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Sound Velocity Anomaly at the Mott Transition: application to organic conductors and V_2O_3

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Close to the Mott transition, lattice degrees of freedom react to the softening of electron degrees of freedom. This results in a change of lattice spacing, a diverging compressibility and a critical anomaly of the sound velocity. These effects are investigated within a simple model, in the framework of dynamical mean-field theory. The results compare favorably to recent experiments on the layered organic conductor κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl. We predict that effects of a similar magnitude are expected for V_2O_3 , despite the much larger value of the elastic modulus of this material.

The Mott transition, which is the metal-insulator transition (MIT) induced by electron-electron interactions, has been investigated theoretically and experimentally for many years [1, 2]. Some materials are poised very close to the Mott transition, which can therefore be induced by varying pressure, temperature, or chemical composition. This is the case of $(V_{1-x}Cr_x)_2O_3$, and of the family of layered molecular crystals κ -(BEDT-TTF)₂X where X is an anion (e.g., X=I₃, Cu[N(CN)₂]Cl, Cu(SCN)₂). In these compounds, one observes a pressure induced, finite temperature, first order phase transition. Pressure increases the bandwidth, reducing the relative interaction strength. The first-order transition line ends at a second-order critical endpoint (P_c, T_c) . The critical behaviour at this endpoint has been recently the subject of remarkable experimental investigations [3, 4].

On the theory side, our understanding of the Mott transition has benefitted from the development of dynamical mean-field theory (DMFT) [5, 6]. In this theory, electronic degrees of freedom are the driving force of the transition, and the critical endpoint is associated with a diverging electronic response function χ_{el} (defined below) [7, 8]. An analogy exists with the liquid-gas transition. The insulating phase is a low-density gas of neutral bound pairs of doubly occupied and empty sites; the metal is a high-density liquid of unbound doubly-occupied and empty sites which therefore conduct. The scalar order parameter is associated with the low-energy spectral weight.

In real materials however, lattice degrees of freedom do play a role at the Mott transition. This is expected on a physical basis: in the metallic phase the itinerant electrons participate more in the cohesion of the solid than in the insulating phase where they are localized. As a result, the lattice spacing increases when going from the metal to the insulator. A discontinuous change of the lattice spacing through the first-order metal-insulator transition line is indeed observed in $(V_{1-x}Cr_x)_2O_3$ [9]. Ra-

man scattering experiments [10] find that in the metallic state the frequency of certain phonons associated with the BEDT-TTF molecules has a non-monotonic temperature dependence below 200 K. The effect of the Mott transition on optical (Einstein) phonons was studied theoretically in [11]. Acoustic experiments [12] find an anomaly in the sound velocity of the organic materials as a function of temperature, with a particularly dramatic reduction recently observed [13] for κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl near the Mott critical endpoint at $T_c \simeq 40K$.

In this paper, we propose a simple theory of the effects connected with lattice expansion through the Mott transition, and the associated divergence of the compressibility. We address in particular the critical anomaly of the sound velocity observed in acoustic experiments. For this purpose, both the electronic degrees of freedom and the ionic positions must be retained in a model description. We adopt the simplest possible framework, previously introduced in Ref.[7], namely the compressible Hubbard model (see also [14]), with the electron correlations being treated within DMFT. Our results compare favorably to the recent acoustic experiments on the layered organic conductor κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl [referred to in the rest of this paper simply as the organic-conductor(OC).] Furthermore, we show that effects of a similar magnitude are expected for V_2O_3 , despite the much larger value of the elastic modulus of this material.

