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## The metal–non-metal transition in displaced atomic terms

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**Abstract.** The theory of the atomic-like electronic structure of metals near their liquid–gas critical points has been generalized for noble and d transition metals. In these metals the valence state may change through excitation of d electrons into the low-lying displaced term which becomes favoured because of the interaction of overlapping atoms. We use percolation theory together with concepts of atomic-like screening and classical localization to discuss the metal–non-metal transition. Interplay between the valence state and the metal–non-metal transition is shown to exist. The electric conductivity and the low-frequency dielectric function near the transition point have been estimated for copper as functions of the density.

### 1. Introduction

Near the liquid–vapour critical point of metals the electronic structure changes from nearly free valence electrons typical of condensed metals to an atomic-like structure with strong electron–ion interaction. In the critical region all electronic properties are strongly density dependent, showing the disappearance of the metallic state owing to expansion. Since the pioneering work by Landau and Zeldovitch [1], much effort has been made to study the gradual transition of mercury and alkali metals with lower critical temperatures, which are available for experiments under static conditions, into a non-metallic state [2]. Such data are still lacking for other metals the critical regions for which can be investigated only by explosion methods.

The electronic theory of the metal–insulator transition in disordered systems has intrinsic difficulties caused by strong electron–ion interactions (see, for example, the recent reviews in [3, 4]). Different approaches propose that either weak scattering or strong localization of electrons is applicable but only far from the transition point. Moreover, the gradual transition in gaseous metals needs special consideration to take into account the thermal excitation generally neglected for low-temperature systems. According to Mott's original concept, the metal state depends on the electron–gas screening of ions. As the screening decreases owing to expansion, an atomic-like level appears, indicating a metal–insulator transition [5]. Some insight can be gained by considering the transition in the opposite direction, i.e. the transition of an atomic gas into a metallic gas owing to compression. Generally, in metal atoms the valence electrons are in quasi-classical states screening an ion core near the boundary of the classical accessible region in the Coulomb potential. These regions in neighbouring atoms can overlap, forming percolation clusters. Overlapping electronic shells virtually screen each other from ion cores, giving rise to valence electrons which are partly

free. Below the threshold, electrons are localized in finite percolation clusters (a classical counterpart of Anderson localization [6]). Above the percolation threshold, electrons diffuse along the classical accessible regions. Thus, the metal–non-metal transition in a strongly coupled atomic-like system relates to percolation.

The electronic properties of mercury and alkali metals have been described by the theory of a quasi-atomic gas on the basis of these concepts [7]. In simple metals the valence electrons are well separated from inner electronic shells. In contrast, a peculiarity of noble and transition metals is that the atom state may change through excitation of an inner *d* electron into the displaced term. In some cases its excitation is energetically advantageous because the interaction energy of atoms is lowered. This paper provides an extension of the theory for noble and transition metals. In particular, we shall consider copper because of its wide applications.

## 2. The valence state

The ground-state electronic configuration of copper is  $3d^{10}4s^2S_{1/2}$  with the ionization potential  $I = 7.7$  eV. The lower excited-state levels are two components of the displaced term of the configuration  $3d^94s^2^2D_{5/2}$  and  $^2D_{3/2}$  with ionization potentials of around 6.2 eV [8]. The ground-state level and the displaced term shift by different amounts owing to the interaction of atoms.

The interaction energy of overlapping atoms can be estimated as the Madelung energy of ions embedded in the uniform background of the valence electrons. Indeed, the electron density is mixed near the percolation threshold radius of the sphere problem, i.e. near  $0.7R$  where  $R$  is the mean interatomic distance or the ion cell radius:  $R = (\frac{4}{3}\pi n_i)^{-1/3}$ . The interaction energy per atom is then

$$u \simeq - \int_{0.7R}^R \frac{ze^2}{r} (1 - \frac{4}{3}\pi r^3 n_e) n_e 4\pi r^2 dr = -\alpha_M z^2 e^2 n_i^{1/3}. \quad (1)$$

Here  $e$  is the electron charge,  $n_e$  and  $n_i$  are the electron and ion densities,  $n_e = zn_i$ ,  $z$  is the valence of the ions and  $\alpha_M$  is the renormalized Madelung coefficient. An estimation of the latter from equation (1) is straightforward.

