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Structural study of the charge-density-wave phase transition of the blue bronze : $K_{0.3}MoO_3$

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Résumé. — Nous présentons une étude par diffusion des rayons X de la transition de Peierls du bronze bleu $K_{0.3}MoO_3$ incluant la variation thermique de l’intensité des réflexions satellites du 1er et 2e ordre en dessous de $T_c$, une complète caractérisation des fluctuations structurales (dépendance en température et anisotropie) au-dessus de $T_c$ et une mesure précise du vecteur d’onde des ondes de densité de charge au-dessous et en-dessous de $T_c$. L’analyse de la transition de phase dans le cadre d’une théorie de champ moyen est justifiée. Elle conduit à des valeurs raisonnables du couplage électron-phonon et de l’interaction de Coulomb entre ondes de densité de charge. La valeur du vecteur d’onde de la distorsion résulte de la présence de 2 bandes de conduction quasi unidimensionnelles coupant le niveau de Fermi $E_F$, et d’une 3e bande située vers 650 K au-dessus de $E_F$. L’ouverture d’une bande d’énergie interdite au niveau de Fermi se produit à la transition de Peierls par recouvrement d’une bande de conduction sur l’autre. Il en résulte un état semiconducteur au-dessous de $T_c$. Finalement, nos mesures ne montrent pas clairement l’existence d’une transition de phase, commensurable-incommensurable en fonction de la température.

Abstract. — We present an X-ray study of the Peierls transition of the blue bronze $K_{0.3}MoO_3$, including the temperature dependence of the intensity of the first order and second order satellite reflections below $T_c$, a complete characterization of the structural fluctuations above $T_c$, a complete characterization of the structural fluctuations above $T_c$, and an accurate determination of the wave vector of the charge density wave above and below $T_c$. An analysis of the phase transition within a mean field theory is justified and yields reasonable values of the electron phonon coupling and of the Coulomb interaction between charge density waves. The value of the modulation wave vector is explained as resulting from the presence of two conducting quasi one dimensional bands crossing the Fermi level $E_F$ and of a third one located about 650 K above $E_F$. The opening of an absolute gap at the Fermi level occurs at the Peierls transition due to the folding of one conduction band on the other, and leads to a semiconducting state below $T_c$. Finally our measurements do not reveal any clear commensurate-incommensurate phase transition in temperature.

1. Introduction.

The so-called blue bronzes are ternary molybdenum oxides of formula $A_{0.3}MoO_3$ where the alkaline metal A can be K or Rb [1]. In these compounds the alkaline metal usually donates its outer electron to the transition metal which thus fills partially the d states which would be otherwise empty in the oxide $MoO_3$. $K_{0.3}MoO_3$ belongs to the monoclinic space group $C2/m$ with twenty formulae per unit cell [2]. The crystallographic structure is built with infinite sheets of $MoO_6$ octahedra separated by the K ions. If the stoichiometry corresponds exactly to the formula $K_{0.3}MoO_3$ all the available alkaline sites are occupied. The $MoO_6$ layers consist of clusters of octahedra linked by corners in the [010] and [102] directions; the cluster itself contains 10 $MoO_6$ octahedra sharing edges. The cluster packing is steplike along the [102] direction and in column along the [010] direction. In spite of its layered-type structure, $K_{0.3}MoO_3$ exhibits a very anisotropic electrical conductivity [3], of maximum value in the monoclinic $b$ direction made of infinite chains of $MoO_6$ octahedra. Actually, recent optical measurements have shown that, at room temperature, $K_{0.3}MoO_3$ can be considered as a quasi-one-dimensional (1D) metal [4].

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Physical studies established that the blue bronze shows a semiconductor to metal transition in the vicinity of 180 K \( (T_c) \) [3-5]. More precisely an X-ray diffuse scattering study [6] proved unambiguously that this transition is a Peierls transition towards an incommensurate charge-density-wave (CDW) state, with the formation below \( T_c \) of well defined satellite reflections at the reduced wave vector \( q_c = (0, q_b, 0.5) \), where the in-chain component is incommensurate and temperature dependent. Above \( T_c \), the structural phase transition is announced by anisotropic X-ray diffuse scattering [6] which corresponds to a Kohn anomaly in the phonon spectrum [7-9]. Simultaneously, non-linear conductivity, presumably due to a sliding of the incommensurate CDW [10], was evidenced, stimulating an important work on non-linear transport in these compounds [11].

Following the earlier X-ray finding of a CDW driven Peierls transition in \( K_{0.3}MoO_3 \) by a photographic method [6], we shall present here a quantitative study of this structural phase transition by a counting method. The purpose of this paper is multi-fold:

- to characterize the structural fluctuations above \( T_c \) and their temperature evolution;
- to measure accurately the temperature dependence of the wave vector of the modulation and investigate a possible commensurate-incommensurate transformation [14];
- to provide a simple description of the Peierls transition and of the temperature dependence of the incommensurate modulation.

2. Experimental procedures.

The single crystal used in this experiment was grown according to reference [12]. It is a platelet of \( 3 \times 1.5 \times 0.2 \text{ mm}^3 \) parallel to the (201) cleavage plane with the \( b \) axis being along the long direction.

The experiment was performed using an X-ray diffractometer equipped with a closed-cycle helium refrigerator providing a controlled temperature between 10 K and 300 K. We used the normal beam geometry with a lifting scintillator detector. The crystal was mounted with the \( b^* \) and \( 2 a^* - c^* \) directions in the horizontal scattering plane. The CuK\(_α\) radiation was obtained by reflection on a monochromator of the X-ray beam produced by a conventional 1.5 kW generator. Two monochromators were successively used:

- a doubly bent graphite monochromator ([002] reflection), giving a longitudinal \( q \) resolution with a half width at half maximum (HWHM) of 0.015 \( \text{Å}^{-1} \), for the measurements of the integrated intensity of \( q \) and \( 2q \) satellites and of the diffuse scattering above \( T_c \);
- a flat LiF monochromator ([002] reflection) giving an improved resolution of 0.003 \( \text{Å}^{-1} \) (HWHM) for an accurate determination of the \( q \) wave vector.