In the following, we assume that the dependence of the free energy on the unit-cell volume v (or, rather on the induced strain, see below) can be written as:

$$F = F_0 - P_0(v - v_0) + \frac{1}{2} B_0 \frac{(v - v_0)^2}{v_0} + F_{el}[D(v)] \quad (1)$$

The last term F_{el} , is the contribution of the electronic degrees of freedom which are active through the transition (e.g the d-shell for V_2O_3). Specifically we take F_{el} to be the free energy of a single band, half-filled Hubbard model [15] with a half-bandwidth $D(v)$ depending on the

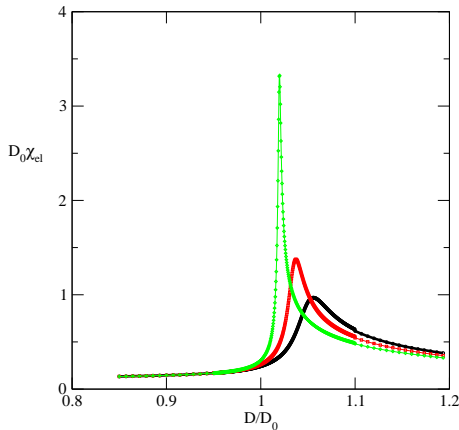


FIG. 1: The variation of the electronic response function χ_{el} with the bandwidth D for various temperatures. The parameters are $U/D_0 = 2.492$ and $T/D_0 = 0.060, 0.055, 0.050$ from right to left. The results are from DMFT solved in the IPT approximation.

unit-cell volume v . The first three terms arise from expanding the free energy due to other degrees of freedom about a reference cell volume v_0 , P_0 and B_0 being the corresponding (reference) pressure and the bulk elastic modulus. Expression (1) can be derived from a microscopic hamiltonian $H = H_{lat}[\mathbf{R}_i] - \sum_{ij\sigma} t(\mathbf{R}_i - \mathbf{R}_j) d_{i\sigma}^\dagger d_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$, involving both the ion positions \mathbf{R}_i and the electronic degrees of freedom, when all phonon *excitations* are neglected, i.e all lattice displacements $\mathbf{R}_i - \mathbf{R}_j$ are taken to be uniform. It is conventional (see e.g [16]) to use an exponential parametrization for $D(v)$, which we linearize since relative changes in v are small: $D(v) = D_0 \exp[-\gamma(v - v_0)/v_0] \simeq D_0 [1 - \gamma(v - v_0)/v_0]$. As a result, the pressure $P = -\partial F/\partial v$ and the “compressibility” $K \equiv -(v\partial P/\partial v)^{-1} = (v\partial^2 F/\partial v^2)^{-1}$ are given by:

$$P = P_0 - B_0(v - v_0)/v_0 - (\gamma D_0/v_0)\mathcal{T}_{el} \quad (2)$$

$$(K v)^{-1} = B_0/v_0 - (\gamma D_0/v_0)^2 \chi_{el} \quad (3)$$

Here \mathcal{T}_{el} is the (dimensionless) electronic kinetic energy $\mathcal{T}_{el}(T, D(v), U) \equiv -\partial F_{el}/\partial D$, and χ_{el} is the electronic response function: $\chi_{el}(T, D(v), U) \equiv -\partial^2 F_{el}/\partial D^2$. Both quantities are associated with the purely electronic Hubbard model. Within DMFT, χ_{el} is found [7, 8] to reach a peak value $\chi_{el}^{max}(T, U)$ for a given temperature T at a specific value of $D = D_m^{el}(T, U)$, and eventually, to diverge at $T = T_c^{el}$, $D = D_c^{el}$. This is illustrated in Fig.1 using DMFT together with iterated perturbation theory (IPT) [5] in which case $T_c^{el} \simeq 0.02U$, $D_c^{el} \simeq 0.4U$. In the compressible model, as pointed out in Ref.[7], the Mott critical endpoint will therefore occur at $T_c > T_c^{el}$ and will be signalled by the divergence of K . From (3), this happens when χ_{el}^{max} has reached a large enough (but not divergent) value such that $D_0 \chi_{el}^{max}(T_c) = B_0 v_0 / (\gamma^2 D_0)$. The corresponding critical half-bandwidth is $D_c = D_m^{el}(T_c, U)$ and the critical cell volume is deter-