Otherwise, this coefficient can be found semiempirically from the critical parameters of the metals which have critical points on the metallic side of the metal–non-metal transition, e.g. caesium or rubidium. We assume a modified van der Waals equation of state for overlapping atoms:

$$p = nT/(1 - n_i b_i) - \frac{1}{3}\alpha_M z^2 e^2 n_i^{4/3} \quad (2)$$

where  $n$  is the total density,  $n = n_e + n_i$  and the minimal volume per atom is  $b_i \sim (e^2/I)^3$ . The second term on the right-hand side of equation (2) is related to the Madelung energy. The critical pressure and temperature are then expressed through the Madelung coefficient. Hence, the latter can be estimated from the experimental parameters. From different estimations,  $\alpha_M$  has a value from 0.45 to 0.65.

As follows from equation (1) the  $^2D$ -state level corresponding to the valence  $z = 2$  shifts as a result of the interaction more than the ground-state level does. Thus, near the metal–non-metal transition point the energy  $E_D - 4\alpha_M e^2 n_i^{1/3}$  of

the two-valence state turns out to be less than the energy  $E_s - \alpha_M e^2 n_i^{1/3}$  of the ground-state configuration. Moreover, since the  $^2D$  term has a major statistical weighting, occupation of the two-valence state turns out to be much more probable for Boltzmann statistics.

Excitation of the displaced term has several consequences. First of all, the increased valence influences the parameters of the plasma critical point. It follows from equation (2) that the critical parameters obey the similarity relations [9]:

$$T_c = 0.0425 z I \quad p_c = 0.405 z^2 I^4 \quad Z_c = 0.1(z + 1). \quad (3)$$

Here  $I$  is the ionization potential from the ground state,  $T_c$  is the critical temperature in electronvolts,  $p_c$  is the critical pressure in bars and  $Z_c$  is the critical compressibility factor. Equations (3) are normalized to the experimental parameters of caesium and rubidium [10]. The critical parameters of copper estimated for  $z = 2$  ( $T_c \simeq 7600$  K,  $p_c \simeq 6 \times 10^3$  bar and  $\rho_c \simeq 2$  g cm $^{-3}$ ) agree reasonably with existing experimental values [11]. This apparently confirms the results of our analysis of the valence state of copper near the critical point.

### 3. Percolation

As mentioned above, in metal atoms the quasi-classical valence electrons screen the ion core potential out of their classical accessible region. As two such regions overlap each other, they extend, comprising the second ion core. Therefore, when atoms form percolation clusters, the ions become virtually screened by the electrons of neighbouring atoms. As a result, the quasi-atomic electron states include some admixture of free motion corresponding to the continuous internal-energy spectrum

$$E = -I + p^2/2m. \quad (4)$$

Here,  $-I$  is the ground-state valence-electron level in a free atom and is the lowest limit of the internal energy,  $p$  is the momentum of asymptotically free motion above a virtual screened potential and  $m$  is the electron mass. The atoms in such mixed states are referred to as quasi-atoms.

All valence electrons are conductive as the density exceeds a percolation threshold, or else the activation energy arises. Thus, the percolation threshold is identified with the metal-non-metal transition point. It can be defined similar to the percolation problem of overlapping spheres as

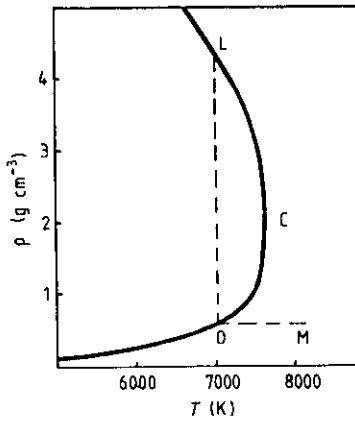
$$\frac{4}{3}\pi(e^2/I)^3 n_a = 0.29 \quad (5)$$

where  $e^2/I$  is the radius of the classical accessible sphere and  $n_a$  is the atom density. The number on the right-hand side of equation (5) corresponds to the metal-non-metal transition point for mercury. For a continuous energy spectrum, it follows from equations (4) and (5) that the metal-non-metal transition spreads out by thermal excitation with the relative width

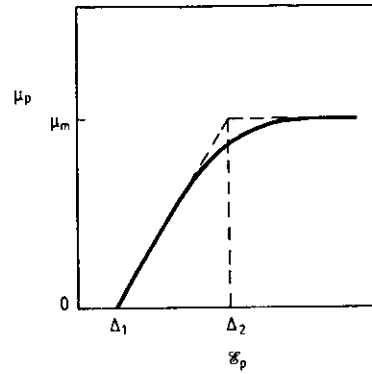
$$\Delta n_a/n_a \sim 3T/I. \quad (6)$$

Evidently, this gradual transition disappears at very high temperatures as a plasma state remains at any density.