Before the X-ray study, the crystal had been used for non-linear transport measurements. At 77 K, it presented a well defined threshold field with a switching from the Ohmic to the non Ohmic regime, announced below this field by precursor voltage pulses when the dc current was varied [13].

3. Results and analysis of the data.

3.1 \( T < T_c \). — Below \( T_c \) we have selected for the measurements four strong first order satellite reflections, namely the \((17, - 1 + q_b, 8.5), (17, 1 - q_b, 8.5), (17, - 1 - q_b, 8.5) \) and \((17, 1 + q_b, 8.5) \) as well as a weak second-order satellite reflection \((16, 2 q_b, 8) \). (As in reference [6] we define \( q_b \) inside the first Brillouin zone, i.e. \( q_b \sim 0.25-0.30 \).)

At 12 K the integrated intensity of the first order reflections \((17, \pm 1 \mp q_b, 8.5) \) that we measured, is about \( 3 \times 10^5 \) counts/min while that of the second-order reflection \((16, 2 q_b, 8) \) is only about 800 counts/min. These intensities are respectively about two and four orders of magnitude less than that of the two closest main Bragg reflections, \((16, 0, 8) \) and \((18, 0, 9) \).

Figure 1 shows the temperature variation of the integrated intensity \( I_q \) of the first-order satellite reflections. \( I_q \) extrapolates to zero around 170 K. This gives a critical temperature a few degrees lower than that usually found (180 K) for the structural and the metal-insulator phase transition of the blue bronzes [11]. This shift can be ascribed to some difficulties with the measurement of the absolute temperature of the sample. It has no significant effect on the analysis and the interpretation of the data. The tempe-
ature dependence of $I_q$ is in good agreement with previous structural measurements [7, 14] and with the square of the quadrupole splitting obtained in a recent NMR study of Rb$_{0.3}$MoO$_3$ [18].

For a given reflection, the satellite intensity is proportional to $\eta^2$, where $\eta$ is the order parameter associated with the lattice distortion [16]. The dotted line of figure 1 gives the temperature dependence of $\eta$ calculated in a mean field treatment (BCS theory) of the Peierls transition [17]. It fits roughly the experimental curve.

The temperature variation of the integrated intensity $I_{2q}$ of the second-order satellite reflection (16, 2 $q_b$, 8) is shown in the insert of figure 1. Within experimental errors, it behaves like the square of the normalized intensity of the first-order satellite reflection ($I_q$)$^2$.

This weak (16, 2 $q_b$, 8) satellite reflection, observed for the first time in this work, can be considered either as a second order diffraction harmonic of the first-order satellite peak, or as the 2 $q_c$ = (0, 2 $q_b$, 0) component of a non sinusoidal modulation, or as a combination of the two effects. However, with a ratio of intensity $I_{2q}/I_q$ comparable to the one between a primary satellite reflection and the corresponding main Bragg reflection, the 2 $q_c$ satellite is likely to be mostly a diffraction harmonic.

Below $T_c$, the incommensurate component $q_b$ of the modulation wave vector was obtained by recording the separation along $b^*$ between the (17, $\pm 1 \mp q_b$, 8.5) and (17, $\pm 1 \mp q_b$, 8.5) reflections, the crystal being accurately aligned with the six closest main Bragg reflections. Figure 2 shows, with the improved resolution, two scans along the (17, 1 $- q_b$, 8.5) reflections obtained at 130 K and 11.5 K. It demonstrates clearly that the 1 $- q_b$ component increases as the temperature decreases, and that, at 11.5 K, the reflection is not perfectly centred on the commensurate value 0.75. Figure 3 reports the temperature variation of 1 $- q_b$, a quantity which is more closely related to 2 $k_F$ of the 1D bands (see ref [6] and the discussion). At $T_c$, 1 $- q_b$ amounts to 0.737 $\pm$ 0.002 then increases as the temperature decreases and saturates below about 80 K at the value 1 $- q_b$ = 0.7495 $\pm$ 0.0005. Below $T_c$, the temperature dependence of 1 $- q_b$ is in agreement with that of reference [14]. Our values are slightly greater, by about 0.002 than that of references [7, 15]. Below 80 K, figures 2 and 3 show that, although the value 1 $- q_b$ = 0.75 is included in the error bars, all our determinations give values slightly lower than this simple commensurate value. The same observation can be made on the data of reference [14]. Other determinations give a low temperature saturation of 1 $- q_b$ at values 0.748 [7, 9] and 0.746 [15], which differ markedly from 0.75. All these data show that there is not an unambiguous commensurate-incommensurate phase transition in the blue bronzes. Differences in the purity and the stoichiometry of the various investigated samples might be the origin of this dispersion in the low temperature values of 1 $- q_b$ (see part 4).

3.2 $T > T_c$ — Above $T_c$ satellite reflections broaden into an anisotropic diffuse scattering. The diffuse scattering corresponding to the (17, $\pm 1 \mp q_b$, 8.5) satellite reflections was followed up to room temperature. At each temperature scans through the diffuse scattering were performed along three nearly perpendicular directions related to the structural anisotropy: namely the directions [010], [102], and perpendicular to the (201) layers of MoO$_6$ octahedra (scans along $b^*$, 2 $a^* + e^*$ and 2 $a^* - e^*$ respectively). Figure 4 gives an example of such scans at 180 K ($= T_c + 10$ K).

