Mechanical-Electric Coupling in Metals

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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. The MEC may lead to a single-electron model which can 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. It may also indicate that the heavy-fermion characteristics of the heavy-fermion systems may originate from the physical picture that the electron chemical potential intersects the narrow conduction *f*-electron band and the correlation effects among heavy-fermions may be weak, as is in contrary to the conventional viewpoint. Furthermore, it was found that the MEC can not only give the right sign of Seebeck coefficients of the monovalent metals but also give the physical origin of the CDW gap, which are in agreement with experimental results. Overall, the MEC may be important for the metals and it should be taken into account seriously for investigating the multi-physical properties of the metals.

keywords: mechanical-electric coupling; metals; electron chemical potential; heavy fermions; 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 (ECP) 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 longstanding 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 [4, 9].

As enlightened by *Yuheng Zhang effect*, a strain can give rise to the shift of ECP and thereby can lead to a mechanical-electric coupling (MEC) in a metal [10, 11]. The MEC was found to induce some new physics such as the electric properties of dislocations and the electric force between dislocations [12]. On another hand, the MEC may also result in the new understandings of the conventional problems, which still needs further investigation.

In this work, the MEC was adopted to modify the free electron model and the important problems in metal physics were thereby addressed, for instance, the magnitude of charge density wave (CDW) gap, the sign of Seebeck coefficients opposite to Hall coefficient for some monovalent metals, and the multi-physical properties of the heavy-fermion systems.

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 alterations of the Fermi surface may be described by *Yuheng Zhang equation* [11, 13],

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

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 [10-14].

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

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

where ε_{F0} stands for 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 ECP 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 ECP 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 ECP 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

$$E_F = \varepsilon_p\left(r_s, \varepsilon_F\right) + \varepsilon_F \tag{3}$$

where ε_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 depends on the electron density which is usually depicted by the dimensionless ratio r_s but also depends on the kinetic energy ε_k, r_s is a dimensionless ratio, $r_s a_0$ 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 ε_p for brevity. And the MEC for an isotropic metal can be defined by

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

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

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

where $g(\varepsilon_F)$ is the common EDS at the 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, 15]

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

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)

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

where $V(r)$ is the position-dependent volume and it satisfies $n_e(r)V(r) = N_e$. 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 σ_e is the electron conductivity and it is commonly expressed as $\sigma_e = en_e\mu_e$, μ_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 totally electrical current must be zero when the electron equilibrium state is reached [10, 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 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, 15], the potential energy ε_p of the conduction electron was popularly neglected for the ECP and the Fermi energy was regarded as the ECP. Some references [1, 10] noted the difference between the ECP and the Fermi energy, but the mathematical expression of the Fermi energy instead of the ECP was still utilized to calculate the diffusion coefficient of conduction electrons [10]. Therefore, the diffusion relation obtained in terms of the Fermi energy in the related references [9, 15] may only be an approximate relation. The precise diffusion relation for the conduction electrons should be given by the MEC which adopts the ECP 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

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

where Z_i is the valence of an ion core, ε_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 linear equation

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

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

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

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 ECP 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 λ_{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

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

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

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

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 commonly 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.

By considering the potential energy of conduction electrons in a metal, the Linhard dielectric function should be modified. Based on the derivation in textbook [1], the expression of the modified Linhard dielectric function may be approximately obtained by substituting the electron mass m_e by the electron effective mass as below

$$m_e^*=\frac{m_e}{1+\frac{\partial\varepsilon_p\left(r_s,\varepsilon_{F0}\right)}{\partial\varepsilon_{F0}}}$$

where m_e^* is the electron effective mass. The important factor in the denominator of the above equation will be addressed in the later.