In the displaced term, the radius of the classical accessible sphere increases because the ionization potential of the  $4s^2$  shell is lower than that of the  $4s$  shell in the ground-state configuration. Therefore, in accordance with equation (5), excitation of the displaced term decreases the metal–non-metal transition density to  $\rho_M \simeq 0.6 \text{ g cm}^{-3}$ , widening the metallic-state domain in the phase diagram. Thus, copper remains a metal when it expands 15 times below the normal density of  $9 \text{ g cm}^{-3}$  (figure 1). Near the critical point, both liquid and gas phases are in a metallic state.



**Figure 1.** The phase diagram of copper: C is the critical point, OM is the metal–non-metal transition line and OL is the boundary between one and two metallic phases. The two-phase region is depicted similarly to those for caesium and rubidium [10].



**Figure 2.** The percolation mobility as a function of the energy of free motion:  $\Delta_1$  is the percolation level,  $\Delta_2$  is the free-motion level and  $\mu_m$  is the minimal gas-kinetic mobility.

#### 4. The electric conductivity

Near the percolation threshold, the valence electrons are in nearly localized atomic-like states, diffusing through random walks between neighbouring atoms. The diffusion coefficient is then

$$D = R^2/3\tau' = \frac{1}{3}v_T R\tau/\tau' \quad (7)$$

where  $R$  is the mean interatomic distance,  $\tau'$  is the time of transfer,  $\tau$  is the time of flight,  $\tau = R/v_T$  where  $v_T$  is the mean thermal velocity,  $v_T = (8T/\pi m)^{1/2}$ ,  $T$  is the temperature, and  $m$  is the electron mass. Thus, the diffusion coefficient is expressed through the gas-kinetic coefficient with the minimal free path  $l = R$  and the factor  $\vartheta = \tau/\tau'$  which characterizes partial localization of electrons. Owing to the Einstein relation, the average mobility is expressed through the minimal gas-kinetic mobility  $\mu_m = e\tau/m$  and the same localization factor:

$$\mu = \mu_m \vartheta. \quad (8)$$

Hence, the localization factor is directly related to the average mobility.

The one-electron theory relates the percolation mobility to the classically accessible volume:

$$\zeta(E) = \frac{4}{3}\pi(e^2/|E|)^3 n_a \quad (9)$$

where the energy spectrum is defined by equation (4). The percolation mobility occurs when  $\zeta(E)$  is above the percolation threshold of the sphere problem and reaches a gas-kinetic value when  $\zeta(E)$  is of the order of the close-packing fraction, i.e. most of the volume is accessible. Hence, the excitation energy  $\Delta_1$  corresponding to the percolation threshold and the excitation energy  $\Delta_2$  corresponding to nearly free motion are expressed by

$$\Delta_i = I - e^2(4\pi n_a/3\zeta_i)^{1/3} \quad (i = 1, 2) \quad (10)$$

where  $\zeta_1 = 0.29$  and  $\zeta_2 = 0.74$ . In the range from  $\Delta_1$  to  $\Delta_2$  a linear approximation of percolation mobility is found (figure 2).

Near the metal-non-metal transition point, the Boltzmann distribution of the quasi-atomic excitations is shown to apply [7]:

$$n(E) \propto (E + I)^{1/2} \exp[-(E + I)/T]. \quad (11)$$

Then the averaged percolation mobility yields the following localization factor:

$$\vartheta = (\frac{3}{2}T - \Delta_1 - TF_2)/(\Delta_2 - \Delta_1) \simeq (\frac{3}{2}T - \Delta_1)/(\Delta_2 - \Delta_1) \quad (\Delta_1 \leq 0, \Delta_2 \gg T) \quad (12)$$