Fig. 2. — Peak profiles along $b^*$, of the (17, 1 $- q_b$, 8.5) satellite reflection at 11.5 K and 130 K. In these scans a flat LiF crystal has been used as a monochromator.
The maximum of the diffuse scattering above the background \( I(q_c) \), more easily defined by the scans along \( b^* \) and \( 2a^* + c^* \), was measured as a function of temperature (Fig. 5). At room temperature \( I(q_c) \) is about 0.3 counts/s above a background of 1.8 counts/s. At this temperature \( I(q_c) \) is about three orders of magnitude smaller than the peak intensity of the \((17, -1 + q_b, 8.5)\) satellite reflection at 11 K (300 counts/s). Figure 5 shows that \( I(q_c) \) increases strongly as the temperature approaches \( T_c \).

The diffuse X-ray scattering intensity, at the scattering vector \( Q = G + q \) is given by:

\[
I(Q) = |F_d(Q)|^2 S(q, t = 0)
\]

where \( G \) is a reciprocal lattice vector, \( F_d(Q) \) (the structure factor of the unstable lattice mode) and \( S(q, t = 0) \) the Fourier transform of the instantaneous correlation function of the order parameter. For temperatures \( kT \) greater than a characteristic frequency \( \hbar \omega_c \) of the fluctuations, the classical limit of the fluctuation-dissipation theorem gives:

\[
S(q, t = 0) = kT \chi(q)
\]

where \( X(q) \) is the susceptibility associated with the order parameter \( \eta \). Thus, in this limit, \( I(Q) \), divided by the thermal population factor \( kT \), measures the susceptibility \( X(q) \). As, for \( q \) equal to the critical wave vector \( q_c \) of a second order phase transition, this quantity diverges, it is more convenient to plot \( X^{-1}(q_c) \) as a function of temperature. Figure 5 shows that \( X^{-1}(q_c) \) decreases linearly below about 210 K, thus following a Curie-Weiss law, and extrapolates to zero at the critical temperature \( T_c = 170 \text{ K} \).

A systematic deviation from this Curie-Weiss behaviour (or more precisely from a \( \log T/T_c \) dependence (see part 4) — dotted line in figure 5) can be observed above about 210 K in spite of large uncertainties in the high temperature data. In this respect it is interesting to point out that the square of the frequency of the Kohn anomaly, \( \omega^2 \), which is also proportional to \( X^{-1} \), in a soft mode description of structural phase transitions, shows the same deviation from the Curie-Weiss behaviour at high temperature [8].

Let us now present the \( q \) dependence of the diffuse scattering, which enters in the \( q \) dependence of the susceptibility \( X(q) \). This susceptibility is maximum at a critical wave vector \( q_c \) and decays with additional \( \delta q \) components with a generally well verified Lorentzian law:

\[
X(q) = \frac{X(q_c)}{1 + \xi^2 \delta q^2}
\]

where \( \xi \), the correlation length, given by the inverse HWHM of \( X(q) \), measures the range of the fluctuations in the \( \delta q \) direction. Real profiles are in fact a convolution of \( X(q) \) and of the resolution function. Moreover when resolution corrections are small and when the base line is well defined the Lorentzian profile can be clearly observed, as in scan (b) of figure 4. In anisotropic compounds such as \( K_{0.3}MoO_3 \), \( \xi^{-1} \) is an anisotropic quantity. It was measured by scans of the diffuse scattering, along the three above quoted nearly perpendicular directions, related to the structural anisotropy.

Figure 6 gives, as a function of the temperature, the observed half width at half maximum (HWHM) \( \Delta q \), of the diffuse scattering along the \( b^* \), \( 2a^* + c^* \) and \( 2a^* - c^* \) directions.

As \( T_c \) is approached, \( \Delta q \) decreases towards the experimental resolution \( R_g \) in the chain and in the transverse directions respectively. In addition to the diffractometric measurements, figure 6 contains photographic determinations of the HWHM along \( b^* \) and \( 2a^* + c^* \) and, for comparison with the X-ray data, it includes the HWHM along \( 2a^* - c^* \) of the central peak in energy observed by neutron scattering a few degrees above \( T_c \) [8].
Because of some limitations at high temperatures in the signal to noise ratio, and in order to extract an intrinsic correlation length we choose, instead of using standard fitting routines, to simply subtract from the width of the experimental profile, the resolution width measured at low temperatures on the (17, ± 1 ± qb, 8.5) satellite reflections. This gives at 180 K very anisotropic correlation lengths of 200 Å, 35 Å and 12 Å along the [010] [102] and [201] directions. At 250 K correlation lengths are respectively 40 Å, 10 Å and 7 Å. The anisotropy of the correlation lengths follows the structural anisotropy and corresponds to the anisotropy of electrical properties [3].

The dotted lines in figure 6 show that in the vicinity of \( T_c \), all the inverse correlation lengths vary as

\[
\xi^{-1} \sim \sqrt{T - T_c}
\]

characteristic of a mean field behaviour close to \( T_c \).

\( \xi_{1(010)} \) increases more strongly than predicted by this law above about 210 K, at about the same temperature at which systematic deviations from the Curie-Weiss law can be detected (see Fig. 5). At room temperature the fluctuations in chain direction still include about 7 MoO₆ octahedra. Within experimental errors, \( \xi_{1(010)} \) follows the square root behaviour for all the temperature range. At 250 K, \( \xi_{1(010)} \) is comparable to the transverse size of the cluster of 10 MoO₆ octahedra. \( \xi_{1(010)}^{-1} \) follows the square root law up to about 180 K (\( T_c + 10 \) K). Above this value its curvature decreases markedly and it has a temperature dependence which is difficult to estimate because of the large uncertainties in the measurements. Around 210 K, \( \xi_{1(010)}^{-1} \) is comparable to the average distance, 8 Å, between layers of MoO₆ octahedra. At this temperature and above, the diffuse scattering is so broad along the 2 \( a^* - c^* \) direction that it has practically the shape of the diffuse platelet described in an earlier work [6]. The structural fluctuations appear as decoupled between neighbouring layers.

