferromagnetic phase transition could also be understood in terms of the simple single-electron model.

### 2.7 Electrical conductivity of the metal

The MEC may affect the electrical conductivity of the metal. Considering the potential energy of the conduction electrons, it is convenient to give the modified electrical conductivity based on the Boltzmann equation [1, 4, 16],

$$\sigma_{me} = \int e^2 \tau_{me} \left[ -\frac{\partial f_0(x)}{\partial x} \right] \frac{\partial x}{\partial \varepsilon_k} \vec{v}_k \vec{v}_k g(x) dx$$

where the variables x is the single-electron energy  $x=\varepsilon_k+\varepsilon_p(r_s, \varepsilon_k)$ ,  $\sigma_{me}$  is the modified electrical conductivity,  $\tau_{me}$  is the modified electron relaxation time,  $v_k$  is the electron velocity with the wave vector k.

Since the function  $\partial f(x) \partial x$  behaves like the Dirac delta function  $\delta(x)$  [1, 4], the only difference between the modified electrical conductivity and the conventional electrical conductivity in some textbooks resides in the electron relaxation time. Upon calculating the electron relaxation time, the energy conservation always holds during the electron scattering processes, *e.g.* electron-phonon scattering and electron-impurity scattering. Considering the potential energy of the conduction electron, the energy conservation guaranteed by the Dirac delta functions should use the functions  $\delta(x-x'\pm\hbar\omega_q)$  and  $\delta(x-x')$  instead of  $\delta(\varepsilon_k\pm\hbar\omega_q-\varepsilon_{k\pm q})$  and  $\delta(\varepsilon_k-\varepsilon_{k'})$ , where the variable is  $x'=\varepsilon_{k\pm q}+\varepsilon_p(r_s,\varepsilon_{k\pm q})$  and  $\omega_q$  is the angular frequency of the phonon. As a result, the electron relaxation time will be modified by the factor  $[1+\partial\varepsilon_p(r_s,\varepsilon_{F0})/\partial\varepsilon_{F0}]$  based on the mathematical formulation of the electron relaxation time [1, 4]. Thus, the modified electron relaxation time can be given by

$$\tau_{me} = \tau_e \left[ 1 + \frac{\partial \varepsilon_p \left( r_s, \varepsilon_{F0} \right)}{\partial \varepsilon_{F0}} \right]$$
(37)

where  $\tau_e$  is the conventional electron relaxation time. And the modified electrical conductivity for an isotropic metal is

$$\sigma_{me} = \frac{n_e e^2 \tau_e}{m_e / \left[1 + \frac{\partial \varepsilon_p \left(r_s, \varepsilon_{F0}\right)}{\partial \varepsilon_{F0}}\right]}$$
(38)

It shows that the consideration of the potential energy of the conduction electrons for calculating the electrical conductivity is equivalent to modifying the electron mass by the factor  $[1+\partial \varepsilon_p(r_s, \varepsilon_{F0})/\partial \varepsilon_{F0}]$ . If this factor approaches zero, the equivalent mass of the conduction electron will be ultra-large, exhibiting the heavy-fermion behaviors and reducing the electrical conductivity greatly. Reversely, if the factor presents a very huge value, the equivalent mass of the conduction electrons will almost vanish, displaying the massless fermions and ultra-high fermion mobility in the metal.

### 2.8 Thermal conductivity of the metal

When a metal undergoes a temperature gradient, the heat flux will flows along the temperature gradient. By taking the potential energy of the conduction electrons into account, the modified thermal conductivity generated by the conduction electrons can be obtained according to the references [4, 16]

$$\kappa_{me} \approx \frac{1}{T} \int \tau_{me} \left( x - E_F \right)^2 \vec{v}_k \vec{v}_k \left[ -\frac{\partial f_0(x)}{\partial x} \right] \frac{\partial x}{\partial \varepsilon_k} g(x) dx$$

where  $\kappa_{me}$  is the modified electron thermal conductivity. By using Equation (37) and

the properties of the function  $\partial f_0(x)/\partial x$ , *i.e.*, the Dirac delta function, it can be written as

