# Charge Density Wave In Low Dimensional Bronzes: A Conceptual Review

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***Abstract:***
*Low-dimensional layered systems exhibit remarkable physical phenomena known as charge density waves (CDWs). Understanding CDW is essential for comprehending strongly correlated electronic behaviors, lattice change, and other associated physical features. Our study provides an overview of recent research on CDW that is becoming apparent in low-dimensional systems. The key issues for this collective transport phenomenon are discussed in this review. First, a brief overview of CDW's primary mechanisms is provided. Second, it describes the CDW phenomenon in molybdenum bronzes. Finally, some examples of possible applications for devices made from CDW materials are shown.*
***Keywords:*** *Charge density wave, Fermi surface, Nesting*

## I. Introduction

The most extensively researched subjects in contemporary condensed matter physics are quantum events [1-6] originating from electron-electron interaction or electron coupling to other degrees of freedom in the solid. As one shifts from the three-dimensional electrical structure and concentrates on the low-dimensional environment, one comes across various material qualities. [7] There are significant ramifications when going from three dimensions to two or one. In a smaller dimension, electron correlations, electron-phonon interactions, and fluctuations have a more pronounced impact. Electronic instabilities are frequently seen in low-dimensional materials with anisotropic electronic structures. In the quasi-low-dimensional systems, where the aforementioned quantum events play a significant role, several intriguing occurrences are observed to occur. It is observed that the traditional metallic behaviour may deviate if the conduction electrons are restricted to one spatial dimension, creating a novel Brillouin zone. Numerous mechanisms contribute to this. The Peierls instability [8], however, is the most well-known one. In this instability, nesting of the 1D Fermi surface in conjunction with electron-phonon coupling results in the spontaneous generation of a charge-density wave (CDW), which is frequently accompanied by a transition into an insulating phase. To put it another way, a charge density wave (CDW) is defined as a periodic distortion of the charge-carrier density accompanied by a periodic distortion of the lattice. The CDWs that arise in bronze systems with highly anisotropic crystal structures and are produced from nesting of the band structure close to the Fermi surface (FS) will be discussed in this review paper.

## II. Peierls Instability

A straightforward illustration of a one-dimensional metallic system may be used to demonstrate Peierls instability. According to Fig. 1(a), the ions are evenly spaced apart, and the electronic density is also homogeneous. Let's assume that in the system's steady state, the Fermi wave vector ($k_F$) is located at half of the Brillouin zone (BZ) and the system has a free parabolic band [Fig. 1(b)]. The periodic lattice distortion (PLD), which causes a periodic modulation of the electron density as seen in Fig. 1(c), occurs when temperature is dropped below the CDW transition temperature $T_{CDW}$. Figure 1(d) displays the band image brought about by CDW formation. Connecting the Fermi level crossings at $+ k_F$ and $- k_F$ is the CDW wave vector q (q = $k_F$). "Nesting" describes this technique, where the distortion vector q connects the $k_F$ points by extending over the Fermi surface (FS). The system now has a new periodicity as a result of the nesting of the Fermi surface with q.
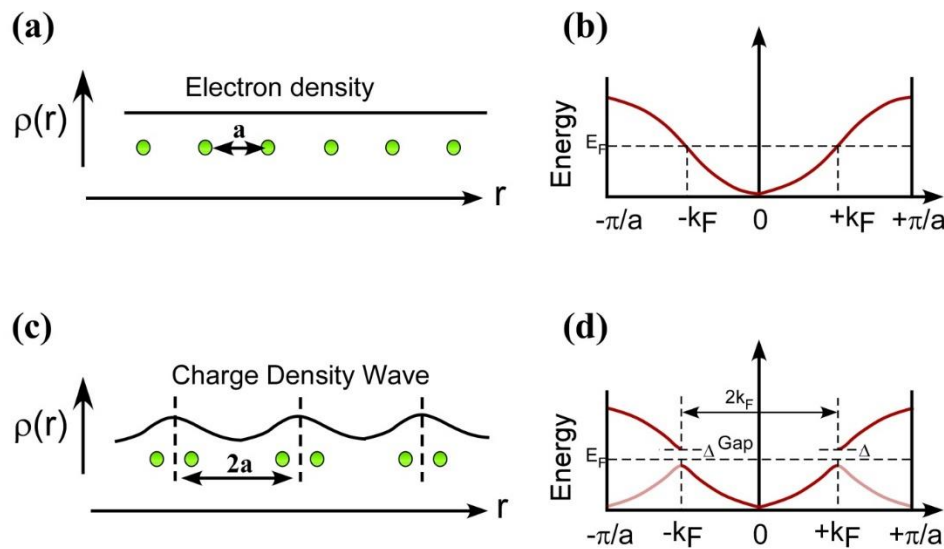
**Fig. 1(a) One-dimensional metallic chain where the ions are equally spaced and the electronic density is uniform (b) Band picture of the normal state where the Fermi wave vector crosses the band at $\pm k_F$ points. (c) Modulation of the electronic charge density after the system temperature is lowered below the CDW transition temperature. (d) Single particle band evolution of the CDW state where the band back folding occurs at the $\pm k_F$ points**