Above \( T_c \), the diffuse scattering remains centred around the (0, \( q_b, 0.5 \)) reduced wave vector. Because of the narrowness of the diffuse scattering along \( b^* \), the incommensurate component \( q_b \) can be significantly determined at all temperature. 1 - \( q_b \) has been obtained between \( T_c \) and room temperature by measuring the separation between the diffuse scattering passing through the (17, ± 1 ± \( q_b, 8.5 \)) reciprocal points. Figure 3 gives the temperature dependence of 1 - \( q_b \). At room temperature 1 - \( q_b \) is equal to 0.71 ± 0.01, in agreement with the previous X-ray photographic determination [6], from which some data points were added in the figure. 1 - \( q_b \) increases when the temperature decreases. Within experimental errors there is no change in the rate of increase of 1 - \( q_b \), at the Peierls transition.

4. Discussion.

4.1 General features of the Peierls transition in the blue bronze \( K_{0.3}MoO_3 \). — It was previously recognized [6] that the observed value of the wave vector of the Peierls distortion along the chain direction \( q_0 \neq 0.75 b^* \) gives a strong indication that two one dimensional bands cross the Fermi level in this compound. Considering that, in the chains built with the MoO₆ octahedra, all the conduction electrons are provided by the potassium atoms, and assuming a perfect stoichiometry, each cluster has three conduction electrons : the resulting 2 \( k_F \) value, in a simple one band picture, should thus be equal to 1.5 \( b^* \) while \( q_0 \) is only half this value.

It is thus interesting to consider the various aspects that a Peierls transition may present in a two band system and to discuss how the Fermi surface is affected. Although the complete discussion deserves a separate study [19], we present in figure 7 three different situations that we believe to be representative :

— In figure 7a, the two bands are degenerate and as a consequence there is only one Fermi wave vector \( k_F \). The Peierls distortion will occur at the wave vector \( q_0 = 2k_F = \rho_0 b^*/4 \) (where \( \rho_0 \) is the number of conduction electrons per units) which thus should not depend upon the temperature. The distortion will open a gap at the Fermi level so that, as in the usual one band compounds, the Peierls transition will reveal itself by a metal-insulator transition in the transport properties.
Schematic band structure of a two band one-dimensional conductor, in the presence of a deformation of the lattice of wave vector \( q \): in a) the two bands are degenerate and \( q_0 = 2k_F \), in b) the two bands are non-degenerate and \( q_0 = k_{F_1} + k_{F_2} \); there is nesting of one band on the other; in c) each band can nest only on itself. The system remains metallic.

In figure 7b: the two bands are no longer degenerate; in the absence of a distortion two Fermi wave vectors \( k_{F_1} \) and \( k_{F_2} \) may be defined, which are related to each other through the law of conservation of the number of electrons \( k_{F_1} + k_{F_2} = \rho_0 b^*/4 \). The Peierls distortion which takes place has the wave vector \( q_0 = k_{F_1} + k_{F_2} \) and there is a folding of one band upon the other. In that way, an absolute gap appears on the whole Fermi surface so that the Peierls transition and the metal-insulator transition occur at the same temperature. In a way similar to the degenerate case (Fig. 7a) one may notice that \( q_0 = k_{F_1} + k_{F_2} = \rho_0 b^*/4 \) is independent on temperature.

In figure 7c a Peierls distortion at a wave vector \( q_0 \) different from \( k_{F_1} + k_{F_2} \) is represented. This may occur if there is no possibility of folding of one band on the other; then a compromise between the instabilities on the two bands leads either to two phase transitions or to only one with \( 2k_F < q_0 < 2k_F \). It is this last case that is depicted: it is quite clear that the Peierls transition is not a metal-insulator transition: the wave vector of the modulation is temperature dependent above and below the Peierls transition \( T_P \). At a temperature \( T_1 < T_P \) it may occur that, due to the increase of the individual gaps, there appears an absolute gap in the electronic spectrum (metal insulator transition). Then the minimization of energy combined with the conservation of the number of electrons gives the wave vector \( q_0 \) at the value \( q_0 = k_{F_1} + k_{F_2} \) for all temperatures \( T < T_1 \) [19].

This discussion shows that the blue bronze \( K_0.3MoO_3 \) belongs to one of the two first categories since the Peierls transition leads to an insulating state. It is not possible to discriminate between the degenerate and the non-degenerate case although some arguments favour the non degenerate one. The first argument lies on the consideration of the orbitals which participate to the formation of the bands [20]: among the \( d \) orbitals of molybdenum of \( t_2g \) character which give rise to the first antibonding states of the \( \pi^* \) type of the \( MoO_6 \) octahedra, two may give rise to quasi-1D dispersive bands, namely \( d_{xz} \) and \( d_{yz} \), with \( z \) the direction of the chains. But due to the considerable deformation of the octahedra in the directions perpendicular to the chains, and the very low symmetry of the crystal, a degeneracy between these states is very unlikely. Moreover non-degenerate 1D bands of the bonding and antibonding type may be built with each of these \( d \) orbitals, due to a small transverse coupling between inequivalent molybdenum sites inside each cluster.

The second argument is just a hint provided by the values of the transverse components of the modulation. In the direction perpendicular to the sheets of octahedra the value \( q_z = 1/2 \), which indicates an out of phase ordering, is well explained by a Coulomb coupling between CDW belonging to neighbouring sheets [6]. But in the layers of octahedra the value \( q_z = 0 \) is rather puzzling, since it is generally admitted in one band systems that the best transverse nesting vector component is \( 1/2 \). A possible explanation is depicted on figure 8 if one assumes that the two bands are not degenerate and possess opposite curvatures in the transverse direction, so that the best nesting wave vector of one band into the other at the Fermi level has a \( q_z = 0 \) transverse component.

