I - INTRODUCTION

The transition metal oxide bronzes belong to the large family of transition metal oxides which often show unusual electronic properties such as metal-non metal transitions or charge density wave (CDW) instabilities.

The oxide bronzes are compounds with the general formula $A_xT_{O_m}$ where $A$ is a monovalent metal, often an Alkali metal and $T$ a transition metal. In the oxide $T_{O_m}$, the d states are usually empty and the $A$ metal donates its outer electron to the conduction band which becomes partially filled in the bronze. The physical properties thus depend strongly on the extension of the d wave function. While the 5d tungsten bronzes are metallic at all temperatures, the 3d vanadium bronzes such as $Na_xV_2O_5$, rather show a semiconducting behavior. The molybdenum bronzes are intermediate as far as the 4d electron localization and the width of the conduction band are concerned. The so-called red bronzes $A_{0.33}MoO_3$ are semiconductors, the blue bronzes of formula $A_{0.30}MoO_3$ show a metal to semiconductor transition and the purple bronzes $A_{0.9}Mo_6O_{17}$ are metallic at all temperatures. In this case, one should note that the partial filling of the conduction band results both from the charge transfer from the alkali metal and from the lack of oxygen, as compared to the oxide $MoO_3$. From this point of view, the molybdenum oxides $Mo_4O_{11}$ are similar to the purple bronzes. In the two compounds, the monoclinic $\eta$ and the orthorhombic $\gamma$ phases, only the lack of oxygen accounts for the metallic conductivity. All these materials, bronzes and oxides, are well-defined compounds in which the alkali or oxygen concentration cannot be changed in a continuous way.

An important property common to these bronzes and oxides is their anisotropic, layer-type crystal structure. This leads to anisotropic electrical properties: the purple bronzes and $Mo_4O_{11}$ oxides are quasi two-dimensional metals, while the blue bronzes, because of the existence of infinite chains of $MoO_6$ octahedra in the structure, are quasi one dimensional metals. In all cases, the Fermi surface is expected to be anisotropic and to provide the possibility of "nesting", giving rise to CDW instabilities.

In a quasi one-dimensional (1 D) metal, the Fermi surface may be described in a first approximation by two parallel planes, distant of $Q$=2$k_F$, $k_F$ being the Fermi wave vector. In a quasi two-dimensional metal the Fermi surface is quasi-cylindrical with respect to an axis perpendicular to the two-dimensional plane and will often show nesting with a wave vector $Q$ parallel to this plane. Such materials are unstable towards a lattice distortion of the wave vector $Q$, which leads to a new Brillouin zone and opens a gap at the Fermi surface. This decreases
the electronic energy of the system. The competition between the increase of elastic energy associated to the lattice distortion and the corresponding decrease of electronic energy may favour the distorted state. This so-called Peierls transition can be described in the mean field theory. The transition (or Peierls) temperature is then expected to be simply related to the zero temperature gap. In a quasi one-dimensional metal, the gap opening at the Fermi surface is normally complete and the Peierls transition is a metal to semiconductor transition. In a quasi two-dimensional metal, the Peierls transition is associated with partial gap openings only and is therefore a metal-metal transition.

In the Peierls distorted state, the lattice distortion is accompanied by a modulation of the electronic density, with a periodicity $2\pi/Q$. This is the charge density wave. This new periodicity, determined only by the degree of filling of the conduction band may be incommensurate with the initial lattice periodicity. The CDW may then be either commensurate or incommensurate and the physical properties are expected to be sensitive to this property.

In spite of some characteristics common to all the compounds mentioned above, this course will concern only the quasi one-dimensional systems, the blue bronzes. Details concerning the quasi two-dimensional systems can be found in ref. 2 and a review in ref. 3.

The potassium blue bronze has been synthesized for the first time in 1964 by Wold et al. by the electrocrystallization technique. The crystal structure was refined by Graham and Wadsley in 1966. Physical studies by Bouchard et al. established that the blue bronze shows a semiconductor-to-metal transition in the vicinity of 180 K. Later, Perloff et al. noticed a large anisotropy of the electrical conductivity in the plane of the layers. Detailed studies of the transport properties were then performed by Fogle and Perlstein. They especially measured the low-temperature behavior of the conductivity and reported a non-ohmic behavior at $T < 20$ K, when the sample is insulating ($\sigma \approx 10^{-14} \Omega^{-1} \text{ cm}^{-1}$). They proposed a model of an excitonic insulator for the semiconducting state.

It is only recently that the anisotropy of the conductivity was rediscovered and studied in greater details by Brusetti et al. Optical reflectivity measurements showed indeed that $K_{0.30}\text{MoO}_3$ is a quasi-one-dimensional (quasi-1 D) metal in the high-temperature phase. Later, X-ray diffuse scattering studies by Pouget et al. led to the conclusion that the metal-to-semiconductor transition is a Peierls transition towards an incommensurate charge density wave (CDW) state. At the same time, in a search for non-ohmic conductivity in the temperature range where the conductivity is not vanishingly small ($T > 50$ K), Dumas et al. established that the blue bronze shows nonlinear transport, due to the sliding of the CDW.

The possible sliding of incommensurate CDW had been predicted long ago by Fröhlich and is known as the Fröhlich mechanism. Nonlinear conductivity attributed to this mechanism was first reported for niobium triselenide in 1976 by Monceau et al. Since then, a considerable amount of work has been devoted to this property and to the related phenomena first in $\text{NbSe}_3$ and $\text{TaS}_3$, then in the blue bronzes and in some transition metal tetrachalcogenides. Reviews on inorganic quasi-one-dimensional compounds have lately been published.

Since the discovery of nonlinear transport, the blue bronzes have been the object of extensive studies. Their physical properties have been surveyed in a recent article. The present course will try to include part of these properties. Other properties related to the dynamics of the CDW are described in ref. 20. The nuclear magnetic resonance results and the optical properties are reviewed in ref. 21 and 22 respectively, and neutron inelastic scattering data in ref. 23.

II - CRYSTAL STRUCTURE

Three compounds which show the same crystal structure and similar properties have now been synthesized and studied: two alkali metal bronzes $K_{0.30}\text{MoO}_3$ and $Rb_{0.30}\text{MoO}_3$ and the thallium compound $Tl_{0.30}\text{MoO}_3$. The crystal structure is monoclinic, space group $C2/m$. 

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