Sound Velocity Anomaly at the Mott Transition: application to organic conductors and V$_2$O$_3$

S.R.Hassan, 1,2 A.Georges, 2,1 and H.R.Krishnamurthy 3,4

1Laboratoire de Physique Théorique-Ecole Normale Superieure
24, rue Lhomond 75231 Paris Cedex 05, France
2Centre de Physique Théorique-Ecole Polytechnique, 91128 Palaiseau Cedex, France
3Centre for Condensed Matter Theory, Department of Physics, Indian Institute of Science, Bangalore 560 012, India
4Condensed Matter Theory Unit, JNCASR, Jakkur, Bangalore 560 064, India.

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 \( \kappa \)-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. We predict that effects of a similar magnitude are expected for V$_2$O$_3$, 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. 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$_x$)$_2$O$_3$, and of the family of layered molecular crystals \( \kappa \)-(BEDT-TTF)$_2$X where X is an anion (e.g., X = I$_3$, 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.

On the theory side, our understanding of the Mott transition has benefited from the development of dynamical mean-field theory (DMFT). 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 \( \chi_{el} \) (defined below). 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$_x$)$_2$O$_3$. Random scattering experiments 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. Acoustic experiments find an anomaly in the sound velocity of the organic materials as a function of temperature, with a particularly dramatic reduction recently observed for \( \kappa \)-(BEDT-TTF)$_2$Cu[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., namely the compressible Hubbard model (see also), with the electron correlations being treated within DMFT. Our results compare favorably to the recent acoustic experiments on the layered organic conductor \( \kappa \)-(BEDT-TTF)$_2$Cu[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 203, 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 203). Specifically we take $F_{el}$ to be the free energy of a single band, half-filled Hubbard model with a half-bandwidth $D(v)$ depending on the
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 \( H = H_{lat}[\mathbf{R}_i] - \sum_{ij} t(\mathbf{R}_i - \mathbf{R}_j) \delta_{i\sigma} \delta_{j\sigma} d_{i\sigma} d_{j\sigma} + U \sum n_{i\sigma} n_{i\bar{\sigma}} \), 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: \( D(v) = D_0 \exp[-\gamma(v - v_0)/v_0] \approx D_0 [1 - \gamma(v - v_0)/v_0] \). As a result, the pressure \( P = -\partial F/\partial v \) and the “compressibility” \( K \equiv -\partial^2 F/\partial v^2 \) are given by:

\[
P = P_0 - B_0(v - v_0)/v_0 - (\gamma D_0/v_0) T_{el} \tag{2}
\]

\[
(Kv)^{-1} = B_0/v_0 - (\gamma D_0/v_0)^2 \chi_{el} \tag{3}
\]

Here \( T_{el} \) is the (dimensionless) electronic kinetic energy \( T_{el}(T, D, v, U) \equiv -\partial F_{el}/\partial D \), and \( \chi_{el} \) 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, \( \chi_{el} \) is found to reach a peak value \( \chi_{el,\text{max}}(T, U) \) for a given temperature \( T \) at a specific value of \( D = D_{m}(T, U) \), and eventually, to diverge at \( T = T_{el} \), \( D = D_{el} \). This is illustrated in Fig.1 using DMFT together with iterated perturbation theory (IPT) in which case \( T_{el}^{\text{el}} \approx 0.02 U \), \( D_{el}^{\text{el}} \approx 0.4 U \).

In the compressible model, as pointed out in Ref. [17], the Mott critical endpoint will therefore occur at \( T_c > T_{el} \) and will be signalled by the divergence of \( K \). From (3), this happens when \( \chi_{el,\text{max}}^{\text{max}} \) has reached a large enough (but not divergent) value such that \( D_0 \chi_{el,\text{max}}^{\text{max}}(T_c) = B_0 v_0 / (\gamma^2 D_0) \). The corresponding critical half-bandwidth is \( D_c = D_{el}(T_c, U) \) and the critical cell volume is determined 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 \( T_{el} \) one can use the form (for \( T > T_{el} \)): \( \chi_{el,\text{max}}^{\text{max}} \approx \alpha_{el}(U) T_{el}^{\text{el}} / (T - T_{el}) \), which follows from mean-field theory [18]. Here, \( \alpha_{el}(U) = \alpha / U \) with \( \alpha \approx 0.5 \) in our calculations. Hence one obtains: \( \Delta T_c/T_c \equiv (T_c - T_{el})/T_{el} = \alpha [\gamma^2 D_0/(B_0 v_0)](D_0/U). \)

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. [17] 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 \( \rho \partial^2 \mu/\partial \rho^2 \) (with \( \rho \) 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, e.g. 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
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 the results of the calculations described in Ref. [7] - chromium-doped V$_2$O$_3$ – 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 the dependence on both polarization and direction of propagation.