Finally one should note that in cases a and b of figure 7 the wave vector of the Peierls distortion cannot vary with temperature. We will come back to that point at the end of this section. We believe that it is due to an additional complication of the band structure.

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Fig. 7. --- Schematic representation of the Fermi surface of a two-band compound in a two-dimensional reciprocal space. When the curvatures of the Fermi surfaces corresponding to the two bands are opposite, a possible good nesting wave vector is \( (k_{F_1} + k_{F_2}, 0) \).

Fig. 8. --- Schematic representation of the Fermi surface of a two-band compound in a two-dimensional reciprocal space. When the curvatures of the Fermi surfaces corresponding to the two bands are opposite, a possible good nesting wave vector is \( (k_{F_1} + k_{F_2}, 0) \).
4.2 MEAN FIELD BEHAVIOUR OF THE PHASE TRANSITION. — The experimental results given in section 3 present several features which suggest that an analysis within the mean field approximation may be reasonably performed. The first point is the good fit of the intensity of the satellite reflections below \( T_c \) with a BCS theory. This behaviour below \( T_c \) is also consistent with the study of the fluctuations above \( T_c \) which never present a one dimensional character. Contrary to compounds such as TTF-TCNQ for example, no diffuse sheets are observed at any temperature. At ambient temperature there is already a short range coupling between the clusters in the layers of the octahedra, since in that transverse direction, the correlation length is about 8 Å, i.e. of the order of the distance between clusters. In the direction perpendicular to the layers of octahedra the correlation length is smaller than the distance between layers in the range \( T > 210 \) K and the layers become coupled only below this temperature. This suggests that, with respect to the structural fluctuations, the blue bronzes are quasi-two dimensional compounds for \( 210 \) K \( < T < 300 \) K and tridimensional compounds below 210 K.

Consequently, we have tried to check whether a simple mean field theory is able to reproduce the temperature dependence of the intensity of the diffuse scattering and of the correlation length above \( T_c \). For this purpose we write the lowest order term of the Landau expansion under the form:

\[
F = \frac{1}{2} \hbar \omega_0 u_q^2 + \frac{1}{2} \chi(q) \delta^2.
\]

(1)

The first term is the deformation energy of the lattice when an atomic displacement \( u_q \) occurs \( (u_q \sim \langle b_q^\dagger b_q \rangle) \) at a wave vector \( q \) for which the bare phonon energy is \( \hbar \omega_0 \). The second term is the decrease of the electronic energy of the system resulting from the opening of a gap \( \Delta_q \) induced by the distortion: \( \Delta_q = g u_q \), where \( g \) is the electron phonon coupling constant. \( \chi(q) \) is the susceptibility of the electrons at the wave vector \( q \), which includes the interactions \( V \) between chains in a RPA approximation:

\[
\chi(q) = \frac{\chi_0(q)}{1 - V \chi_0(q)}.
\]

(2)

In a one band conductor, \( \chi_0(q) \) would be the usual one dimensional susceptibility at the wave vector \( q \) which reads for \( q = 2 k_F \):

\[
\chi_0(2 k_F) = -N(0) \log \frac{1.14 E_F}{kT}.
\]

(3)

\( N(0) \) is the density of states at the Fermi level, proportional to the inverse of the Fermi velocity \( V_F \).

In a two-band compound the most divergent part of the susceptibility for wave vectors \( q \) close to the value \( q_0 = k_{F_1} + k_{F_2} \) is essentially similar with a multiplicative constant

\[
N'(0) = 4 \times N_1(0) \times N_2(0)/(N_1(0) + N_2(0)) \sim \frac{4(V_{F_1} + V_{F_2})}{V_{F_1}^2 + V_{F_2}^2}
\]

\( N_1(0) \) and \( N_2(0) \) being respectively the density of states at the Fermi level for the band 1 and the band 2 (cf. appendix). To simplify the notations we will keep \( N(0) \) in the following. Equation (1) may thus be rewritten under a form suited to a structural analysis:

\[
F = \frac{1}{2} \hbar \omega_0 + g^2 \chi_0(q) \frac{\delta^2}{1 - V \chi_0(q)}
\]

(4)

which allows to define the susceptibility \( \chi(q) \) associated to the order parameter:

\[
\chi(q) = \frac{1}{\hbar \omega_0 \left(1 + \frac{g^2}{\hbar \omega_0} \chi_0(q) \right)}.
\]

(5)

The transition temperature \( T_c \) is obtained when \( \chi(q) \) diverges, i.e.:

\[
kT_c = 1.14 E_F e^{-1/N(0)V_{eff}}
\]

(6)

with

\[
V_{eff} = \frac{g^2}{\hbar \omega_0} - V
\]

and the intensity of the diffuse scattering \( I(q) = kT X(q) \) depends upon temperature according to the law:

\[
I(q) \simeq kT \left[ \frac{1 - V \chi_0(q_0)}{1 + \frac{g^2}{\hbar \omega_0} - V \chi_0(q_0)} \right] \chi(q_0)
\]

\[
\propto kT \frac{\log (T_c/T)}{\log (T/T_c)}
\]

(7)

if one defines \( T_1 \) as the temperature such that

\[
1 - V \chi_0(q_0) = 0, \quad \text{i.e.} \quad kT_1 = 1.14 E_F e^{+1/N(0)V_{eff}}.
\]

(8)

Figure 5 demonstrates that the law \( X^{-1}(q_0) \sim \log T/T_c \) (dotted line) is obeyed close to \( T_c \), but that there is a systematic deviation at high temperature. A better agreement with the high temperature experimental data is obtained using equations (7) with \( T_1 \approx 85 \) K (solid line).