Since we have only studied a band that is half full, nesting cuts the BZ in half, which in actual space equates to a time of doubling. A metal-insulator transition results from energy gaps being opened at the Fermi vectors as a result of the CDW-induced back folding. As already mentioned, that for a crystal with a half-filled band, the CDW state corresponds to a periodic structure with a lattice constant that is twice as large as the periodicity of the basic structure. However, in general, the filling of the conduction band is not associated with the lattice periodicity of the crystal. The CDW state of the crystal is therefore characterized by an incommensurately modulated structure, and $k_F$ can be any proportion of the reciprocal lattice's basis vector. These incommensurate CDWs are particularly intriguing because they exhibit physical characteristics that are distinct from those of typical crystals. The system's overall energy is decreased and two energies are in competition during the CDW phase. One energy corresponds to the cost of elastic energy for making the PLD. The other one is given by the gap opening and is associated to the lowering of the energy of the occupied states right at $k_F$.

The main feature in the CDW phenomenon is the Lindhard electric susceptibility $\chi(q)$ which provides the response function of the electron system behaving under the influence of an external potential $\phi(\vec{q})$. The following discussion of the CDWs closely follows the treatment given by G. Gruner in "Density Waves in Solids". [9]

The response of an electron gas to an externally applied potential is given by

$$\rho^{ind}(\vec{q}) = \chi(\vec{q})\phi(\vec{q}) \tag{1.1}$$

where the potential $\phi$ and the induced charge $\rho^{ind}(\vec{q})$ are considered in terms of their fourier components and are related through the Lindhard response function. The Lindhard response function, or susceptibility, $\chi(\vec{q})$ is given in $n$ dimensions by

$$\chi(q) = \int \frac{d\vec{k}}{2\pi^n} \frac{f_k - f_{k+q}}{\epsilon_k - \epsilon_{k+q}} \tag{1.2}$$

where $f_k = f(\epsilon_k)$ is the Fermi function or the occupation function at the wave vector $k$ and $\epsilon_k$ is the band energy. From this expression it is very clear that contributions come only from the Fermi level and it is very sensitive to the topology of the band structure near the Fermi surface. The states $k$ and $k + q$ that contribute most to the integral are those for which the denominator of the integrand is small (states close in energy) and the numerator is close to one *i.e* a pair consisting of an occupied and unoccupied state near the Fermi surface.
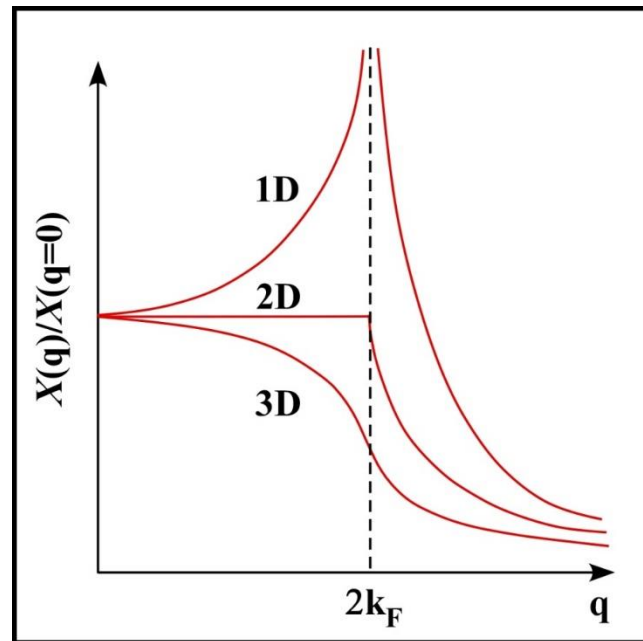
**Fig. 2 Electronic susceptibility as a function of wave vector q. In 1D the susceptibility assumes a singularity at $2k_F$ and thus lead to CDW instability [9]**