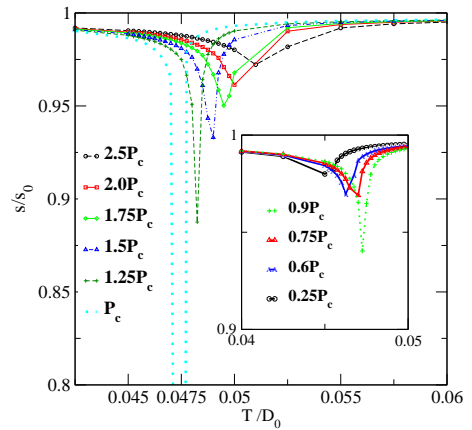


FIG. 2: Temperature dependence of the sound velocity at various pressures for parameters corresponding to OC. Inset: position and amplitude of anomaly below P_c

mined from $(v_c - v_0)/v_0 = -(D_c - D_0)/(\gamma D_0)$. The critical pressure can then be determined using Eq. (2). If T_c is close enough to T_c^{el} one can use the form (for $T > T_c^{el}$): $\chi_{el}^{max} \simeq \alpha_{el}(U)T_c^{el}/(T - T_c^{el})$, which follows from mean-field theory [8]. Here, $\alpha_{el}(U) = \alpha/U$ with $\alpha \simeq 0.5$ in our calculations. Hence one obtains: $\Delta T_c/T_c \equiv (T_c - T_c^{el})/T_c^{el} = \alpha [\gamma^2 D_0 / (B_0 v_0)] (D_0/U)$.

The inverse “compressibility” K^{-1} is directly proportional to the square of the sound velocity s : $s \propto 1/\sqrt{K}$. At T_c , since K *diverges*, the sound-velocity *vanishes*. Hence, right at the critical point the acoustic phonon branch under consideration disperses anomalously. If the crystal has inversion symmetry, the dispersion should go as $\omega \propto q^2$. Thus from a calculation of the inverse compressibility along lines similar to that in Ref. [7] one can determine the dependence of the sound velocity on temperature and pressure, including its critical anomaly, as reported below. Note that a similar critical behaviour of the sound-velocity is well known in the context of the usual liquid-gas transition [17].

We note that the “pressure” and inverse “compressibility” in Eqs. (2,3) are associated with the stiffness with respect to changes in the unit-cell volume, i.e. to bulk strain at *fixed number* of ions and electrons per unit cell. General thermodynamics relates $\rho^2 \partial \mu / \partial \rho$ (with ρ the total density) to the inverse compressibility provided the latter is defined from volume changes *at zero strain* (i.e stemming from vacancy diffusion). Hence, this relation does not apply to K (which is related to the stress-stress correlation function rather than to the density-density one). This also implies that K is not related to the “charge compressibility” $\kappa_{el} = \partial n_{el} / \partial \mu_{el}$ (studied theoretically, eg. in [18]), as the latter involves changes of the electron density under conditions of zero strain. The correspondence between the sound velocity and the “compressibility” K as calculated above can be shown to be exact for the simplest compressible Hubbard model of

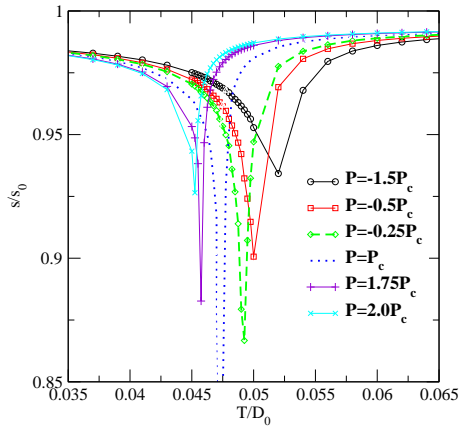


FIG. 3: Temperature dependence of the sound velocity at various pressures for parameters corresponding to pure V_2O_3 . “Negative” pressures can be reached by chromium-substitutions: for $(V_{1-x}Cr_x)_2O_3$, experiments establish that $x = 1\%$ corresponds to $\Delta P = -4\text{kbar}$ ($\simeq P_c$) (see e.g [2]).