The correlation length along the chains, \( \xi_{||} \), is obtained when the susceptibility \( X(q) \) is developed as a function of the wave vector in the neighbourhood of its maximum; if \( q = q_0 + \delta q \):

\[
X(q) = X(q_0) \left(1 - \xi_{||}^2 \delta q^2 \right).
\]

(9)

The dependence of \( X \) upon \( q \) lies in the dependence
of the electronic susceptibility upon \( q \). Usually:

\[
\chi_0(q) = \chi_0(q_c) + \frac{N(0)}{16 \pi^2} \psi(3) \frac{V_F^2 \delta_q}{kT^2} \]

\[
= \chi_0(q_c) + 0.053 \, N(0) \left( \frac{V_F^2 \delta_q}{kT} \right)^2. \tag{10}
\]

Replacing in equation (5) \( \chi_0(q) \) by its development yields:

\[
X(q) = X(q_c) \left[ 1 - \frac{0.053}{1 - V \chi_0(q_c)} \right] \left[ 1 + \left( \frac{g^2}{\hbar \omega_0} - V \right) X_0(q_c) \right] \cdot \left( \frac{V_F \delta_q}{kT} \right)^2. \tag{11}
\]

So that the inverse of the correlation length, which is directly related to the HWHM of the diffuse scattering in the chain direction, is equal to:

\[
\xi_{\parallel}^{-1} = 4.34 \frac{kT}{V_F} \sqrt{\frac{\log \left( \frac{T}{T_c} \right) \log \left( \frac{kT}{1.14 E_F} \right)}{\log \left( \frac{kT}{1.14 E_F} \right) \cdot \log \left( \frac{kT}{1.14 E_F} \right)}}. \tag{12}
\]

Figure 6 demonstrates that the law in \( \sqrt{T - T_c} \) (dotted line) is obeyed close to \( T_c \) but that there is a deviation at high temperature. This deviation could not be fitted without taking into account the prefactor \( kT \) in equation (12). Using the value of \( T_c = 170 \) K and \( T_1 = 85 \) K obtained from the fit of the temperature dependence of \( X(q_c) \), one gets the excellent fit shown by the solid line of figure 6. Due to the large error bars in figures 5 and 6 it is not possible to extract an accurate value of \( T_1 \) from only one of these figures but the satisfactory point is that both \( \xi_{\parallel} \) and \( \xi\) may be interpreted with the same theory and the same parameters.

From the determination of \( T_c \) and \( T_1 \) and from the absolute values of \( \xi_{\parallel} \) (Fig. 6) and the renormalized phonon frequency:

\[
\hbar^2 \Omega_1(q_c) = \hbar^2 \omega_0^2 \left( 1 + \frac{g^2}{\hbar \omega_0} \cdot \frac{X_0(q_c)}{1 - V \chi_0(q_c)} \right) \tag{13}
\]

obtained by neutron scattering [8] it is possible to derive values of the coupling constants, the cut-off energy and the Fermi velocity. Using equations (6), (8), (12) and (13) one obtains the set of parameters:

\[
\frac{g^2}{\hbar \omega_0} N(0) = 0.60
\]

\[
VN(0) = -0.66
\]

\[
1.14 E_F = 400 \text{ K}
\]

\[
\frac{2V_{F_1}V_{F_2}}{V_{F_1} + V_{F_2}} = 2.4 \times 10^4 \text{ K} \times \text{Å}. \tag{14}
\]

It is thus seen that in this system the Coulomb coupling between charge density waves is attractive and non negligible compared to the electron-phonon coupling. The electron-phonon coupling found compares very well with that which can be deduced from the decrease \( \Delta \omega_0 \), of the frequency, \( \omega_0 \), of the optical branch showing the Kohn anomaly, when its wave vector takes a non zero \( q_0 \) component : \( \Delta \omega_0 / \omega_0 \sim 0.4 \) [8, 9]. The band width deduced from the Fermi velocities is of the order of the electron-volt if \( V_{F_1} \neq V_{F_2} \) which is in reasonable agreement with calculated values [20]. Finally the use of the cut-off \( E_F \) is questionable since its order of magnitude is close to the thermal energies.

We have tried to analyse the temperature dependence of the two correlation lengths in the transverse directions with a similar approach. For this purpose it is necessary to discuss which kind of coupling determines the value of the wave vector of the distortion in a transverse direction. Three different processes may play a rôle:

i) a band structure effect in which \( q_1 \) is determined by the best nesting wave vector of the bands,

ii) a Coulomb coupling between neighbouring CDW's,

iii) a preexisting minimum (or anomaly) in the phonon spectrum : this last coupling may exist in the direction \( 2a^* + c^* \) of the blue bronze since X-ray photographs reveal at room temperature (Fig. 2 in Ref. [6]) that critical diffuse scattering are superimposed on a preexisting and larger diffuse scattering. However there is no proof that iii) constitutes the dominant coupling process.

For each of the above mentioned cases the temperature dependence of \( \xi_{\parallel} \) may be written as a function of \( V_{F_1}, T_c, T_1 \) but also as a function of the strength of the Coulomb or phonon coupling. Additional parameters thus occur, except in case i) where it is clear that \( \xi_{\parallel} \) will be proportional to \( \xi_{\parallel} \). Considering the large error bars on \( \xi_{\parallel} \) we have not been able, within this analysis, to assign a non ambiguous microscopic origin to the chain couplings in the directions \( 2a^* + c^* \) and \( 2a^* - c^* \). Other arguments should be searched in the study of different physical properties of this system.
4.3 CONSIDERATIONS ON THE ELECTRONIC STRUCTURE OF \(K_{0.3}MoO_3\). — In this subsection we come back to the temperature dependence of the wave vector \(q_0\) of the modulation in chain direction above and below \(T_c\). We have stressed in the first part that, since the Peierls transition is accompanied by a metal insulator transition at \(T_c\), the value of the component of the wave vector in the chain direction \(q_0 = 1 - q_b\) is directly related to the number of electrons in the two conduction bands by \(q_0 = \frac{\rho b^*}{4}\). Thus the only possibility that \(q_0\) varies with temperature is that \(\rho\) also varies, i.e. that the total number of electron \(\rho_0\) provided by the potassium atoms does not go entirely in these two conduction bands. We propose that it exists a third band situated above the Fermi level, the population of which depends upon temperature through the Fermi occupation factor, in such a way that the sum of its population plus the population \(\rho\) of the two conducting bands remains constantly equal to \(\rho_0 = 3\) electrons per units. In order to check the validity of our idea we have tried to fit the experimental curve \(1 - q_b\) in this context by assuming that the third band is not dispersive and located at the energy \(E_0\) above \(E_F\). In this way there is only one adjustable parameter \(E_0 - E_F\). The equation of conservation of the number of electrons per units reads:

