Mechanic-Electric Coupling in Metals

Yuanjie Huang*

Mianyang, *Sichun province*, *People's Republic of China*

*Corresponding author's E-mail: hyj201207@163.com

Abstract

In metal physics, the free electron model and the related Fermi-Dirac distribution was usually utilized to investigate multi-physical properties of metals. However, they neglected the important mechanic-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 could not only monitor 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 modified free electron model which could offer a simple way of interpreting the electron heat capacity and the Pauli magnetic susceptibility 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 the investigation of the physical properties of the metals.

keywords: mechanic-electric coupling; metals; 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 bottom energy of the conduction band 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 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 mechanic-electric coupling (MEC) in a metal [9, 10]. The MEC was found to induce new physics such as the electric properties of dislocations and the electric force between dislocations [11]. On another hand, the MEC could also cause some modifications on the free electron model which was interestingly found to result in 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 heavy-fermions 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. Upon equilibrium state, the physical relation between the electric field and the correlated Fermi surface alterations may be described by *Yuheng Zhang equation* [12],

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

where e is electron (positron) charge, E_F is the position-dependent electron (positron) chemical potential at the equilibrium state.

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]

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

where ε_{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 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. Thereby it could be written as

$$E_F = \varepsilon_p + \varepsilon_F \tag{3}$$

where ε_F stands for the Fermi energy, and ε_p denotes the potential energy of the conduction electron. 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, the direct Coulomb energy among the electrons, the electron exchange energy, electron correlation energy and contributions of surface dipole layer [1, 2]. It may be of paramount importance in some physical effects and would be discussed in the followings.

2.1 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, 16-20], it is written as

$$S_{th} = \frac{E}{\nabla T} \tag{4}$$

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, 19]

$$S_{ex} = \frac{-\Delta V}{\Delta T} \tag{5}$$

where ΔV is the voltage difference, ΔT the temperature difference. 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 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 [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.

Thermoelectric effect is a non-equilibrium phenomena and the measured voltage difference arises from 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 chemical potential was considered [19], 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

$$-\frac{V_{ex}\left(T+\Delta T\right)-V_{ex}\left(T\right)}{\Delta T}=\frac{\left[E_F\left(T+\Delta T\right)+e\phi\left(T+\Delta T\right)\right]-\left[E_F\left(T\right)+e\phi\left(T\right)\right]}{e\Delta T} \quad (6)$$

where $V_{ex}(T+\Delta T)$, $V_{ex}(T)$ is the experimentally measured voltage at the hot end and cool end, respectively, $\phi(T+\Delta T)$, $\phi(T)$ the respective internal potential caused by the drift of electrons at the hot end and cool end. Based on Equations (5) and (6), the experimental Seebeck coefficient could be simplified to be

$$S_{ex}=\frac{\vec{E}_c-\vec{E}_r}{\nabla T} \quad (7)$$

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, 26] and the metals such as Ag, Cu and Au with higher electrical conductivity usually exhibit a smaller 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 (7) could be expressed in another manner,

$$S_{ex} = \frac{dE_F}{edT} - \frac{\vec{E}_r}{\nabla T} \tag{8}$$

Seen from Equations (6) (7) and (8), 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 (8) could be written as

$$\frac{dE_F}{edT} = \left(\frac{\partial E_F}{e\partial T}\right)_V + \frac{\alpha_V(T)C_{m-e}}{e} \tag{9}$$

where $\alpha_V(T)$ is the temperature-dependent volume expansion coefficient of the metal and it could be $\alpha_V(T)=\partial V/V\partial T=3\alpha_l(T)$ for the isotropic metals, $\alpha_l(T)$ the temperature dependent linear expansion coefficient, and $C_{m-e}=V\partial E_F/\partial V$ is the MEC of an isotropic metal. Based on Equation (3), the first term in the above equation could be written as

$$\left(\frac{\partial E_F}{e\partial T}\right)_V = \left(\frac{\partial \varepsilon_p}{e\partial T}\right)_V + \left(\frac{\partial \varepsilon_F}{e\partial T}\right)_V \tag{10}$$