A 1D electron gas with such a singularity at $2k_F$ will thus be unstable against creation of a CDW state since a singularity in $\chi(\vec{q})$ corresponds to the requirement of Fermi-surface nesting for the Peierls instability. There is a drastic dependence on dimensionality, as illustrated in Fig. 2, where in 1D $\chi(\vec{q})$ becomes singular at $q = 2k_F$. The main driving force underlying Peierl's instability is this singularity of (q). Thus, redistribution of charge creates a gap at the Fermi surface as a result of CDW production, which ultimately results in a metal-insulator transition. This results in a gain in one-electron energy as occupied states near the Fermi surface are lowered in energy. The charge redistribution pulls the lattice away from its neutral positions. This lattice modulation costs energy, balancing the gain in one-electron energy. In 1D CDW system, a single wave vector is able to nest all portions of the Fermi surface. However, this is no longer the true for higher dimensions. It can be seen that for the 2D case the Fermi surfaces is a circle and for 3D case it is a sphere. The corresponding susceptibility curves, shown in Fig. 2, do not show a divergence at $q = 2k_F$. It totally depends on the FS topology whether the system matches the CDW instability.
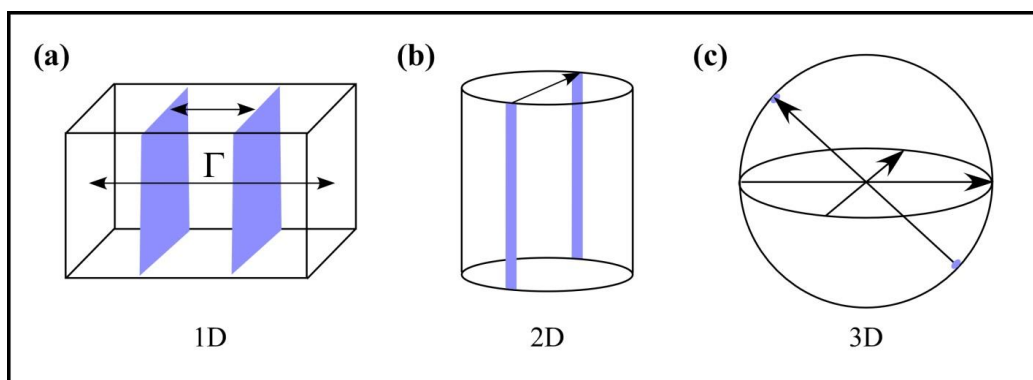


**Fig. 3. Role of dimensionality for Fermi surface nesting in a free electron gas for (a) one dimension (b) two dimension and (c) three dimension. A Fermi surface in 1D provides the largest number of states for nesting.**

Figure 3 illustrates the FS nesting for a free-electron band in 1D, 2D and 3D. It is evident that the nesting condition strongly depends on the dimensionality. In the ideal 1D system this requirement is matched by the parallel planes of the FS as shown in Fig. 3 (a). They are perfectly nested because the wave vector $2k_F$ matches them identically onto each other. The gap develops in the same way as in 2D [see Fig 3(b)] and 3D [see Fig 3(c)] systems if they fulfill the nesting conditions.