2.3 Seebeck coefficient

The thermoelectric effect is an important physical effect and is usually described by Seebeck coefficient. According to the theoretical definition in textbooks and literatures [1, 16-20], it was written as

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

where S_{th} is theoretical Seebeck coefficient, E is the temperature-gradient-induced electric field in the metal. But the experimentalists usually use the experimental definition of the Seebeck coefficient [1, 19]

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

where ΔV is the voltage difference, ΔT the temperature difference, S_{ex} is experimental Seebeck coefficient. Based on these definitions [1, 4, 8, 16-19], 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, 21]. It was an interesting but longstanding 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 [22, 23]. 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 [24, 25]. 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 the electrochemical potential difference [19]. So it was noted and revealed that the theoretical definition of Seebeck coefficient is different from the experimental definition [19]. However, only the temperature-induced lift of the ECP was considered [19], but another important contribution was neglected, *i.e.*, the thermal expansion-induced lift of the ECP [10]. When an end of a metal would be heated, the related ECP would be altered. The electrons would flow from the region with high ECP to the region with low ECP. 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

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

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

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

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 state, *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, 26] and the metals such as Ag, Cu and Au with the high electrical conductivity usually exhibit a small Seebeck coefficient [4, 26]. 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,

$$S_{ex} = \frac{dE_F}{edT} - \frac{\vec{E}_r}{\nabla T} \tag{18}$$

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

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

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

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

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 ε_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, 20], the temperature-dependent Fermi energy ε_F is

$$\varepsilon_F\approx\varepsilon_{F0}-\frac{\pi^2}{6}\frac{g'(\varepsilon_{F0})}{g(\varepsilon_{F0})}(k_BT)^2 \tag{21}$$

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

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

The MEC term on the right-hand side of Equation (19) was ever neglected [19], but it is important for understanding the experimental Seebeck coefficient [10]. Substituting Equations (5) and (22) into Equation (19) may yield

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

As is shown, of great importance is the density of states and the potential energy ε_p whose accurate expressions may be difficult to obtain. Nevertheless, for alkali metals and some monovalent noble metals, the free electronic density of state at Fermi surface could be employed approximately [2, 4, 8, 20]

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

and the potential energy ε_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, $Ry=e^2/8\pi\varepsilon_0 a_0=13.6\ eV$, ε_0 the vacuum permittivity. The above estimation of ε_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

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

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

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

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 [9, 26-31] and the results were shown in Table 1. It can 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 ECP 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 controlled by dE_F/edT and especially the MEC C_{m-e}. A positive MEC C_{m-e} generally gives birth to a negative

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 ε_{F0} at zero temperature, linear expansion coefficient α_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
C_{m-e} (eV)	–0.158	0.617	1.03	1.10	1.15	–1.72	–0.638	–0.664
dE_F/edT $(\mu V/K)$	+	–	–	–	–	+	+	+
S_{ex} $(\mu V/K)$	10.6 [27]	–5.8 [27]	–12.9 [27]	–9.5 [27]	–0.9 [27]	1.83 [26,28]	1.51 [26,28]	1.94 [26,28]
ε_{F0} (eV) [8]	4.72	3.23	2.12	1.85	1.58	7.00	5.48	5.51
α_l $(10^{-6}/K)$	46 [9]	71 [9]	79.64 [29]	66 [30]	72 [31]	16.5 [9]	18.9 [9]	14.2 [9]
r_s [8]	3.25	3.93	4.86	5.20	5.63	2.67	3.02	3.01

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 [20] 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

$$U_e = N_e E_{F0} - \frac{2}{5} N_e \varepsilon_{F0} \tag{27}$$

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

$$\bar{P}_e = -n_e \left(C_{m-e} + \frac{4}{15} \varepsilon_{F0} \right) \tag{28}$$

where $\bar{P}_e$ 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 $C_{m\text{-}e}>-4\varepsilon_{F0}/15$, 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 $C_{m\text{-}e}<-4\varepsilon_{F0}/15$ 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
$C_{m\text{-}e}$ (eV)	–0.158	0.617	1.03	1.10	1.15
n_e $(\times10^{28}/m^3)$ [8]	4.70	2.65	1.40	1.15	0.91
ε_{F0} (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

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

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 ε_p must include the contributions of Coulomb energy, exchange energy and correlation energy. The calculation of the real potential energy ε_p at finite temperatures may be very complex and difficult. But all the necessarily calculated terms for the potential energy ε_p may be in the form $\int_0^\infty \varepsilon_p(\varepsilon) f(\varepsilon) d\varepsilon$ (where ε_p (ε) is any continuous function and $f(\varepsilon)$ is Fermi-Dirac function) [1], so the potential energy ε_p could be calculated formally according to the Sommerfeld expansion [2-4, 6, 7].