In 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 $\partial\varepsilon_p/\partial T=0$. According to the Sommerfeld expansion in textbooks [2-4, 6, 7, 20], the temperature-dependent Fermi energy ε_F is

$$\varepsilon_F \approx \varepsilon_{F0} - \frac{\pi^2}{6}\frac{g'(\varepsilon_{F0})}{g(\varepsilon_{F0})}(k_B T)^2 \tag{11}$$

where ε_{F0} is the Fermi energy at zero temperature, k_B the Boltzmann constant, $g(\varepsilon_{F0})$ the density of states at the 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 (10) could be obtained

$$\frac{\partial\varepsilon_F}{e\partial T} = -\frac{\pi^2}{3e}\frac{g'(\varepsilon_{F0})}{g(\varepsilon_{F0})}k_B^2 T \tag{12}$$

In Equation (9), the MEC term on the right was ever neglected [19], but it is important for understanding the experimental Seebeck coefficient [9]. Using Equations (3) and the relation [2, 4, 8, 20],

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

where r_s is a dimensionless ratio, a_0 the Bohr radius, and $r_s a_0$ is the average radius of a sphere containing a single conduction electron in metals, the MEC could be given by

$$C_{m-e} = \frac{r_s}{3}\frac{\partial\varepsilon_p}{\partial r_s} - \frac{n_e\partial\varepsilon_{F0}}{\partial n_e} \tag{13}$$

In the related calculations, the relation $V\partial\varepsilon_{F0}/\partial V = -n_e\partial\varepsilon_{F0}/\partial n_e$ was employed and the approximations $\partial\varepsilon_F/\partial V \approx \partial\varepsilon_{F0}/\partial V$ was used, because the relation $k_B T \ll \varepsilon_{F0}$ may persist for the metals in the concerned temperature range $T<300$ K.

Substituting Equations (12) and (13) into Equation (9), one may obtain

$$\frac{dE_F}{edT}=-\frac{\pi^2}{3e}\frac{g'(\varepsilon_{F0})}{g(\varepsilon_{F0})}\frac{k_B^2T}{\varepsilon_{F0}}+\frac{\alpha_V(T)}{e}\left[\frac{r_s}{3}\frac{\partial\varepsilon_p}{\partial r_s}-\frac{n_e\partial\varepsilon_{F0}}{\partial n_e}\right] \tag{14}$$

As is shown, of great importance is the real density of states $g(\varepsilon_{F0})$ 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 electron density of state at Fermi surface could be employed approximately [2, 4, 8, 20]

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

and the potential energy ε_p could be estimated simply in terms of a central potential [2]

$$\varepsilon_p\approx\frac{-3Ry}{r_s}\left(1-\frac{1}{r_s^2}\right) \tag{15}$$

where Ry is Rydberg, $Ry=e^2/8\pi\varepsilon_0a_0=13.6\ eV$, 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. Despite a rough estimation, it could still be utilized to investigate the related phenomena. Thus, the MEC is

$$C_{m-e}=\left[\frac{Ry}{r_s}\left(1-\frac{3}{r_s^2}\right)-\frac{2}{3}\varepsilon_{F0}\right] \tag{16}$$

and Equation (14) becomes

$$\frac{dE_F}{edT}=-\frac{\pi^2}{6}\frac{k_BT}{\varepsilon_{F0}}\frac{k_B}{e}+\frac{\alpha_V(T)}{e}\left[\frac{Ry}{r_s}\left(1-\frac{3}{r_s^2}\right)-\frac{2}{3}\varepsilon_{F0}\right] \tag{17}$$

To examine whether Equation (17) 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 [26-32] and the results was shown in Table 1. It could be seen that the sign of calculated values dE_F/edT and the MEC $C_{m\text{-}e}$ 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 controlled by dE_F/edT and especially the MEC $C_{m\text{-}e}$. A positive MEC $C_{m\text{-}e}$ generally gives birth to a negative Seebeck coefficient and a negative value of $C_{m\text{-}e}$ 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 $C_{m\text{-}e}$. In a word, for the types of carriers, what Hall coefficient predicts may be more accurate than that predicted by Seebeck coefficient.

