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Incommensurate-commensurate transition in TaS_3

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Résumé. — Par des mesures de diffraction électronique, nous montrons que la transition de Peierls qui apparaît à $T_0 = 215$ K dans le composé orthorhombique TaS_3 a une période, le long de l'axe des champs, faiblement incommensurable avec le réseau cristallin. Cette période varie avec la température jusqu'à $T'_0 = 140$ K où elle devient égale à quatre fois la période du réseau. Cette transition incommensurable-commensurable est mise en évidence dans les mesures de transport et dans les propriétés dynamiques de l'onde de densité de charge. Pour expliquer cette transition, nous proposons un modèle qui couple fortement les ondes de densité de charge qui apparaissent sur deux ensembles de chaînes.

Abstract. — Careful electron diffraction measurements show that the Peierls distortion, which appears in TaS_3 with the orthorhombic structure at $T_0 = 215$ K, is weakly incommensurate with the underlying lattice. The periodicity of the distortion is temperature dependent and locks at $T'_0 = 140$ K to a value equal to four times the lattice constant. This incommensurate-commensurate transition is observable in transport measurements and also in dynamical properties of the charge density wave. We explain this transition with a model where the charge density waves on two sets of chains are strongly coupled.

1. Introduction.

In the last decade the properties of restricted dimensional systems have been successfully understood. It was shown that many one-dimensional compounds are unstable at low temperature and undergo structural phase transitions, or Peierls transitions, associated with the formation of

charge density waves (CDWs). However the dynamical properties of these CDWs have been studied only recently. $NbSe_3$ was the first example for which a CDW current-carrying state was demonstrated [1] as proposed by Fröhlich in 1954 [2]. The non-linearity in transport properties is observed only above a threshold electric field because of the pinning of the CDW [3]. Another member of the transition metal trichalcogenides family behaves similarly [4, 5] but whereas $NbSe_3$ remains metallic at low temperature, the ground state of TaS_3 below the Peierls transition is semiconducting. Two polytypes of TaS_3 can be synthetized : one with an orthorhombic unit cell but an unknown structure undergoes a Peierls transition at $T_0 = 215$ K [6]. It was shown that the wavelength of the lattice distortion was commensurate with the lattice and equal to four times the lattice constant along the chain axis [7]. The other polytype has a monoclinic unit cell and its structure is isotypical with the $NbSe_3$ one [8]. Two independent CDWs appear at $T_1 = 240$ K and $T_2 = 160$ K, incommensurate with the lattice [9]. A critical study of the CDW dynamics in these two polytypes will be reported later [10]. But anomalies in the transport properties of the orthorhombic TaS_3 lead us to reexamine the superlattice structure obtained by electronic diffraction patterns. Hereafter we present evidence that the wave length of the CDW along the chains at $T_0 = 215$ K is weakly incommensurate and temperature dependent and locks to four times the lattice constant at $T'_0 \sim 140$ K. This incommensurate-commensurate transition is observable in the temperature variation of the resistivity along the chain axis and also in the non linear properties associated with the motion of the CDW submitted to an electric field. These are the temperature variation of the electric threshold field and the number of electrons affected by the CDW gap formation. We propose a model with two types of chains with parallel and nearly equal wave-vector lattice distortions $\mathbf{q}$. At the Peierls transition T_0 a set of chains becomes modulated and forces a CDW transition on the second set of chains by adjusting its wave-vector down to $T'_0 = 140$ K where an energetically stable commensurate distortion prevails.