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

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

The kinetic energy dependence of the potential energy may arise from the exchange-correlation 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 will be discussed in the following sections. Consequently, the total energy can be written in the integral form

$$U = V\int_{x_0}^{\infty} x_k g\left(x_k\right) f\left(x_k\right) dx_k$$

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

$$g(\varepsilon_k)=g(x_k)\frac{dx_k}{d\varepsilon_k} \tag{30}$$

Since the EDS $g(\varepsilon_k)$, $g(x_k)$ are always positive, the value of the derivative $dx_k/d\varepsilon_k$ is surely positive. Therefore the single-electron energy x_k must be a monotonically increasing function with the kinetic energy ε_k, giving the one-to-one mapping relationship between the single-electron energy x and the kinetic energy ε_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_BT) can be evaluated

$$U=V\left[\int_{x_0}^{x_F} x_k g(x_k)\,dx_k+\frac{\pi^2(k_BT)^2}{6}\frac{\partial x_F g(x_F)}{\partial x_F}\right]$$

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.*, $x_F - x_0 >> k_BT$. 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

$$U=U_0+V\frac{\pi^2(k_BT)^2}{6}g(x_F)$$

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 γ is

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

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 [32-39]. Hence, according to Equation (32) the temperature dependence of the ECP 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 [40].

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 can be written as

$$U = V\left[\int_{x_0}^{x_{F0\uparrow}} x_k \frac{g(x_k)}{2} dx_k + \int_{x_0}^{x_{F0\downarrow}} x_k \frac{g(x_k)}{2} dx_k - n_\uparrow \mu_B B + n_\downarrow \mu_B B\right]$$

where $n_\uparrow$ is the number density of up-spin conduction electrons, $n_\downarrow$ is the number density of down-spin electrons, $\varepsilon_{F0\uparrow}$, $\varepsilon_{F0\downarrow}$ are the Fermi energies of up-spin electrons and down-spin electrons at zero temperature, respectively, the single-electron energies are $x_{F0\uparrow}=\varepsilon_{F0\uparrow}+\varepsilon_p(r_s,\varepsilon_{F0\uparrow})$, $x_{F0\downarrow}=\varepsilon_{F0\downarrow}+\varepsilon_p(r_s,\varepsilon_{F0\downarrow})$, μ_B denotes the Bohr magneton, B is the externally applied magnetic field, $g(x_k)/2$ is the density of states for the up-spin conduction electrons and down-spin conduction electrons. When the conduction electrons reach 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

$$x_{F0\uparrow} \frac{g(x_{F0\uparrow})}{2} \frac{\partial x_{F0\uparrow}}{\partial n_\uparrow} - x_{F0\downarrow} \frac{g(x_{F0\downarrow})}{2} \frac{\partial x_{F0\downarrow}}{\partial n_\downarrow} - 2\mu_B B = 0 \qquad (33)$$

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,

$$n_\uparrow = \int_{x_0}^{x_{F0\uparrow}} \frac{g(x_k)}{2} dx_k$$

$$n_\downarrow = \int_{x_0}^{x_{F0\downarrow}} \frac{g(x_k)}{2} dx_k$$

$$n_e = n_\uparrow + n_\downarrow$$

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

$$\frac{\partial x_{F0\uparrow}}{\partial n_{\uparrow}} = \frac{2}{g\left(x_{F0\uparrow}\right)}$$

$$\frac{\partial x_{F0\downarrow}}{\partial n_{\downarrow}} = \frac{2}{g\left(x_{F0\downarrow}\right)}$$

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

$$\varepsilon_{F0\uparrow} + \varepsilon_p\left(r_s, \varepsilon_{F0\uparrow}\right) - \mu_B B = \varepsilon_{F0\downarrow} + \varepsilon_p\left(r_s, \varepsilon_{F0\downarrow}\right) + \mu_B B \tag{34}$$

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) can be expanded into Taylor's series to first order,