2.2 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 and n_e is the electron density. 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

$$E_e = N_e E_{F0} - \frac{2}{5} N_e \varepsilon_{F0} \tag{18}$$

Table 1 The calculated mechanic-electric coupling $C_{m\text{-}e}=V\partial E_F/\partial V$ and the sign of dE_F/edT for the alkali metals and some monovalent noble metals based on Equations (16) and (17). 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
$C_{m\text{-}e}$ (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 [29]	71 [29]	79.64 [30]	66 [31]	72 [32]	16.5 [29]	18.9 [29]	14.2 [29]
r_s [8]	3.25	3.93	4.86	5.20	5.63	2.67	3.02	3.01

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

$$\bar{P}_e = -n_e \left(C_{m-e} + \frac{4}{15} \varepsilon_{F0} \right) \tag{19}$$

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 could 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 (15) and (16), 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 $(\times 10^{28}/m^3)$ [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

2.3 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. To compare with experimental results, 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 $\varepsilon_p(\varepsilon)$ 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

$$U = 2\sum_{\vec{k}} \left[\varepsilon_p\left(r_s, \varepsilon_k\right) + \varepsilon_k\right] f\left(\varepsilon_k + \varepsilon_p\left(r_s, \varepsilon_k\right)\right) \tag{20}$$

where $\varepsilon_p(r_s, \varepsilon_k)$ is the potential energy of the conduction electron, 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 ε_k. 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 was not considered in previous discussions but it is important for electron heat capacity and magnetic susceptibility which would be discussed in the next section. 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

$$g(\varepsilon_k) = g(x)\frac{dx}{d\varepsilon_k} \tag{21}$$

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 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) could be evaluated

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

In the calculations, it is 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 (11), the total energy could be simplified to be

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

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

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

Using Equation (21), the heat capacity of conduction electrons per unit volume could be expressed in the form $c_e=\gamma T$ where the parameter γ is

$$\gamma = \frac{\pi^2 k_B^2}{3}\frac{g(\varepsilon_{F0})}{1+\dfrac{\partial \varepsilon_p (r_s, \varepsilon_{F0})}{\partial \varepsilon_{F0}}} \tag{22}$$

As shown in Equation (22), 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 (22), 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 modified free 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

$$\frac{dE_F}{dT} \approx \alpha_V C_{m-e} \tag{23}$$

The heavy-fermion systems usually exhibits the thermal expansion coefficient several orders of magnitude larger than that of normal metals at low temperatures [33-40]. Hence, according to Equation (23) 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 [41].

2.4 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 down-spin electrons, respectively, the single-electron energies are $x_{F\uparrow}=\varepsilon_{F\uparrow}+\varepsilon_p(r_s,\varepsilon_{F\uparrow})$, $x_{F\downarrow}=\varepsilon_{F\downarrow}+\varepsilon_p(r_s,\varepsilon_{F\downarrow})$, μ_B the Bohr magneton, B the externally applied magnetic field, $g(x)/2$ 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

$$x_{F\uparrow}\frac{g\left(x_{F\uparrow}\right)}{2}\frac{\partial x_{F\uparrow}}{\partial n_{\uparrow}}-x_{F\downarrow}\frac{g\left(x_{F\downarrow}\right)}{2}\frac{\partial x_{F\downarrow}}{\partial n_{\downarrow}}-2\mu_B B=0 \tag{24}$$

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,

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

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

Substituting these equations into the Equation (24), it is

$$\varepsilon_{F\uparrow}+\varepsilon_p\left(r_s,\varepsilon_{F\uparrow}\right)-\mu_B B=\varepsilon_{F\downarrow}+\varepsilon_p\left(r_s,\varepsilon_{F\downarrow}\right)+\mu_B B \tag{25}$$

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 (25) could be expanded into Taylor's series to first order,