### III. Molybdenum Bronzes

Molybdenum bronzes are the materials which have been discovered almost three decades back.[10] These bronzes have been investigated extensively because of their unusual physical properties which include quasi low dimensional behavior, charge density wave driven metal insulator transition. [11,12] The general formula for the molybdenum bronzes is $A_xMo_yO_z$. Generally, they all have the layered structure. The molybdenum bronzes are available in three different stoichiometric compositions and structure, *Blue bronzes*, *Red bronzes* and *Purple bronzes*. These materials exhibit different electronic properties. The *blue bronzes* are quasi-one-dimensional (quasi-1D) metals, the *red bronzes* are semiconductors, and the *purple bronzes* are quasi-two-dimensional metals, except for the Li *purple bronze*, which is a quasi-1D metal.

*Blue bronzes* are layered type materials which have the general formula $A_{0.3}MoO_3$ where, *A* is the alkali metal (*A*= K, Rb, Tl). [13,14] Transport measurement studies carried out on potassium blue bronze showed that the system is metallic [15] and undergoes a metal-semiconductor transition at $T_p$ = 180 K. [16] Further studies showed that the electrical conductivity in the plane of the layers is quite anisotropic.[17] It is predicted on the basis of optical reflectivity data that the potassium *blue bronze* is a quasi-1D metal above $T_p$ and the metal-semiconductor transition is of a Peierls type.[18] Formation of the CDW in the *blue bronze* was found from *x*-ray diffuse-scattering study.[19] Thereafter, other studies *like x*-ray [20], neutron [21] and electron diffractions [22] also confirmed this finding. Similar results have been found for the rubidium and thallium *blue bronzes*. The *blue bronzes* show quasi-one dimensional electronic properties due to the infinite chains of $MoO_6$ octahedra along the monoclinic *b*-axis as shown in Fig. 4. It is the first quasi one-dimensional oxide which shows non-linear transport due to sliding of the CDW.[23]
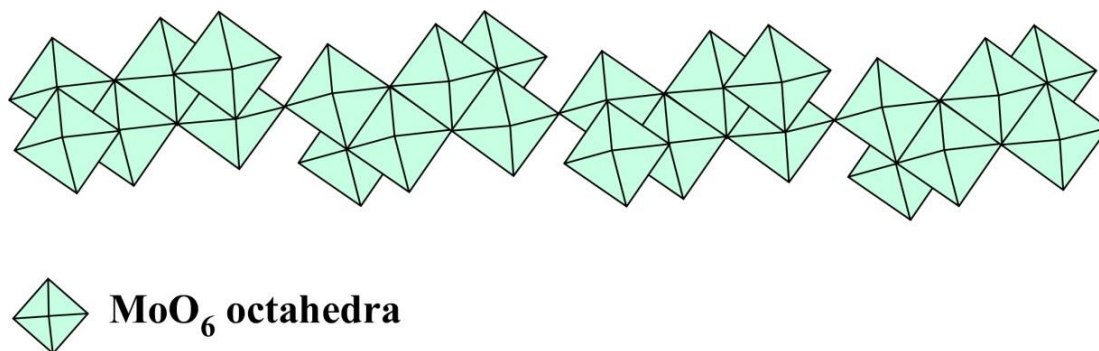


**Fig. 4. Schematic diagram of the infinite chains of MoO₆ octahedra along the monoclinic *b*-axis.**

The general formula for the *red bronzes* is $A_{0.33}MoO_3$ (A=Li, Na, K, Rb, Cs, Tl), which are semiconducting. On the other hand, *purple bronzes* have the general formula $A_{0.9}Mo_6O_{17}$ (A=Li, Na) and $AMo_6O_{17}$ (A=K, Tl) which are generally quasi two-dimensional metals. The layered crystal structure of this family lead to quasi-low-dimensional electronic properties, either one dimensional or two dimensional, depending on the molybdenum-oxygen polyhedra arrangement. The corresponding Fermi surfaces show the so-called nesting properties, which favor the onset of the Peierls transition.