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

$$\varepsilon_p\left(\varepsilon_{F0\uparrow}\right) \approx \varepsilon_p\left(r_s, \varepsilon_{F0}\right) + \left.\frac{\partial \varepsilon_p\left(r_s, \varepsilon_{F0\uparrow}\right)}{\partial \varepsilon_{F0\uparrow}} \frac{\partial \varepsilon_{F0\uparrow}}{\partial n_{\uparrow}}\right|_{\varepsilon_{F0\uparrow}=\varepsilon_{F0}} \frac{\partial n_{\uparrow}}{\partial B} B$$

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

$$\varepsilon_p\left(\varepsilon_{F0\downarrow}\right) \approx \varepsilon_p\left(r_s, \varepsilon_{F0}\right) + \left.\frac{\partial \varepsilon_p\left(r_s, \varepsilon_{F0\downarrow}\right)}{\partial \varepsilon_{F0\downarrow}} \frac{\partial \varepsilon_{F0\downarrow}}{\partial n_{\downarrow}}\right|_{\varepsilon_{F\downarrow}=\varepsilon_{F0}} \frac{\partial n_{\downarrow}}{\partial B} B$$

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

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

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

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

The corresponding magnetic susceptibility can 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

$$\chi_p = \frac{\mu_0 \mu_B^2 g(\varepsilon_{F0})}{1 + \frac{\partial \varepsilon_p(r_s, \varepsilon_{F0})}{\partial \varepsilon_{F0}}} \tag{36}$$

It demonstrates that compared with the common results in textbooks and literatures the potential energy of the conduction electrons leads to the same modification on both the magnetic susceptibility and the electron heat capacity. The conduction electrons in a metal exhibit the Landau diamagnetic susceptibility χ_l whose magnitude is one third of the Pauli magnetic susceptibility [15], *i.e.*, $\chi_l=-\chi_p/3$. So the experimentally measured magnetic susceptibility χ_e would be $\chi_e=2\chi_p/3$. And the ratio between the experimentally magnetic susceptibility χ_e and the parameter γ, 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 [41]. 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 χ_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, 15],

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

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

Since the function $\partial f(x_k)/\partial x_k$ behaves like the Dirac delta function $\delta(x_k)$ [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 $\delta(x_k-x'\pm\hbar\omega_q)$ and $\delta(x_k-x')$ 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 ω_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

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

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

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

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, 15]

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

where κ_{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

$$\kappa_{me} = \kappa_e \left[1 + \frac{\partial \varepsilon_p \left(r_s, \varepsilon_{F0} \right)}{\partial \varepsilon_{F0}} \right] \tag{39}$$

where κ_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 also 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. And it will be investigated in the following section.

2.9 Determination of the factor

Despite that the modified factor $[1+\partial\varepsilon_p(r_s, \varepsilon_{F0})/\partial\varepsilon_{F0}]$ is a phenomenological parameter, it may be very convenient to uncover the physical behaviors of the metals. In the section, the modified factor $[1+\partial\varepsilon_p(r_s, \varepsilon_{F0})/\partial\varepsilon_{F0}]$ will be discussed. In the actual metals and alloys, the conduction electrons are customarily consisted of electrons in the initially atomic orbitals such as the outer *s*, *p*, *d* and *f* orbitals. Hence, based on the number conservation of the conduction electrons the following relation may be valid at zero temperature

$$\int_{x_0}^{x_{F0}} g_f\left(x_k\right) dx_k + \sum_{l=s,p,d} \int_{x_0}^{x_{F0}} g_l\left(x_k\right) dx_k = \int_0^{\varepsilon_{F0}} g_c\left(\varepsilon_k\right) d\varepsilon_k \tag{40}$$

where the $g_c(\varepsilon_k)$ is the EDS with the kinetic energy ε_k and it is $g_c(\varepsilon_{F0})=3n_e/2\varepsilon_{F0}$ in the free-electron model, n_e is the conduction electron density, $g_f(x_k)$ and $g_l(x_k)$ stand for the density of the outer conduction *f*-electron states and electron states in the outer orbitals such as *s*, *p*, *d*, respectively. Carrying out the partial derivative with respect to the Fermi energy ε_{F0} will yield

$$1+\left.\frac{\partial\varepsilon_p\left(r_s,\varepsilon_k\right)}{\partial\varepsilon_k}\right|_{\varepsilon_k=\varepsilon_{F0}}=\frac{g_c\left(\varepsilon_{F0}\right)}{g_f\left(x_{F0}\right)+\sum\limits_{l=s,p,d}g_l\left(x_{F0}\right)} \tag{41}$$