$$\kappa_{me} = \kappa_{e} \left[ 1 + \frac{\partial \varepsilon_{p} \left( r_{s}, \varepsilon_{F0} \right)}{\partial \varepsilon_{F0}} \right]$$
(39)

where  $\kappa_e$  is the conventional electron thermal conductivity of the metal. Seen from Equation (39), the factor  $[1+\partial \varepsilon_p(r_s, \varepsilon_{F0})/\partial \varepsilon_{F0}]$  can influence the electron thermal conductivity. Analogous to the case of the electrical conductivity, if the factor exhibits a small value, the electron thermal conductivity will be weakened. On the contrary, if the factor displays a large value, the electron thermal conductivity will be enhanced.

In view of the Equations (30) (31) (36) (38) and (39), the modified factor  $[1+\partial \varepsilon_p(r_s, \varepsilon_{F0})/\partial \varepsilon_{F0}]$  may play a very important role in understanding the variously physical properties of the metals. Despite that it is a phenomenological parameter and needs to be investigated deeply in the future, it may be very convenient to uncover the physical behaviors of the metals.

# 2.9 Peierls transition and charge density wave

Peierls ever pointed out that a one-dimensional metal could not be stable with respect to a crystalline deformation at low temperatures and the ground state may be characterized by both a band gap and a periodic CDW [44, 45]. CDW is a widespread phenomenon in solid state physics. And it is generated by the decrease of the electron energy but limited by the increase of deformation energy [4, 8]. To introduce the related physics, a one-dimensional strain is usually taken for the sake of simplicity

$$\xi(x) = \xi_0 \cos 2k_F x$$

where  $\xi(x)$  is position-dependent one-dimensional strain,  $\xi_0$  is the largest strain,  $k_F$  is the wave vector. The popular quantum theory of CDW unravels that the emerged deformation potential opens up a band gap for the conduction electrons at the Fermi surface and thereby lowers the total electron energy [8, 45]. Despite so much research on CDW, the underlying physics of the deformation potential and the induced band gap, including their magnitude and physical origin, has been seldom addressed. In the section, the problems will be uncovered.

According to Equation (1) and the MEC  $C_{m-e}$ , the statically periodic strain would give birth to a periodic variation of chemical potential and a periodic electrostatic field,

$$E_{F}(x) = E_{F0} + C_{m-e}\xi_{0}\cos 2k_{F}x$$
(40)

$$\vec{E}(x) = -2\frac{C_{m-e}}{e}k_F\xi_0\sin 2k_Fx \tag{41}$$

where  $E_F(x)$  is the position-dependent electron chemical potential,  $C_{m-e}=\partial E_F/\partial \zeta$  is the MEC in the case of the one-dimensional strain,  $\vec{E}(x)$  is the electric field. The periodically electrostatic field would inevitably exert a potential on the conduction electrons and the potential amplitude could be  $|C_{m-e}\zeta_0|$ . The potential enables the initial gapless conduction band to open up a CDW gap whose magnitude could be obtained according to the degenerate perturbation theory [4, 8],

$$\Delta_{\rm CDW} = \left| C_{m-e} \xi_0 \right| \tag{42}$$

where  $\Delta_{CDW}$  is the CDW gap. As indicated by the equation, the CDW gap is anticipated to be proportional to the strain, which is consistent with the experimental observations [46]. On another hand, the magnitude of CDW gap may also rest with the MEC of the material. And a larger magnitude of the MEC would usually yield a larger CDW gap which may cause the CDW transition more easily. Because the driving force of CDW transition, *i.e.*, the condensation energy of electrons, was established to be proportional to the square of the CDW gap [46]. As a result, the MEC  $C_{m-e}$  governs the CDW gap and CDW transition. In light of the experimentally measured CDW gap, the corresponding magnitude of the MEC can be estimated according to Equation (41), as shown in Table 3.