Table. 1, one sees that the (dimension-less) combination $B_0 v_0/(\gamma^2 D_0)$ is large for both compounds ($\simeq 14.7$ for 2o3 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 2o3 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 2o3), the combination $B_0 v_0/(\gamma^2 D_0)$ 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 $K_0 v_0/v = 1 - (\gamma^2 D_0/B_0 v_0) D_0 \chi_{el}$. We emphasize that there is a significant difference between our choice of parameters and that made in Ref. [7] for 2o3: 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 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 2o3 and for several pressures. At the critical pressure $P = P_c$, the sound-velocity

| Parameter | V$_2$O$_3$ | OC |
|-----------|------------|----|
| $D_0$     | 1 eV       | 13 eV |
| $v_0$     | 100 Å$^2$  | 1700 Å$^2$ |
| $B_0$     | 2140 kbar  | 122 kbar |
| $\gamma$  | 3          | 5   |
| $B_0 v_0$ | 133 eV     | 129 eV |
| $U/D_0$   | 2.468      | 2.492 |
| $B_0 v_0/(\gamma^2 D_0)$ | 14.7 | 40 |

Table 1: Table of parameter values for 2o3 and the organic-conductor $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (OC)
according to the mean-field law \( s \propto (T - T_c)^{1/2} \) \((K \) diverges as \( 1/(T - T_c) \), as follows from Eq. 4). 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 \( \Delta s / s_0 \approx 10\% \) for \( P \approx 1.3P_c \), 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 \( \chi_{el} \) 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 \( 2\varepsilon_0 \). 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 \( D_{tr}^{el}(T) = D(v_{i,m}^{el}(T)) \) be the half-bandwidth for metal-insulator co-existence in the purely electronic problem at temperature \( T \). For \( T \) well below \( T_c \), the fractional differential volumes \( d\nu_{i,m}/v_0 \equiv (\nu_{i,m} - v_{i,m}^{el}(T))/v_0 \) of the coexisting insulating and metallic phases and the transition pressure \( P_{tr} \) in the presence of lattice coupling are approximately \( \delta \nu_{i,m}/v_0 \approx -\delta v_{i,m}/v_0 \approx \gamma (T_m - T_c)/2B_0v_0/D_0 \) and \( P_{tr} \approx B_0(D_{tr}^{el}(T) - D_0)/(\gamma D_0 - (\gamma D_0/v_0)(T_m + T_c)/2 \) (compare 2). Here \( T_{i,m} \) are \( T_c \) evaluated in the coexisting insulating and metallic phases respectively. These expressions are in good agreement with the numerical results reported above and in Ref. [14]. 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) \( T_c \) 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 \( 2\varepsilon_0 \). 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 \( T_{i,m} \).

We acknowledge discussions with S. Florens, L. de Medici, D. Jerome, E. Kats, G. Kotliar, P. Limelette, R. McKenzie, M. Poirier, A.M. Tremblay, P. Wizetek and with M. Rozenberg (who also provided some of his codes). This work has been supported by an Indo-French collaborative grant (IFCPAR-2404-1), by CNRS and by École Polytechnique.

[1] N. F. Mott, Metal-Insulator Transitions (Taylor and Francis, London, 1974).
[2] Imada, M., Fujimori, A., and Tokura, Y., Rev. Mod. Phys., 70, 1030 (1998).
[3] Limelette, P., Georges, A., Jérome, D., Wizetek, P., Metcalf, P., and Honig, J. M., Science, 302, 89-92 (2003).[4] Kagawa, F., Itou, T., Miyagawa, K., and Kanoda, K. Phys. Rev. B 69, 064511 (2004).
[5] A. Georges, G. Kotliar, W. Krauth and M. Rozenberg Rev. Mod. Phys. 68, 13 (1996).
[6] For a brief review of the Mott transition within DMFT, see e.g. A. Georges, S. Florens and T.A. Costi, J. Phys. IV (France) 114, 165 (2004) [cond-mat/0311520].
[7] P. Majmudar and H. R. Krishnamurthy, Phys. Rev. Lett. 73, 1525(1994);74, 3303(1995) (erratum); and Phys. Rev. B 52, R5479 (1995)
[8] Rozenberg, M. J., Chitra, R., and Kotliar, G., Phys. Rev. Lett., 83, 3498 (1999).
[9] A. Jayaraman, D. B. McWhan, J. P. Remeika, and P. D. Dernier, Phys. Rev. B 2,3751(1970).
[10] Y. Lin et al., Phys. Rev. B 58, R599 (1998).
[11] J. Merino and R. H. McKenzie, Phys. Rev. B 62, 16442 (2000).
[12] K. Frikach, M. Poirier, M. Castonguay, and K.D. Truong, Phys. Rev. B 61, R6491 (2000)
[13] D. Fournier, M. Poirier, M. Castonguay, and K.D. Truong, Phys. Rev. Lett. 90, 127002 (2003).
[14] Cyrot, M., and Lacour-Gayet, P., Sol. State Comm., 11, 1767 (1972).
This is appropriate for the organics. For $\text{ZnO}$, a more quantitative description (beyond the scope of this paper) would require the consideration of orbital degeneracy and two d-electrons.

W. A. Harrison *Electronic Structure and properties of Solids*, (W. H. Freeman, 1980).

M. Barmatz *Phys. Rev. Lett.* **24**, 651 (1970); M. A. Anisimov *Critical Phenomena in Liquids and Liquid Crystals*, (Taylor and Francis, London, 1991).

G. Kotliar., Sahana Murthy, and M. J. Rozenberg, *Phys.Rev.Lett.* **89**, 046401 (2002).

Limelette, P., Wzietek, P., Florens, S., Georges, A., Costi, T. A., Pasquier, C., Jérome, D., Mézière, C., and Batail, P., *Phys. Rev. Lett.*, **91**, 016401 (2003).