As is seen, the dimensionless factor depends on the ratio between the EDS in the free-electron model and the summation of the EDS for the conduction electrons in different bands at ECP, and thus it is always positive, which is consistent with the previous analysis. Its magnitude may dominate the physical properties of the electrons and should be addressed in the followings. The bandwidth of the *f*-electron band may be quite narrow because of the ignoring overlap between the *f*-electron state and other states, thereby giving rise to an ultra-high EDS for the *f* electrons. As a result, once the ECP intersects the *f*-electron band, the above dimensionless factor may reach a very small value, leading to the heavy-fermion behaviors that was discussed in the foregoing sections. On the contrary, the heavy-fermion behaviors may not emerge in the case that the ECP of the metal is separated with the *f*-electron band. Interestingly, if the ECP of the heavy-fermion system can be tuned to depart from the *f*-electron band using the techniques such as high pressure, *i.e.*, $g_f(x_{F0})=0$ in the denominator, the heavy-fermion behaviors may disappear. Reversely, the heavy-fermion behaviors may appear in the case that the ECP of the non-heavy-fermion system will be shifted to intersect the *f*-electron band.

To see the important role of EDS for the *f*-electron in the heavy-fermion systems, the magnitude of the dimensionless factor should be estimated in the followings. The half width of the *f*-electron band and the number of the *f*-electrons may be denoted by $\Delta\varepsilon_f$

and n_{ef}, respectively. The EDS for the f-electron may be approximately given by $g_f(x_{F0})= n_{ef}/\Delta\varepsilon_f$, so the dimensionless factor may read

$$1+\left.\frac{\partial\varepsilon_p\left(r_s,\varepsilon_k\right)}{\partial\varepsilon_k}\right|_{\varepsilon_k=\varepsilon_{F0}}\approx\frac{n_e}{n_{ef}}\frac{3\Delta\varepsilon_f}{2\varepsilon_{F0}}\tag{42}$$

where the half-width of the f-electron band may be comparable to the half-width of the related fluorescence peaks. The experimental observations showed that the half-width of the fluorescence peaks is customarily several nanometers [42, 43], implying the half-width of the f-electron band in the range 1 *meV*-10 *meV*. The Fermi energy may be the order of 1 *eV*, therefore enabling the f- electrons near the ECP to exhibit the mass in the range 10^2 m_e-10^3 m_e which may agree with the customarily experimental observations [44, 45].

The total conduction electron density arising from different bands may be as follows,

$$\sum_{l=s,p,d,f}\int_{x_0}^{x_{F0}}g_l\left(x_k\right)dx_k=n_e\tag{43}$$

The derivation of the ECP with respect to the conduction electron density may generate the relation

$$1=\frac{dx_{F0}}{dn_e}\sum_{l=s,p,d,f}g_l\left(x_{F0}\right)-\frac{dx_0}{dn_e}\sum_{l=s,p,d,f}g_l\left(x_0\right)\tag{44}$$

If the locally bound electrons in these bands are totally ionized to the conduction electrons, the potential energy x_0 may lie below these bands, making the EDS at the potential energy x_0 be zero. It is equivalent to the case that the first term on the right hand in Equation (5) is zero. So the following relation may hold right

$$\frac{dx_{F0}}{d\ln V}=-\frac{n_e}{\sum_{l=s,p,d,f}g_l\left(x_{F0}\right)}\tag{45}$$

It may be written in in another form

$$C_{m-e} = -\frac{n_e}{\sum\limits_{l=s,p,d,f} g_l\left(x_{F0}\right)} \tag{46}$$

It is the MEC of the metal. As is shown, the MEC may be negative for the MEC of the metal whose EDS $g_l(x_0)$ at the potential energy is zero. The magnitude of MEC may be large when the total density of state at the ECP is small. On the contrary, the MEC will display a small magnitude in the case that the total density of state at the ECP is very large, *e.g.*, the heavy-fermion systems.