Table 3 The physical parameters of some typical CDW materials and the calculated magnitude of the mechanical-electric coupling  $|C_{m-e}|$ .

materials	displacement	lattice	strain	CDW gap	$ C_{m-e} $
	(Å)	parameter (Å)	(%)	(meV)	( <i>eV</i> )
КСР	0.027 [46]	2.894 [46]	0.933	150 [47]	16
K0.3MoO3	0.05 [46]	7.56 [48]	0.661	130 [49]	17
(TaSe4)2I	0.09 [46]	3.206 [46]	2.81	250 [12, 50]	8.9
2H-NbSe2	0.042 [51]	3.4583 [51]	1.21	60 [52]	5.0

At the end, some comments should be made. The model used in this work may be a single-electron model, but it may be different from the common free electron model. Because it takes both the potential energy and the important MEC into account for the conduction electrons in the metals. The utilized potential energy may be the mean field result of the totally complex interactions for the conductions electrons. Despite that its precisely mathematical form has not been obtained yet, the introduction of the potential energy and MEC may be very economical and can grasp some key physical features of the conduction electrons in the metal.

#### 3. Conclusion

In summary, the MEC in metals was investigated in the work. The MEC may not

only determine the diffusion relation of conduction electrons and the sign of Seebeck coefficients but also dominate the electron degeneracy pressure and the magnitude of the CDW gap. In addition, the MEC may also indicate that the potential energy of conduction electron in a metal must be considered and the free electron model should be correspondingly modified. The modified free electron model could offer a simple way of understanding the variously physical properties such as the electron heat capacity, the Pauli magnetic susceptibility, the electrical conductivity and the electron thermal conductivity of the metals, especially the related characteristics of the heavy fermion systems. In a word, the MEC may be important and could help understand multi-physical behaviors of the metals.

# Reference

[1] Gerald D. Mahan, Many-Particle Physics, third edition, Kluwer Academic/PlenumPublishers, New York, 2000, pp. 296-302, pp.499-505, pp. 545-549.

[2] Philip Phillips, Advanced Solid State Physics, Westview Press, Boulder, 2003, pp.1-

8, pp.35-49, pp. 115-118, pp.187-196.

[3] Zhicheng Wang, Thermodynamics •Statistical Physics, Higher Education Press,
 Beijing, 5<sup>th</sup> edition, 2013, pp. 240-245.

[4] Shousheng Yan, Foundation of Solid State Physics, Peking University Press, Beijing, third edition, 2011, pp.4-13, pp.22-24, pp. 71-74, pp.144-161, pp. 188, pp.315-326, pp. 338-340.

[5] 朗道,栗弗席兹,统计物理学,杨训恺等译,北京,人民教育出版社,1964, pp.199-207.

[6] Roberto Piazza, Statistical Physics, Springer International Publishing Switzerland,2017, pp.303-308.

[7] Carlo Heissenberg, Augusto Sagnotti, Classical and Quantum Statistical Physics, Cambridge University Press, 2022, pp. 150-155.

[8] Charles Kittel, Introduction to Solid State Physics, eighth edition, John Wiley & Sons, Inc, Hoboken, 2005, pp.133-147, pp.153-156, pp.422-424.

[9] Yuanjie Huang, Strain-Induced Electric Effect in Metals, Journal of Materials Sciences and Applications, 5(3), 58-62(2019).

[10] Yuanjie Huang, Strain Induced Electric Effect in Condensed Matters, Journal of Materials Sciences and Applications, 5(3), 44-57(2019). [11] Yuanjie Huang, Electric features of dislocations and electric force between dislocations, Mathematics and Mechanics of Solids, V. **26**(4), 616-628(2021).

[12] J. Gooth, B. Bradlyn, S. Honnali, C. Schindler, N. Kumar, J. Noky, Y. Qi, C. Shekhar, Y. Sun, Z. Wang, B. A. Bernevig, C. Felser, Axionic charge-density wave in the Weyl semimetal (TaSe4)2I, Nature, V. 575, pages315–319 (2019).

[13] Yuanjie Huang, Liusen Hu, Phase transition-induced contact electric potential,Phase Transitions, V.94, 270-279(2021).

[14] Yuanjie Huang, Discovery of A New Transport Mechanism and Physical Origin of Hume-Rothery Rules, viXra:1902.0264.

[15] Yuanjie Huang, Tangential Electrostatic Field at Metal Surfaces, Open Physics, V.21, 20220270(2023).