2. Electron diffraction measurements.

Measurements of the components of the superlattice in the reciprocal space have been previously reported : for TaS_3 in the orthorhombic structure at 15 K by X-rays [7] and at 90 K [9, 11] and 130 K [6] by electron diffraction studies, which seemed to indicate no temperature variation. However we have undertaken a systematic study of the electron diffraction patterns as a function of the temperature. We used two electron microscopes : a Phillips EM 400 (the accelerating voltage being 120 kV) with a sample holder cooled with liquid nitrogen and a 3 MeV microscope (2 MV accelerating voltage) with a sample holder cooled with liquid helium. Typical diffraction patterns were previously published [9]. In figure 1 we draw the temperature variation of the components of the superlattice measured on ten crystals from different batches and different origins along the chain axis c^* and in figure 2 along b^* in one direction of the plane perpendicular to the chains. Temperatures reported in figures 1 and 2 were measured on the sample holder. The temperature gradient (approximately 20 K to 30 K by defect) can be estimated from the temperature difference between the Peierls transition of TaS_3 and the temperature measured on the sample holder where superlattice spots start to appear. The lengths of the unit cell in the reciprocal space a^* and b^* and the wave length of the lattice distortion were measured on the diffraction patterns. Each point in figures 1 and 2 is the average of 15 to 20 measurements on each pattern. The length of the error bars (twice the standard deviation) depends on the quality of the diffraction pattern such as the shape, the dimension and the separation of the spots. The amplitude of the error bars has the same order of amplitude as the difference between the extremal values of the components. However the average values show a weak dispersion and clearly indicate a temperature variation. At the Peierls transition T_0 the component along c^* is 0.255 c^* and it decreases with temperature. It becomes locked to the commensurate value 0.25 c^* at around 100 K-110 K measured on the sample holder which corresponds to a temperature of the sample T'_0 around 130 K. The component along b^* increases from 0.1 b^* and locks to 0.125 b^* at the same temperature. We have no

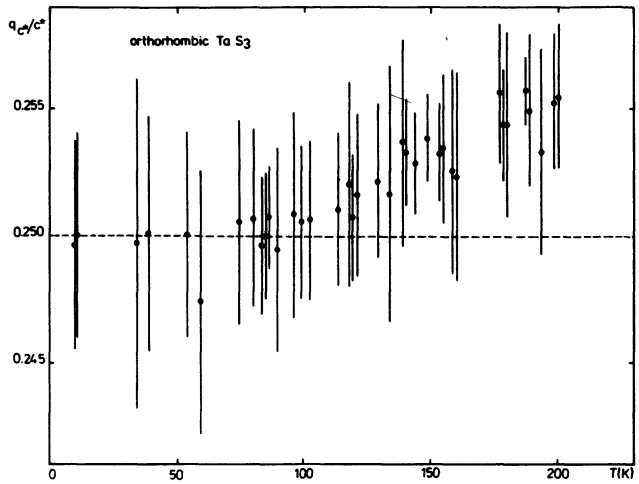

Fig. 1. — Variation of the component of the distortion wave vector **q** along the chain axis c^* in the reciprocal space for TaS_3 with the orthorhombic structure as a function of the temperature measured on the sample holder. The temperature gradient between the sample and the sample holder is estimated as 30 degrees per defect. Data involve ten samples.

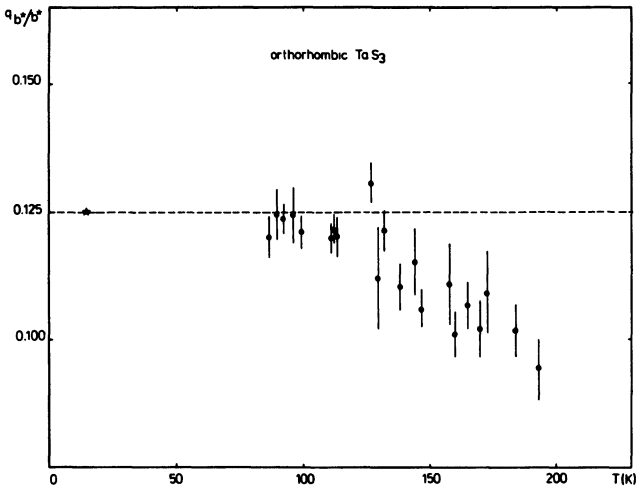

Fig. 2. — Variation of the component of the distortion wave vector along the direction b^* in the plane perpendicular to the chains for TaS_3 with the orthorhombic structure as a function of the temperature measured on the sample holder. The star is the result obtained at $T = 15$ K in reference 7.