Substitution of Equation (46) into Equation (10) may yield the modified Thomas-Fermi screening wave vector

$$q_{TF}^2 = \frac{e^2}{\varepsilon_0} \sum_{l=s,p,d,f} g_l\left(x_{F0}\right) \tag{47}$$

and the modified Thomas-Fermi screening length

$$\lambda_{TF}^2 = \frac{\varepsilon_0}{e^2} \frac{1}{\sum\limits_{l=s,p,d,f} g_l\left(x_{F0}\right)} \tag{48}$$

It may indicate that a large EDS at the ECP may lead to a short Thomas-Fermi screening length, resulting in a small Coulomb interaction. Therefore, the electron system such as the heavy-fermion system which exhibits a very large EDS at the ECP may display very small Coulomb interaction, as is completely contrary to the conventionally widespread viewpoint that the heavy-fermion systems result from the strong correlation effect. Reversely, if the actual EDS at the ECP is very small, the factor shown in Equation (41) will be very large. As a result, the effective mass of the electrons may be very small and the Thomas-Fermi screening length may be very long, corresponding to a notable

Coulomb interaction between the electrons. And the related properties may be shown in Table 3.

Table 3 The related physical parameters and properties for the different electron systems whose electronic density of states (EDS) at the potential energy x_0 is zero.

electron systems	EDS	MEC	screening length	Coulomb interaction
heavy-fermions	large	small	short	small
light-fermions	small	large	long	large

2.10 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 [46, 47]. 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

$$\xi\left(x\right)=\xi_0\,cos\,2k_Fx$$

where $\xi(x)$ is position-dependent one-dimensional strain, ξ_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, 47]. 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 $C_{m\text{-}e}$, the statically periodic strain would give birth to a periodic variation of the ECP and a periodic electrostatic field,

$$E_F\left(x\right)=E_{F0}+C_{m\text{-}e}\xi_0\,cos\,2k_F x \tag{49}$$

$$\vec{E}\left(x\right)=-2\frac{C_{m\text{-}e}}{e}k_F\xi_0\,sin\,2k_F x \tag{50}$$

where $E_F(x)$ is the position-dependent ECP, $C_{m\text{-}e}=\partial E_F/\partial\xi$ 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 $|C_{m\text{-}e}\xi_0|$. The potential enables the initial gapless conduction band to open up a CDW gap whose magnitude can be obtained according to the degenerate perturbation theory [4, 8],

$$\Delta_{\text{CDW}}=\left|C_{m-e}\xi_0\right| \tag{51}$$

where Δ_{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 [48]. 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 [48]. As a result, the MEC $C_{m\text{-}e}$ 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 (51), as shown in Table 4.

Table 4 The physical parameters of some typical CDW materials and the calculated magnitude of the mechanical-electric coupling $|C_{m\text{-}e}|$.

materials	displacement (Å)	lattice parameter (Å)	strain (%)	CDW gap (meV)	$\lvert C_{m\text{-}e}\rvert$ (eV)
KCP	0.027 [48]	2.894 [48]	0.933	150 [49]	16
K0.3MoO3	0.05 [48]	7.56 [50]	0.661	130 [51]	17
(TaSe4)2I	0.09 [48]	3.206 [48]	2.81	250 [52, 53]	8.9
2H-NbSe2	0.042 [54]	3.4583 [54]	1.21	60 [55]	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 metals.

3. Conclusion

In summary, the MEC in metals was investigated in the work. The MEC may 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 single-electron model can offer a simple way of understanding the variously physical properties of the metals such as the electron heat capacity, the Pauli magnetic susceptibility, the electrical conductivity and the electron thermal conductivity, especially the related characteristics of the heavy fermion systems. On another hand, the MEC may be used to not only obtain the right sign of Seebeck coefficients for some monovalent metals such as Li, Cu, Ag and Au but also give the magnitude of the CDW gap. In a word, the MEC may be important and could help understand variously physical behaviors of the metals in a simple manner.

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