[16] Giuseppe Grosso, Giuseppe Pastori Parravicini, Solid State Physics, 2<sup>nd</sup> edition,Waltham, Elsevvier Ltd. 2014, pp.502-512, pp.659.

[17] A. Haug, Theoretical Solid State Physics, Pergamon Press, Oxford, 1972.

[18] G. D. Mahan, Good thermoelectrics, Solid State Phys. V. 51, 81-157(1998).

[19] P. Taylor and O. Heinonen, A Quantum Approach to Condensed Matter Physics Cambridge University Press, Cambridge, U.K., 2002. pp. 308-312.

[20] Jianwei Cai, G. D. Mahan, Effective Seebeck coefficient for semiconductors, Phys.Rev. B 74, (2006) 075201 (1-3).

[21] Neil W. Ashcroft, N. David Mermin, Solid State Physics, Harcourt. Inc. Orlando, 1976, pp.30-52.

[22] C. L. Foiles, Electronic Transport Phenomena, in Landolt-Bornstein: Numerical

Data and Functional Relationships in Science and Technology, New Series, Group 3, eds. J. Bass, J. S. Dugdale, C. L. Foiles and A. Myers (Springer, Berlin, 1985), p. 68. [23] J. E. Robinson, Thermoelectric Power in The Nearly-Free-Electron Model, Phys. Rev. V. **161**, 533-539 (1967).

[24] J. E. Robinson, J. D. Dow, Electron-Phonon Interaction in Solid Alkali Metals. I.Scattering and Transport Coefficients, Phys. Rev. V. 171, 815-826 (1968).

[25] H. Jones, The Thermoelectric Power of Monovalent Metals, Proc. Phys. Soc. A V.68, 1191-1193(1955).

[26] Bin Xu, Matthieu J. Verstraete, First Principle Explanation of the Positive SeebeckCoefficient of Lithium, Phys. Rev. Lett. V. 112, 196603(1-5) (2014).

[27] Frank J. Blatt, Peter A. Schroeder, Carl L. Foiles, Denis Greig, ThermoelectricPower of Metals, Plenum Press, New York, 1976, pp.4-5, pp.22.

[28] J. S. Dugdale, J. N. Mundy, The Pressure Dependence of the Thermoelectric Power of the Alkali Metals at Room Temperature, Philosophical Magazine, V. 6:72, 1463-1473(1961). DOI: 10.1080/00318086.1961.11643275

[29] N. Cusack and P. Kendall, The Absolute Scale of Thermoelectric Power at High Temperature, Proc. Phys. Soc. V. 72, 898-901 (1958).

[30] Host Stöcker, Taschenbuch der Physik, Xizhen Wu *et.al.* translated, Peking University Press, Beijing, 2004, pp.700-701.

[31] D. R. Schouten, C. A. Swenson, Linear-Thermal-Expansion Measurements on Potassium Metal from 2 to 320 K, Phys. Rev. B, V. 10, 2175-2185(1974).

[32] F. M. Kelly, W. B. Pearson, The Rubidium Transition at ~180 K, Canad. J. Phys.

V. 33, 17-24 (1955).

[33] M. S. Anderson, E. J. Gutman, J. R. Packard, C. A. Swenson, Equation of State for Cesium Metal to 23 kBar, J. Phys. Chem. Solids, V. 30, 1587-1601(1969).

[34] K. Andres, The Measurement of Thermal Expression of Metals at low Temperatures, Cryogentics, 93-97(1961).

[35] McLean, Kent Otho, Low temperature thermal expansion of copper, silver, gold and aluminum (1969). Retrospective Theses and Dissertations. 4127. https://lib.dr.iastate.edu/rtd/4127

[36] G. Oomi, K. Takahashi, F. J. Ohkawa, Y. Ōnuki, T. Komatsubara, Thermal Expansion of Single Crystalline CeCu6, J. Mag. Mag. Mater. V. 76&77,145-146(1988).

[37] A. de Visser, N. H. Van Dijk, K. Bakker, J. J. M. Franse, Search for Antiferromagnetic order in Ube13 via Magnetovolume effects, Phy. Rev. B V. 45,2962-2968 (1992).