on the metallic side of the transition, and

$$\begin{aligned} \vartheta &= T(F_1 - F_2)/(\Delta_2 - \Delta_1) \\ &\simeq [2(\Delta_1 T)^{1/2}/\pi^{1/2}(\Delta_2 - \Delta_1)] \exp(-\Delta_1/T) \quad (\Delta_2 > \Delta_1 \gg T) \end{aligned} \quad (13)$$

on the other side. Here the functions  $F_i$  are the combination of the non-full gamma functions  $\Gamma(m, x)$ :

$$\begin{aligned} F_i &= (2/\pi^{1/2})[\Gamma(\frac{5}{2}, \Delta_i/T) - (\Delta_i/T)\Gamma(\frac{3}{2}, \Delta_i/T)] \\ &\simeq (2/\pi^{1/2})(\Delta_i/T)^{1/2} \exp(-\Delta_i/T) \quad (\Delta_i \gg T). \end{aligned}$$

The conductivity is given by the modified Drude formula

$$\sigma = e^2 n_e \tau \vartheta / m \quad (14)$$

where  $n_e = z n_i$  is the density of valence electrons. First of all, excitations of the displaced term influence the conductivity because they double the free-electron density. Also, according to equation (10), the parameters  $\Delta_i$  decrease by the excitation energy of the  $^2D$  term. Therefore, the localization factor and conductivity increase. In figure 3 the calculated conductivity of copper is shown as a function of the density near the metal-non-metal transition point at the critical isotherm. Note that, in the wide range of densities from the normal melting value to the transition point, the conductivity changes slowly, but it rapidly decreases below this point. There are still no data to compare the calculated conductivity with experiment. In the range of applicability in the vicinity of the transition point it may deviate by a factor of 2-3, as for mercury or alkali metals.

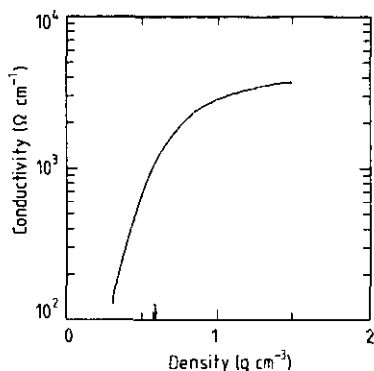


Figure 3. The electric conductivity of copper at 7600 K as a function of the density. The metal-non-metal transition is shown by an arrow.

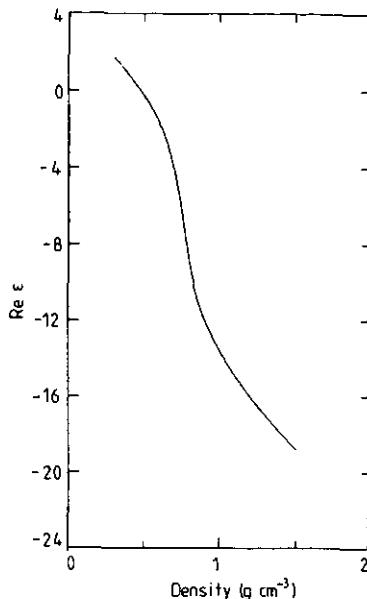


Figure 4. The real part of the low-frequency dielectric function of copper at 7600 K as a function of the density.

## 5. The dielectric function

The response of the quasi-atomic gas to the electromagnetic field includes polarization of the valence electrons in nearly localized states equally with drift. Accordingly, the real part of the dielectric function has both dielectric and conduction parts. For low frequencies,  $\omega\tau < 1$  and  $\hbar\omega < T$ ; thus

$$\text{Re } \epsilon = 1 + 4\pi\chi(1 - \vartheta) - 4\pi\tau\sigma \quad (15)$$

where  $\chi$  is the dielectric susceptibility. Equation (15) contains the initial terms of the  $\text{Re } \epsilon$  power expansion in the localization factor  $\vartheta$  [12]. The dielectric term gives the main contribution when localization is strong ( $\vartheta \rightarrow 0$ ), but it disappears if localization is weak ( $\vartheta \rightarrow 1$ ). In the weak-localization case, equations (14) and (15) turn into the usual Drude expressions for free electrons. In the intermediate-localization case,  $\text{Re } \epsilon$  changes sign.