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

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

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

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

Insertion of these expanded function into Equation (25) will yield

$$\left(1 + \frac{\partial \varepsilon_p\left(r_s, \varepsilon_{F0}\right)}{\partial \varepsilon_{F0}}\right) \frac{2}{g\left(\varepsilon_{F0}\right)} \left(\frac{\partial n_{\uparrow}}{\partial B} - \frac{\partial n_{\downarrow}}{\partial B}\right) = 2\mu_B \tag{26}$$

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 (26), the Pauli magnetic susceptibility of the conduction electrons could be obtained

$$\chi_p = \frac{\mu_0 \mu_B^2 g\left(\varepsilon_{F0}\right)}{1 + \frac{\partial \varepsilon_p\left(r_s, \varepsilon_{F0}\right)}{\partial \varepsilon_{F0}}} \tag{27}$$

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 χ_l whose magnitude is one third of the Pauli magnetic susceptibility [42], *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 (22) and (27), 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 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 according to Equations (22) and (27), 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 by the modified free electron model.

2.5 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

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

where $\xi(x)$ is position-dependent one-dimensional strain, ξ_0 is the largest strain, k_F the wavevector. 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 would be uncovered.

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

$$E_F(x) = E_{F0} + C_{m\text{-}e}\xi_0 \cos 2k_F x \tag{28}$$

$$\vec{E}(x) = -2\frac{C_{m\text{-}e}}{e} k_F \xi_0 \sin 2k_F x \tag{29}$$

where $E_F(x)$ is the position-dependent electron chemical potential, the MEC is $C_{m\text{-}e}=\partial E_F/\partial\xi$ 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 could be obtained according to the degenerate perturbation theory [4, 8],

$$\Delta_{\mathrm{CDW}} = \left|C_{m-e}\xi_0\right| \tag{30}$$

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 [46]. On another hand, the magnitude of CDW gap may also rest with the MEC strength of the material. And a larger MEC strength would usually yield a larger CDW gap which could induce 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 MEC strength could be estimated according to Equation (30), as shown in Table 3.

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

materials	displacement (Å)	lattice parameter (Å)	strain (%)	CDW gap (*meV*)	$\lvert C_{m-e}\rvert$ (*eV*)
KCP	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

Conclusion

In summary, the MEC in metals was investigated in the work. The MEC may not only determine 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 electron heat capacity and the Pauli magnetic susceptibility of the conduction electrons in metals, especially the related characteristics of the heavy fermion systems. In a word, the MEC may be important and could help understand variously physical properties of the metals.

Reference

[1] Gerald D. Mahan, Many-Particle Physics, third edition, Kluwer Academic/Plenum Publishers, 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.187-196.

[3] Zhicheng Wang, Thermodynamics •Statistical Physics, Higher Education Press, Beijing, 5th 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.315-326.

[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, viXra:2110.0054.

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

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

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

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

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

[21] 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.

[22] J. E. Robinson, Thermoelectric Power in The Nearly-Free-Electron Model, Phys.

Rev. V. **161**, 533-539 (1967).

[23] 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).

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

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

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

[27] 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

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

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

[30] 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).

[31] F. M. Kelly, W. B. Pearson, The Rubidium Transition at ~180 K, Canad. J. Phys. V. **33**, 17-24 (1955).

[32] 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).

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

[34] 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

[35] 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).

[36] 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).

[37] 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).

[38] 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).

[39] 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). https://doi.org/10.1103/PhysRevB.82.052502

[40] 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).

[41] 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).

[42] Giuseppe Grosso, Giuseppe Pastori Parravicini, Solid State Physics, 2nd edition, Waltham, Elsevvier Ltd. 2014, pp.659.

[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 Density Waves 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 $K_{0.3}MoO_3$ $(20\bar{1})$ 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 $K_{0.3}MoO_3$ and $Rb_{0.3}MoO_3$, 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 $(TaSe_4)_2I$, Solid State Communication, V. **46**, 325-328(1983).

[51] Christos D. Malliakas and Mercouri G. Kanatzidis, Nb−Nb Interactions Define 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-$TaSe_2$, Phys. Rev. B V. **72**, 121103(R) (2005).