measurement for the third component. The orthorhombic unit cell of TaS_3 is huge ; it is comprised of 24 chains [12]. Previously we determined the relative orientation of the orthorhombic and monoclinic unit cells of TaS_3 reproduced in the monoclinic structure [9]. The orthorhombic can be described formally as being formed by 4 monoclinic unit cells, the correspondence between the axis being : $c_{ortho} = b_{mono}$, $b_{ortho} = c_{mono}$ and $a_{ortho} \cong 4\, a_{mono}$. Using X-rays, the components of the distorsion vector **q** were found at low temperature to be $0.5\, a^*_{ortho}$, $0.125\, b^*_{ortho}$ and $0.25\, c^*_{ortho}$ [7]. If expressed in the monoclinic cell for further comparison with TaS_3 monoclinic the new compo-

nents would be 0.125 a^*_{mono}, 0.25 b^*_{mono} and 0.125 c^*_{mono}, that is to say that the distortion vector is nearly parallel to the chain axis in this monoclinic reference frame.

In figure 3 we have drawn the temperature variation of the distortion component of two CDWs along the chain axis b^* for TaS_3 with the monoclinic structure. The measurements indicate that along b^* the wave lengths of the distortions are incommensurate with the lattice and are temperature independent (although it might be possible to suggest that the component of the upper CDW is very slightly temperature dependent down to the temperature where the lower CDW appears However the accuracy of the measurements is not good enough to confirm this statement). The wave-vector components are : below T_1 (0 a^*, 0.253 b^*, 0 c^*) and below T_2 ($\frac{1}{2}$ a^*, 0.247 b^*, $\frac{1}{2}$ c^*) [9].

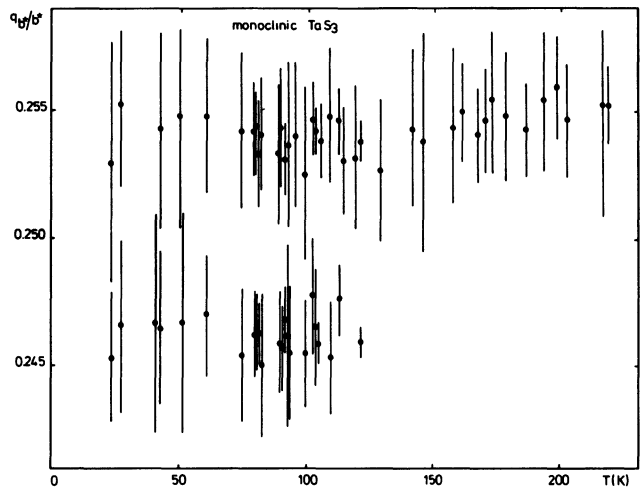

Fig. 3. — Variation of the component of the two distortion wave vectors along the chain axis b^* for TaS_3 with the monoclinic structure as a function of the temperature measured on the sample holder. Data involve eight samples.

3. Transport properties.

3.1 RESISTIVITY. — Very often phase transitions are detectable in the electrical conduction. We have measured the resistivity of needles of TaS_3 with a low frequency bridge. Four contacts were made with silver paint or gold paint. For some experiments contacts in gold were directly evaporated on the crystal. The temperature variation of the resistance along the chain axis and of the logarithmic derivative are plotted in figure 4. The Peierls transition develops at $T_0 = 215$ K where d Log R/d(1/T) has a peak. But d Log R/d(1/T) shows also a broad maximum around $T'_0 = 140$ K at the incommensurate-commensurate transition.

3.2 NON LINEAR PROPERTIES. — Similarly to $NbSe_3$ [1, 3], when a dc current is swept through a TaS_3 sample, the V(I) characteristics become non-linear above a critical current or threshold electric field E_c [4]. Above this field, the electrical force applied to the CDW overcomes the forces which pin the CDW. Therefore the CDW can move and carry a current. Sources of pinning can be either impurity or commensurability. It is believed that the strength of the latter is much higher. In figure 5 we have drawn the temperature variation of E_c for several samples of TaS_3. In the incommensurate temperature range, E_c is nearly constant and equals to 0.5 V/cm. This field is much lower than the values reported in reference [4], which indicates the better quality of our crystals. However at $T'_0 \sim 140$ K, when the CDW becomes commensurate along the chain axis,