Generally, the dielectric susceptibility is given by the Clausius-Mossotti formula

$$\chi = n_a\alpha/(1 - \kappa) \quad \kappa = \frac{4}{3}\pi n_a\alpha \quad (16)$$

where  $\alpha$  is the polarizability. As is known, the pole at  $\kappa = 1$  corresponds to spontaneous polarization which is possible in the solids but not in a gas. Indeed, without an external field, induced dipoles obey the equations

$$d_i = \sum_k a_{ik}(r_{ik})d_k \quad (17)$$

where  $d_i$  are the components of the dipoles and  $a_{ik}(r_{ik})$  are coefficients dependent on the interatomic distances. In general, a determinant  $|a_{ik}(r_{ik}) - \delta_{ik}| \neq 0$ ; so the only solution of equations (17) is  $d_i = 0$ , i.e. there is no spontaneous polarization. Thus, for disordered systems, the Clausius-Mossotti formula needs regularization by the expansion

$$(1 - \kappa)^{-1} = 1 + \kappa + \kappa^2 + \dots \quad \kappa \leq 1. \quad (18)$$

As a compromise we use just a few terms in equation (18) so that the addition of one more does not strongly change the sum of the asymptotic expansion.

Polarization of the quasi-classical  $s$  electrons in the external field is related to the shift of the classical accessible sphere together with the electron charge located mainly near its surface. The shift can be found from the following equation:

$$-e^2/r - e\mathcal{E}r \cos \vartheta_a = -I \quad (19)$$

where  $\mathcal{E}$  is the electric field, and  $r$  and  $\vartheta_a$  are the polar coordinates. The polarizability is then

$$\alpha = ze\delta x/\mathcal{E} = z(e^2/I)^3 \quad (20)$$

where  $\delta x = \delta r/\cos \vartheta_a$  is the shift opposite to the electric field. Both the valence and the radius of the classical accessible sphere increase for the displaced term; so the polarizability increases fourfold, up to  $165a_B^3$  where  $a_B$  is the Bohr radius.

An additional contribution gives the polarization of overlapping atoms with transfer of electron charge between atoms, or polarization of bonds or quasi-molecules. This means virtual excitation of the ion term  $U(R) \simeq I - e^2/R \simeq I/2$  where  $R$  is the interatomic distance. For weak polarization the excitation energy equals  $I\delta^2/2$  where the degree  $\delta$  of polarization is zero in a free quasi-molecule, and unity at full polarization. Minimization of the energy in the electric field with the equation

$$(d/d\delta)[I\delta^2/2 - \delta e\mathcal{E}(2e^2/I) \cos \vartheta_m] = 0 \quad (21)$$

gives for the polarizability of bonds

$$\alpha_b = 4(e^2/I)^3 \langle \cos^2 \vartheta_m \rangle = \frac{4}{3}(e^2/I)^3 \quad (22)$$

where  $\vartheta_m$  is the angle of the quasi-molecular axis to the electric field. The total polarizability becomes

$$\alpha = (z + \frac{4}{3}c)(e^2/I)^3 \quad (23)$$

where  $c$  is the mean number of quasi-molecules per atom. If we neglect the interatomic correlation, the latter is

$$c = \frac{2}{3}\pi(2e^2/I)^3 n_a. \quad (24)$$

As can be seen from equations (23) and (24), for the displaced term the total polarizability also increases fourfold. Thus, excitation of the displaced term changes both the drift and the polarization characteristics of the quasi-atomic gas. Figure 4 depicts the real part of the low-frequency dielectric function of copper against the density near the metal-non-metal transition point at the critical isotherm. It is worth noting that the zero of  $\text{Re } \epsilon$  does not necessarily coincide with the transition point because its definition for the continuous transition is somewhat conditional.



## 6. Conclusion

Thus, the excitation of d electrons into the valence shell changes all the electronic properties. The reason is the low-lying displaced term which lowers more than the ground-state term as a result of the interaction between atoms. Such displaced terms are equal for those elements in which the regularity of d-shell occupation is violated and the ground-state configuration  $d^{n+1}s$  appears instead of  $d^n s^2$ . Besides copper, low-lying displaced terms exist, e.g. in gold, chromium, niobium and molybdenum which are thus objects of the present analysis, too.

In the general case, when a displaced atomic term is high lying, its contribution to the electric characteristics is proportional to the Boltzmann population, which increases because of lowering of the energy level. Excitation of the displaced term is then analogous to thermal ionization.

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