[38] R. Modler, M. Lang, C. Geibel, C. Schank, F. Steglich, Thermal Expansion of the Heavy-Fermion Superconductor UNi2Al3, Phys. B V. 199&200, 145-147(1994).

[39] Tetsuya Takeuchi, Hiroaki Shishido, Shugo Ikeda, Rikio Settai, Yoshinori Haga, Yoshichika Ōnuki, Thermal expansion and magnetostriction studies in a

heavy-fermion superconductor, CeCoIn5, J. Phys.: Condens. Matter V. 14, L261–L266(2002).

[40] Gasparini, A., Huang, Y. K., Hartbaum, J., v. Löhneysen, H., & de Visser, A.
Thermal expansion of the superconducting ferromagnet UCoGe. Phys. Rev. B, V. 82(5), 052502(2010). <u>https://doi.org/10.1103/PhysRevB.82.052502</u>

[41] K. Grube, L. Pintschovius, F. Weber, J. P. Castellan, S. Zaum, S. Kuntz, P. Schweiss, O. Stockert, S. Bachus, Y. Shimura, V. Fritsch, H. v. Löhneysen, Magnetic and Structural Quantum Phase Transitions in CeCu6–xAux are Independent, Phys. Rev. Lett. V. 121, 087203(1-5) (2018).

[42] Q. Y. Chen, D. F. Xu, X. H. Niu, J. Jiang, R. Peng, H. C. Xu, C. H. P. Wen,Z. F. Ding, K. Huang, L. Shu, Y. J. Zhang, H. Lee, V. N. Strocov, M. Shi, F. Bisti, T. Schmitt, Y. B. Huang, P. Dudin, X. C. Lai, S. Kirchner, H. Q. Yuan, D. L. Feng, Direct observation of how the heavy-fermion state develops in CeCoIn5, Phy. Rev. B V. 96, 045107(1-10)(2017).

[43] Helmut Kronmüller, Stuart Parkin, Handbook of Magnetism and Advanced Magnetic Materials. Volume 1: Fundamentals and Theory. John Wiley & Sons, Ltd.
2007, pp. 102.

[44] R. E. Peierls, Quantum Theory of Solids, Oxford University, New York/London, 1955.

[45] G. Grüner, The dynamics of charge-density waves, Rev. Mod. Phys., V. 60, 1129-1181(1988).

[46] George Grüner, Density Waves in Solids, Perseus Publishing, USA, 1994, pp.18-30, pp. 43, pp.67-68.

[47] R. H. Friend, D. Jérome, Periodic Lattice Distortions and Charge DensityWaves in One- and Two-Dimensional Metals, J. Phys. C: Solid State Phys. V.12, 1441-1477 (1979).

[48] Nikiforov, M. P., Isakovic, A., Bonnell, D. A. Atomic structure and charge-density

waves of blue bronze  $K_{0.3}MoO_3$  (201) by variable-temperature scanning tunneling microscopy, Phys. Rev. B, V. **76**, 033104(1-4) (2007).

[49] W. J. Schutte and J. L. De Boer, The incommensurately modulated structures of the blue bronzes K<sub>0.3</sub>MoO<sub>3</sub> and Rb<sub>0.3</sub>MoO<sub>3</sub>, Acta Crystallogr. Sect. B V. **49**, 579-591 (1993).

[50] Z. Z. Wang, M. C. Saint-Lager, P. Monceau, M. Renard, Charge Density Wave in (TaSe<sub>4</sub>)<sub>2</sub>I, Solid State Communication, V. 46, 325-328(1983).

[51] Christos D. Malliakas and Mercouri G. Kanatzidis, Nb–Nb InteractionsDefine the Charge Density Wave Structure of 2H-NbSe2, J. Am. Chem. Soc. V.135, 1719-1722(2013).

[52] K. Rossnagel, Eli Rotenberg, H. Koh, N. V. Smith, L. Kipp, Fermi Surface, Charge-Density-Wave Gap, and Kinks in 2H-TaSe<sub>2</sub>, Phys. Rev. B V. 72, 121103(R) (2005).