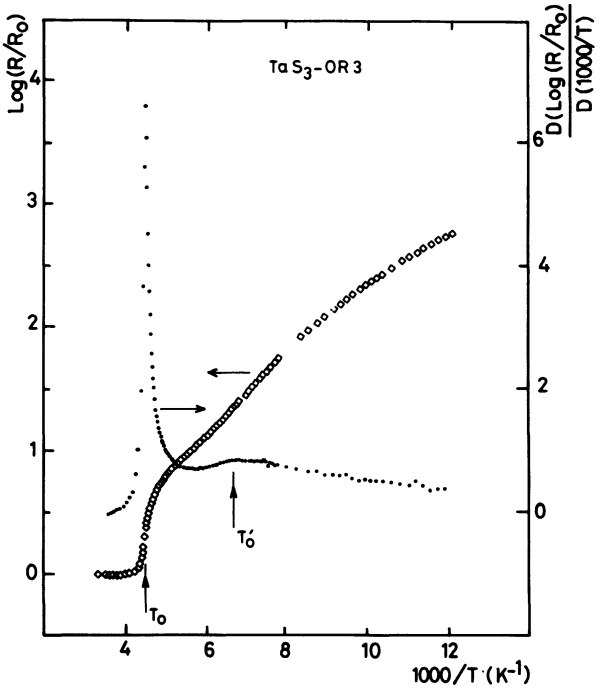

Fig. 4. — Variation of the resistance (normalized to room temperature) of TaS_3 with the orthorhombic structure and variation of the logarithmic derivative as a function of $10^3/T$. $T_0 = 215$ K is the Peierls transition, T'_0 is the incommensurate-commensurate transition.

E_c decreases approximately by a factor 2 down to 90 K. The increase of E_c near T_0 can be explained by a smaller number of condensed electrons because the CDW gap is not completely developed. But the physical reason of the increase at low temperature is not understood, as it is for $NbSe_3$.

All the models for CDW transport take into account the motion of the CDW in a periodic pinning potential. In the commensurate case the period of the pinning is the lattice constant i.e. c [13, 14]. In the impurity pinning case, if the pinning is not too strong, it can be shown that the pinning potential has the CDW periodicity i.e. for TaS_3 $\lambda = 4\,c$ [1]. Above E_c the velocity of the CDW in motion is not uniform but oscillates at the fundamental frequency v corresponding to the periodicity of the pinning. In the ideal case when the sample is formed with an unique CDW domain the current carried by the CDW is formed by a continuous current and an ac current at the frequency v. But there are many domains in the sample without phase coherence and the frequencies mix together to give a broad band noise. The Fourier analysis of this noise reveals the periodic part of correlated domains for which the CDW motion is coherent. We have done a Fourier analysis of the voltage accross the sample as a function of the electric field and measured the variation of the fundamental frequency inside this noise [10]. The current carried by the CDW is $J_{CDW} = nev$ with $v = \lambda\nu$ and ne the electron concentration in the band affected by the CDW gap. So

$$\frac{J_{CDW}}{\nu} = ne\lambda\,.$$

Without any hypothesis on λ, we have drawn in figure 6 the variation of J_{CDW}/ν with temperature. In the incommensurate temperature range J_{CDW}/ν equals 15-20 A/MHz.cm^2. Below $T'_0 =$ 140 K in the commensurate range J_{CDW}/ν increases and equals 30-40 A/MHz.cm^2. The same mea-