Parameter	V_2O_3	OC
D_0	1 eV	.13 eV
v_0	100 \AA^3	1700 \AA^3
B_0	2140 kbar	122 kbar
γ	3	5
B_0v_0	133 eV	129 eV
U/D_0	2.468	2.492
$B_0v_0/(\gamma^2 D_0)$	14.7	40

TABLE I: Table of parameter values for V_2O_3 and the organic-conductor κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Cl (OC)

phonons modulating the nearest neighbour hopping on a cubic lattice, and for longitudinal sound propagation along the [111] direction. We hence present it as a reasonable zeroth-order description of real systems. A more realistic description of anisotropic materials should take into account the dependence on both polarization and direction of propagation.

The details of the calculational procedure have been described in Ref. [7], and we avoid repeating them here. The parameter values we have chosen for the two materials are given in Table 1. Our approach is to consider pure V_2O_3 and the OC at ambient pressure (i.e., $P_0 = 1$ bar is essentially zero) as reference compounds, for which v_0 and B_0 are taken from experiments. For the OC, we take the values $D_0 \simeq 0.13$ eV and $\gamma = 5$, which were found in [19] to be consistent with transport data. For V_2O_3 , we take $D_0 = 1$ eV and $\gamma = 3$ (values considered standard for d-electron systems [16]). Finally, the value of U/D_0 is adjusted so that the critical pressure is reproduced correctly ($P_c \simeq -4$ kbar for V_2O_3 , $P_c \simeq +200$ bar for the OC). This requires U/D_0 to be poised very close to the Mott critical value for the pure electronic problem (1.26 in our calculations). Using the parameters in

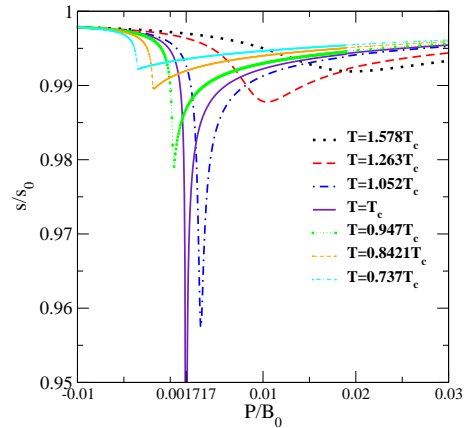


FIG. 4: The sound velocity as a function of pressure at various fixed temperature for parameters corresponding to OC

Table. 1, one sees that the (dimension-less) combination $B_0v_0/(\gamma^2 D_0)$ is large for both compounds ($\simeq 14.7$ for V_2O_3 and $\simeq 40$ for the OC). This implies that the Mott transition arises for large values of $D_0\chi_{el}$, i.e., the experimentally observed transition is definitely driven by the electronic degrees of freedom, and very close to the purely electronic Mott transition. Specifically, we find that the relative shift $\Delta T_c/T_c$ of the critical temperature due to the coupling to the lattice, is as small as 1.4% for V_2O_3 and even smaller for the organic conductors. In fact it is remarkable that despite the very different values of the bulk modulus of the two materials (the OC being much softer than V_2O_3), the combination $B_0v_0/(\gamma^2 D_0)$ only differs by a factor of 3 between them. As a result, the order of magnitude of the sound-velocity anomaly is expected to be similar in both materials, since $K_0v_0/Kv = 1 - (\gamma^2 D_0/B_0v_0)D_0\chi_{el}$. We emphasize that there is a significant difference between our choice of parameters and that made in Ref. [7] for V_2O_3 : there, a much smaller value of B_0 (much smaller than the measured experimental value) and somewhat larger values of U/D were used in order to obtain volume jumps comparable to what is seen experimentally, resulting in a large relative shift $\Delta T_c/T_c$, on the scale of 40%. Because the contribution of the electronic degrees of freedom to the total bulk modulus is comparatively small, it is hard to reconcile the choice made in Ref. [7] with experimental data for this quantity. On the other hand, with our choice of B_0 , the calculated fractional volume jump $\Delta v/v_0$ through the transition is $\sim 0.2\%$, too small compared to the observed [9] jump ($\sim 1\%$). We comment on a possible resolution of this problem towards the end of this paper.