### IV. Lanthanum Molybdenum Bronzes

One of these intriguing compounds, which fall under the category of quasi-low dimensional systems, is rare earth molybdenum bronze $La_2Mo_2O_7$. $La_2Mo_2O_7$ transport investigations, such as resistivity and magnetic susceptibility, reveal a metal to insulator type phase transition (MIT) at a temperature of about 125 K. [24] The orthorhombic crystal structure of $La_2Mo_2O_7$ comprises a layer of $MoO_6$ octadedra on its ac plane, which forms $Mo_2O_{10}$ clusters when two $MoO_6$ units share an edge. Corner sharing occurs in the crystallographic a and c directions for the $Mo_2O_{10}$ clusters. $La^{3+}$ cations are sandwiched between the $Mo_2O_7$-layers in the ab-plane of $La_2Mo_2O_7$, which illustrates the material's apparent quasi-two-dimensional crystal structure. Fig. 5's rectangular box symbolises a single unit cell made up of two layers of $Mo_2O_7$.
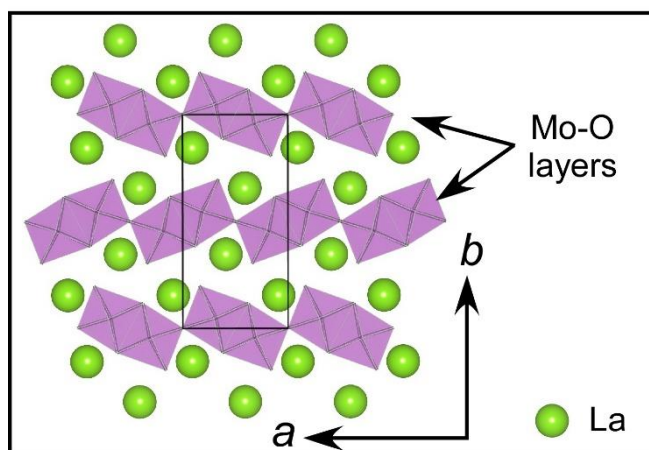
**Fig.5. (Color online) Corner sharing of the Mo₂O₁₀ units in the La₂Mo₂O₇ structure as seen in the crystallographic ac plane. A diagram of the Mo-O layers in the ab plane showing the sandwich of lanthanum cations. A rectangular box serves as the index for a single unit cell.**

The molybdenum oxide bronzes, blue [$A_{0.3}MoO_3$ (A = K, Rb, Tl)] and purple [$A_{0.9}Mo_6O_{17}$ (A = Li, Na)], which are quasi-one-dimensional systems and go through a CDW-driven phase transition at low temperatures, are analogous to $La_2Mo_2O_7$ in many ways, including their structural and transport properties. [25,26,27] Whangbo and Canadell used Extended Huckel tight-binding (EHTB) approach, to explore the electronic structure of $La_2Mo_2O_7$. In order to investigate the nature of the phase transition in $La_2Mo_2O_7$, S. Paul et.al also used a tight-binding Extended Huckel method computation of the electronic band structure and compared the $La_2Mo_2O_7$ electronic structure derived from their first principle and tight-binding simulations. [28,29] In contrast to the EHTB band calculation, the FP-LAPW band calculations show band bilayer splitting along the high symmetry Z-G-X direction. Its low dimensional character is shown by the predicted electronic band structure's lack of dispersion along the *b*-direction. Partial nesting is feasible, according to the study's analysis [29] of the Femi Surface. They predicted that the CDW condition associated with these nesting vectors is the reason for the observed irregularity in the $La_2Mo_2O_7$ transport characteristics.

## V.    Conclusion

The CDW instability in a low dimensional system is the main topic of this review. The Peierls transition induced by the $2k_F$ divergence of the electron-hole response function is the context that is mostly covered. Over the years, this topic has grown significantly, and much has been learnt about the computational work around CDWs in 2D materials, as well as some significant investigations that supported those computational approaches. The ability of materials like $La_2Mo_2O_7$ to acquire unique electrical and functional characteristics makes it important to understand and manage CDW events in these materials. They might be applied to the manufacture of electrical devices, energy conversion, and information storage. $La_2Mo_2O_7$ and similar materials' CDW behaviour is still being studied in terms of its underlying processes and prospective uses.

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