\[
\frac{4q_0}{b^*} + \frac{2}{e^{(E_0-E_F)/kT} + 1} = \rho_0
\]

or equivalently:

\[
q_0 = b^*\left(\frac{\rho_0}{4} - \frac{0.5}{e^{(E_0-E_F)/kT} + 1}\right).
\]  

When \(T\) approaches zero, the population of the third band goes to zero since \(E_0\) is above \(E_F\) and \(q_0\) tends to an asymptotic value \(q_0 = b^*\rho_0/4\). Figure 3 shows that this value is slightly lower than 0.75 \(b^*\) and indeed all the experimental determinations of \(q_0\) at low temperature give values below 0.75 \(b^*\), the deviation depending upon the sample. It is clear that such an effect is expected if the ideal stoichiometry of 3 potassium atoms per 10 \(MoO_3\) is not completely achieved. For example, the value of \(q_0 = 0.749\) \(b^*\) obtained at low temperature would correspond to a stoichiometry of 0.2996 K per \(MoO_3\), i.e. a lack of 4 atoms of K per 3 000. It is likely that such a non-ideal stoichiometry may be due to the preparation of the sample. Nevertheless one has to note that the deviations of \(q_0\) from the value 0.75 \(b\) occur always with the same sign, i.e. in the same sense of a lack of potassium atoms, since it is not possible to exceed the stoichiometry of 3 K per 10 \(MoO_3\) because all the available sites of K are occupied.

The fit of the data with equation [13] in which \(\rho_0 = 0.749\) and \(E_0 - E_F = 650\) K is presented on figure 3 as a solid line. Considering the excellent agreement on the whole temperature range we have not tried to improve the model by adding for example a dispersion in the third band. Although it would be possible to get a fit as good as the previous one, only the distance between the Fermi level and the bottom of the third band would be unambiguously determined because the number of thermally excited electrons is small (0.16 electron at \(T \sim 300\) K). As a consequence we think that the good fit supports the assumption of a third band but we are not able to discriminate between the two possibilities of either a dispersive or a non dispersive band.

\(A\ posteriori\) the existence of a third band not very much separated from the Fermi level is not surprising. As we have briefly commented at the beginning of this section the richness of the band structure lies in the degeneracy of the d orbitals and in the existence of inequivalent Mo sites in the unit cell. It is thus specific to compounds containing transition metal atoms and it does not occur in 1D conductors made with organic molecules (\(\pi\) molecular levels are well separated). This seems to be confirmed by a recent band structure calculation of \(K_{0.3}MoO_3\) [20]. Nevertheless it is interesting to note that the value \(E_0 - E_F = 650\) K derived from the fit is not high compared to typical values of the Peierls gap in 1D conductors. This means that if, at a given temperature, the Peierls gap \(\Delta\) (total gap is 2 \(\Delta\)) becomes larger than \(E_0 - E_F\) then below this temperature the thermal excitations of lowest energy will preferentially populate the third band instead of the split part of the conduction band. We believe that this may be an explanation to the fact that the gap derived from susceptibility measurements [21] saturates at a value which is close to 600 K.

Finally we want to make two additional comments concerning the varying number of conduction electrons \(\rho\) above \(T_c\) and the existence of the third band. As it may be checked from equation (13) \(\rho\) decreases when \(T\) increases, a behaviour which is consistent with the increase of the Hall constant \(R_H\) above \(T_c\) [11, 22]. On the contrary the population of the third band \(\rho_0 - \rho\) increases as \(T\) increases, which gives an increasing contribution to the Pauli susceptibility. This latter may be written above \(T_c\):

\[
\chi_{\text{Pauli}} \propto \int_{E_{\text{min}}}^{E_{\text{max}}} N(0) \left( -\frac{\partial f}{\partial E} \right) dE + \int n_3(E) \left( -\frac{\partial f}{\partial E} \right) dE \equiv \\
\int n_3(E) \left( 1 - \frac{f(E_{\text{min}} - E_F)}{1 - f(E_{\text{min}})} \right) dE,
\]

where

\[
\rho\left( \frac{e^{(E_{\text{max}} - E_F)/kT} + 1}{e^{(E_{\text{min}} - E_F)/kT} + 1} \right) + \int n_3(E) \left( -\frac{\partial f}{\partial E} \right) dE.
\]
The first term is the usual slightly decreasing function of temperature displayed by the metallic Pauli susceptibility while the second term is the contribution of the third band, the exact form of which depends upon the density of states \( n_3(E) \). Nevertheless it is clear that for \( kT < E_o - E_F \) this contribution increases with temperature due to the thermal filling of the band. This increase of the susceptibility with the temperature was noticed in reference [21] and attributed to the existence of a large pseudo gap (of the order of one half the Peierls gap at \( T = 0 \)). Although we are not able to prove quantitatively that the third band is responsible for the whole of the effect, we propose that it can explain at least a large part of it.