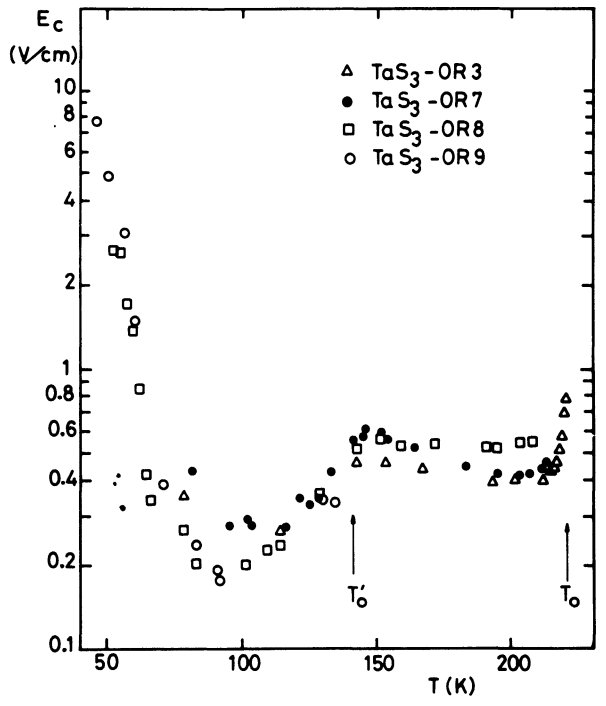

Fig. 5. — Variation of the threshold electric field as a function of temperature for several orthorhombic TaS_3 samples.

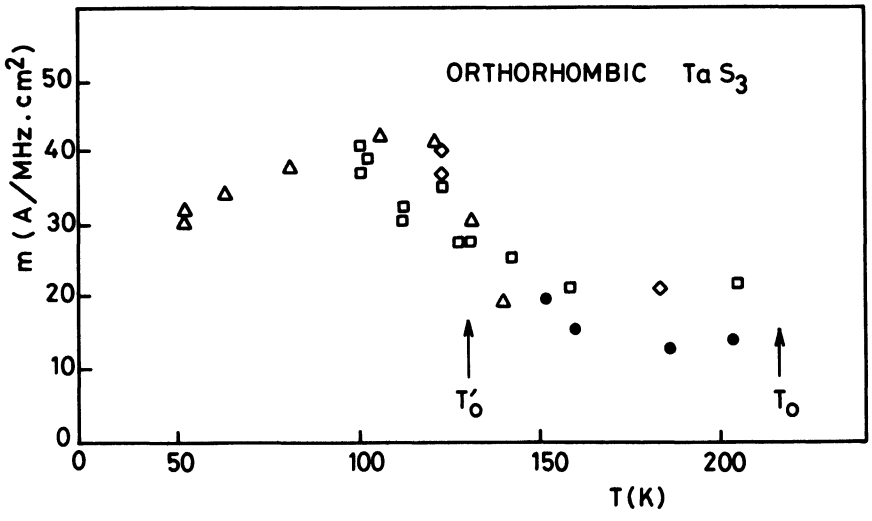

Fig. 6. — Variation of $m = J_{CDW}/v$ as a function of temperature for several orthorhombic TaS_3 samples. m is the slope obtained from the linear variation between the current carried by the CDW in the non linear state and the fundamental frequency of the CDW motion in the Fourier analysis of the voltage accross the sample. m is proportional to a carrier concentration moving in the CDW.

surements made on TaS_3 monoclinic give the same value, approximatively 20 A/MHz.cm^2 [10], for each CDW which is also the same result for each CDW in $NbSe_3$ [1]. The increase of J_{CDW}/v

at T'_0 is not the increase of the supposed change of the pinning potential periodicity because in this case we would expect a decrease of J_{CDW}/v by a factor of 4.

4. Two CDWs locking model.

Our results can be summarized as following : in TaS_3 with the monoclinic structure, two independent CDWs occur with their distortions $\mathbf{q}_1$ and $\mathbf{q}_2$ temperature independent : for the upper CDW the distortions in adjacent unit cells are in phase ; for the lower CDW distortions are antiphase ordered. In TaS_3 with the orthorhombic structure a unique CDW appears at $T_0 = 215$ K with a distortion $\mathbf{q}$ temperature dependent down to $T'_0 = 140$ K where the longitudinal component locks to a commensurate value. This locking is detectable by a very slight anomaly in the transport properties. At the commensurate transition the electric field for which the CDW becomes unpinned decreases by a factor 2 and the number of carriers in the bands affected by the CDW increases by a factor 2. Orthorhombic TaS_3 has an unknown structure but if we consider the transition metal trichalcogenides family it is likely that its structure is formed by chains with different S-S bond strengths. In $NbSe_3$ and TaS_3 it is supposed that the CDWs appear on two types of chains. Without knowing the delicate structural differences which prevents orthorhombic TaS_3 to crystallize in a higher symmetry unit cell (smaller unit cell) let us suppose that this compound can be defined by two chain types. There are two bands crossed by the Fermi level at $\mathbf{q}_1$ and $\mathbf{q}_2$.