Figs. 2 and 3 show our results for the temperature-dependence of the sound velocity computed using the method described above, for the parameters representative of the OC and V_2O_3 and for several pressures. At the critical pressure $P = P_c$, the sound-velocity van-

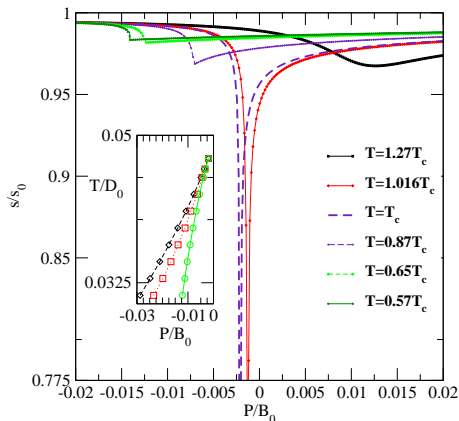


FIG. 5: The sound velocity as a function of pressure at various fixed temperatures for parameters corresponding to V_2O_3 . Inset: The corresponding phase diagram. The central line and the lines on either side correspond to the transition pressure P_{tr} and the spinodal pressures respectively

ishes according to the mean-field law $s \propto (T - T_c)^{1/2}$ (K diverges as $1/(T - T_c)$, as follows from Eq. (3)). A pronounced dip remains visible in a rather extended range of pressure both above and below P_c . The overall shape of these curves, as well as the typical order of magnitude of the effect are in quite good agreement with the experimental data for the OC, recently published in [13]. For example, we obtain a dip of relative size $\Delta s/s_0 \simeq 10\%$ for $P \simeq 1.3P_c$, consistent with the experimental observation.

In Fig.4 and 5, we show the sound-velocity as a function of pressure for various temperatures. This has been studied in a less systematic manner in the experiments on the OC, but the overall shape and magnitude of our results are again consistent with the published data [13]. In particular, the curves in Figs.4-5 show a marked asymmetry: on the low-pressure (insulating) side the pressure dependence is rather weak and a dip appears only very close to P_c , while a more gradual and sizeable pressure-dependence is observed on the high-pressure (metallic) side. This reflects the asymmetry in the electronic response function χ_{el} observed on Fig.1. It is expected qualitatively, since electrons participate much less to the cohesive energy on the insulating side, and is also observed experimentally [13].

The inset of Fig. 5 shows the temperature-pressure phase diagram for parameters corresponding to V_2O_3 . The slope dP_{tr}/dT obtained is too large compared to the observed value. We believe that this, as well as the problem mentioned above, namely the smallness of the calculated $\Delta v/v_0$, can be resolved as follows. Let $D_{tr}^{el}(T) = D(v_{tr}^{el}(T))$ be the half-bandwidth for metal-insulator coexistence in the purely electronic problem at temperature T . For T well below T_c , the fractional differential volumes $\delta v_{i,m}/v_0 \equiv (v_{i,m} - v_{tr}^{el}(T))/v_0$ of the coexisting insulating and metallic phases and the transition pres-

sure P_{tr} in the presence of lattice coupling are approximately $\delta v_i/v_0 \simeq -\delta v_m/v_0 \simeq \gamma(T_m - T_i)/(2B_0v_0/D_0)$ and $P_{tr} \simeq B_0(D_{tr}^{el}(T) - D_0)/(\gamma D_0) - (\gamma D_0/v_0)(T_m + T_i)/2$ (compare 2). Here $T_{i,m}$ are T_{el} evaluated in the coexisting insulating and metallic phases respectively. These expressions are in good agreement with the numerical results reported above and in Ref. [7]. In the context of more realistic models for the electronic problem, one expects that differential screening effects would reduce (enhance) the effective Hubbard U and correspondingly enhance (reduce) T , in the metallic (insulating) phase, leading to an overall enhancement of $(v_i - v_m)/v_0$. An additional enhancement factor might come from the orbital degeneracy in V_2O_3 . These effects could be addressed in future studies of multi-band Hubbard models, including screening effects in a self-consistent manner. High-precision experimental measurements of optical spectral weights in the coexisting insulating and metallic phases would also be very interesting, and could provide information on the kinetic energies $T_{i,m}$.

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