Concerning the structure of the modulation of the lattice in the temperature range where the wave vector is close to 0.75, it was already pointed out in the third section that we had no unambiguous evidence of any commensurate-incommensurate transition. Nevertheless even in the case where the phase modulation remains incommensurate, it is likely that the influence of the commensurate potential of the undistorted lattice due for example to the potassium ions cannot be forgotten and will create commensurate segments (wave vector \( q_{\text{com}} \)) of the chains separated by walls (or discommensurations). In X-ray diffraction such a situation will not be strongly different from a pure incommensurate case: the main satellite reflections will stay at the incommensurate value \( q_{\text{inc}} \) but they will be accompanied by weaker satellite reflections at the distance 4 \( (q_{\text{inc}} - q_{\text{com}}) \) in the reciprocal space (since the order of commensurability is \( n = 4 \) in the blue bronzes) if the discommensurations present a sufficient long-range order. These additional satellites were not observed but, since the best conditions to observe such an effect are at low temperature where \( 4(q_{\text{inc}} - q_{\text{com}}) \) is very small, a special study would be necessary. Evidence of discommensurations below about 90 K has been recently demonstrated by an NMR study of \( \text{Rb}_{0.3}\text{MoO}_3 \) [18] which clearly reveals a drastic change of the \(^{87}\text{Rb}\) lineshape. In any case the value of \( q_{\text{inc}} \) would still be determined by the available number of conduction electrons in the conduction bands so that our explanation would also apply to the non uniform modulation case.

5. Conclusion

Our X-ray measurements on the blue bronze \( \text{K}_{0.3}\text{MoO}_3 \) have given:

i) the fluctuations above the transition temperature \( T_c \) which are related to the susceptibility associated to the order parameter and the correlation lengths \( \xi_|| \) and \( \xi_\perp \),

ii) the temperature dependence of the order parameter below \( T_c \) and

iii) the temperature dependence of the wave vector of the modulation both in the fluctuative regime and below \( T_c \).

The interpretation of the data gives some new contributions to the understanding of the physical properties of this compound:

— Although the system is likely to possess two conducting bands crossing the Fermi level, the Peierls transition looks as simple as in a one band conductor; using the fact that the system becomes insulator below \( T_c \), we propose that the wave vector of the modulation connects the two bands, i.e. that the Peierls transition results from the nesting of one band into the other.

— In the absence of a purely one dimensional fluctuative regime, revealed by the presence of sizeable correlation lengths in the transverse directions, a consistent mean field description of the structural phase transition has been proposed.

— We have interpreted the variation of the wave vector of the modulation with temperature as resulting from an effect of thermal population of the conduction bands in presence of a third band located about 650 K above \( T_c \). Due to the proximity of this third band to the Fermi level, we believe that its presence should not be forgotten in any interpretation of the electronic properties of \( \text{K}_{0.3}\text{MoO}_3 \).

— Although our measurements do not reveal any commensurate-incommensurate phase transition, the existence of commensurate regions separated by discommensurations cannot be excluded, although it would not change our interpretation.

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Appendix.

Let us consider a one dimension electron gas in which two conduction bands cut the Fermi level. These bands will be labelled respectively by the index 1 and 2. Linearizing the dispersion relations in the vicinity of the Fermi level yields

\[
\begin{align*}
\epsilon_k^{(1)} &= V_F(k - k_F) & k > 0 \\
\epsilon_k^{(1)} &= -V_F(k + k_F) & k < 0
\end{align*}
\]

and

\[
\begin{align*}
\epsilon_k^{(2)} &= V_{F2}(k - k_{F2}) & k > 0 \\
\epsilon_k^{(2)} &= -V_{F2}(k + k_{F2}) & k < 0
\end{align*}
\]  

For wave vectors close to \( k_{F1} + k_{F2} \) the most divergent part of the susceptibility of this electron gas reads:

\[
\chi(q) \approx \frac{1}{\pi} \sum_k \frac{f(\epsilon_k^{(1)}) - f(\epsilon_{k-q}^{(1)})}{\epsilon_k^{(1)} - \epsilon_{k-q}^{(1)}} + \frac{1}{\pi} \sum_k \frac{f(\epsilon_k^{(2)}) - f(\epsilon_{k-q}^{(2)})}{\epsilon_k^{(2)} - \epsilon_{k-q}^{(2)}}.
\]  

(A.1)

Writing \( q = k_{F1} + k_{F2} + \delta q \), the first integral appearing in \( \chi(q) \) may be developed with respect to \( \delta q \) in the following way:

\[
I_1 = \sum_k \frac{f(\epsilon_k^{(1)}) - f(\epsilon_{k-q}^{(1)})}{\epsilon_k^{(1)} - \epsilon_{k-q}^{(1)}} = \frac{4a}{\pi(V_{F1} + V_{F2})} \int_{-\infty}^{+\infty} \frac{de}{(e^2 + 1)} \left( e - \delta q \right) \left( \frac{V_{F1} V_{F2}}{V_{F1} + V_{F2}} \right)
\]  

(A.2)

and \( G \) is a constant.

Due to the symmetric rôle played by the two bands in the value of \( I_1 \), it is readily seen that the second integral appearing in \( \chi(q) \) is equal to the first one.

As a consequence:

\[
\chi(k_{F1} + k_{F2} + \delta q) \approx \frac{4}{V_{F1} + V_{F2}} \cdot \frac{kT}{e_B} + \frac{4G}{V_{F1} + V_{F2}} \cdot \left( \frac{2V_{F1} V_{F2}}{kT} \right)^2.
\]  

(A.3)

This result may be compared with the development of the susceptibility around \( 2k_F \) when only one band is present, calculated under the same assumptions

\[
\chi(2k_F + \delta q) = \frac{1}{V_F} F \left( \frac{kT}{e_B} \right) + \frac{G}{V_F} \left( \frac{\delta q V_F}{kT} \right)^2.
\]  

(A.4)
References

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