If we define δ_1 and δ_2 as the complex order parameters on each type of chain, the Ginzburg-Landau density of energy will contain a coupling term of the form $A\delta_1\,\delta_2^*$, the constant A arising from electrostatic, or elastic interaction through the deformations of the lattice.

If $\mathbf{q}_1 \neq \mathbf{q}_2$ this coupling contribution to the energy is zero to first order, by volume integration, but gives a weak second order term [15].

The system may choose another solution, with a unique $\mathbf{q}$ vector, between $\mathbf{q}_1$ and $\mathbf{q}_2$, for which A gives a first order decrease in the energy : $-\,|\,A\delta_1\,\delta_2\,|$, where δ_1 and δ_2 are now the scalar amplitudes of the order parameter :

$$\delta_i\, e^{iqr}\,.$$

The energy necessary for this is given by

$$\delta_1^2\,\xi_1^2\,|\,(q - q_1)\,|^2 + \delta_2^2\,\xi_2^2\,|\,(q - q_2)\,|^2\,,$$

when ξ_1 and ξ_2 are the CDW coherence lengths along the two chains. For every trichalcogenide compound [9] the « along the chains » components of q_1 and q_2 are such that

$$q_1 - q_2 \# 0.010$$
$$q_1 + q_2 \# 0.500\,.$$

In the case of $NbSe_3$ or TaS_3 monoclinic $\mathbf{q}_1 = (0\,a^*, q_1\,b^*, 0\,c^*)$ and $\mathbf{q}_2 = (0.5\,a^*, q_2\,b^*, 0.5\,c^*)$, if $\mathbf{q}$ equals the mean value of $\mathbf{q}_1$ and $\mathbf{q}_2$ we can estimate the relative weight of the longitudinal and transverse components of $(\mathbf{q} - \mathbf{q}_1)^2$: the « along the chains » component is proportional to 10^{-4} whereas the transverse component is proportional to 0.5. Even by considering a strong anisotropy of 100 on the ξ^2 values the cost in transverse energy would be 50 times higher than for the longitudinal energy. Consequently, the coupling is not strong enough and in these components the two waves develop independently.

A different situation may occur of the $\mathbf{q}_1$ and $\mathbf{q}_2$ vectors are nearly parallel and a single $\mathbf{q}$ solution can be the true fundamental one. We do not know why it seems to be the case in orthorhombic TaS_3. We assume that in this system, as in parent trichalcogenide compounds, the Fermi level cuts

two kinds of bands at two wave-vectors $\mathbf{q}_1/2$ and $\mathbf{q}_2/2$ along the chains, disregarding the components of the distortion vectors in other directions. At $T = T_0$, a gap Δ_1 opens on the first band at $q = q_1$ inducing a gap Δ_2 with the same wave-vector on the second band. This model, analoguous to the Bak and Emery calculation on TTF-TCNQ [16], is different, since here, we have essentially a variation of the longitudinal component of q, due to the conservation of the number of electrons. At low temperature, the unique $\mathbf{q}$ vector has to stand at $\frac{q_1 + q_2}{2}$, since all the states under $q/2$ are occupied (below the gaps) in the two bands, instead of $q_1/2$ and $q_2/2$ in the normal phase, above T_0.

We have drawn in figure 7*a* schematic variation with temperature of the gaps Δ_1 and Δ_2. At the incommensurate-commensurate temperature T'_0, the two gaps are completely developed. If A is high enough, every Δ_1 and Δ_2 can reach very rapidly kT(case a) giving an explanation for the high values of the resistivity contrarily to the monoclinic phase where, between T_{c_1} and T_{c_2}, the resistivity stands at about twice its value in the metallic state, due to the condensation of carriers in only one band. If A is moderate (case b) the strong increase of Δ_2 will be near T'_0. In the incommensurate phase principally only one band is affected and the number of carriers that we find is the same as for $NbSe_3$ or monoclinic TaS_3. Below T'_0 the two bands lock and the carriers of these two bands move together. Experimentally we find twice the number of the incommensurate case. However in this case we cannot explain the temperature variation of the resistivity. Another problem remains concerning why the threshold electric field decreases at the commensurate locking. Keeping this discussion for later it might be said that the CDW can be described as commensurate domains separated by discommensurations walls. Following Weger and Horovitz [17] the threshold field would be the depinning field for commensurate domains, and these authors have calculated a decrease of the threshold field when the system becomes commensurate.

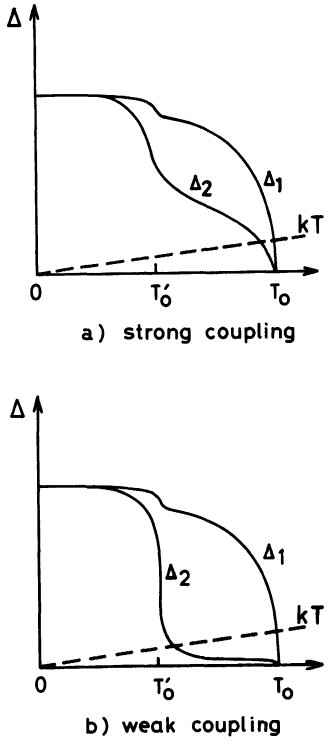

Fig. 7. — Schematic temperature variation of the gaps Δ_1 and Δ_2 which appear on the two sets of chains : the dotted lines indicate kT ; case a, in the strong coupling limit $\Delta_2 > kT$; case b, in the weak coupling limit.

References

[1] For a review see MONCEAU, P., RICHARD, J., RENARD, M., *Phys. Rev. B* **25** (1982) 931 and RICHARD, J., MONCEAU, P., RENARD, M., *Phys. Rev. B* **25** (1982) 948.
[2] FRÖHLICH, H., *Proc. R. Soc. London Ser. A* **223** (1954) 296.
[3] FLEMING, R., GRIMES, C. C., *Phys. Rev. Lett.* **42** (1969) 1423.
[4] THOMPSON, A. H., ZETTL, A., GRÜNER, G., *Phys. Rev. Lett.* **47** (1981) 64.
[5] GRÜNER, G., ZETTL, A., CLARK, W. G., THOMPSON, A. H., *Phys. Rev. B* **23** (1981) 6813.
[6] SAMBONGI, T., TSUTSUMI, K., SHIOZAKI, Y., YAMAMOTO, M., YAMAYA, K., ABE, Y., *Solid State Commun.* **22** (1977) 729.
[7] TSUTSUMI, K., SAMBONGI, T., KAGOSHIMA, S., ISHIGURO, T., *J. Phys. Soc. Japan* **44** (1978) 1735.
[8] MEERSCHAUT, A., GUEMAS, L., ROUXEL, J., *C.R. Hebd. Sea. Acad. Sci.* C. 215 (1980).
[9] ROUCAU, C., AYROLES, R., MONCEAU, P., GUEMAS, L., MEERSCHAUT, A., ROUXEL, J., *Phys. Status Solidi* (*a*) **62** (1980) 483.
[10] SALVA, H., WANG, Z. Z., MONCEAU, P., RICHARD, J., RENARD, M., to be published.
[11] VAN TENDELOO, G., VAN LANDUYT, J., AMELINCKX, S., *Phys. Status Solidi* (*a*) **43** (1977) K 137.
[12] BJERKELUND, E., KJEKSHUS, A., *Z. Anorg. Allg. Chem.* **328** (1964) 235.
[13] ARTEMENKO, S. N., VOLKOV, A. F., *Zh. Eksp. Teor. Fiz.* **81** (1981) 1872 ; *Sov. Phys. JETP* **54** (1981) 992.
[14] BARDEEN, J., *Phys. Rev. Lett.* **42** (1979) 1498.
[15] EMERY, V. J., MUKAMEL, D., *J. Phys. C* **12** (1979) L677.
[16] BAK, P., EMERY, V. J., *Phys. Rev. Lett.* **36** (1976) 978.
[17] WEGER, M., HOROVITZ, B., *Solid State Commun.* **43** (1982) 583.