

**Enhancement of thermal expansion of organic charge-transfer salts by strong electronic correlations**J. Kokalj<sup>1,\*</sup> and Ross H. McKenzie<sup>2,†</sup><sup>1</sup>*J. Stefan Institute, SI-1000 Ljubljana, Slovenia*<sup>2</sup>*School of Mathematics and Physics, University of Queensland, Brisbane, 4072 Queensland, Australia*

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Organic charge-transfer salts exhibit thermal expansion anomalies similar to those found in other strongly correlated electron systems. The thermal expansion can be anisotropic and have a nonmonotonic temperature dependence. We show how these anomalies can arise from electronic effects and be significantly enhanced, particularly at temperatures below 100 K, by strong electronic correlations. For the relevant Hubbard model the thermal expansion is related to the dependence of the entropy on the parameters ( $t$ ,  $t'$ , and  $U$ ) in the Hamiltonian or the temperature dependence of bond orders and double occupancy. The latter are calculated on finite lattices with the finite-temperature Lanczos method. Although many features seen in experimental data, in both the metallic and Mott insulating phase, are described qualitatively, the calculated magnitude of the thermal expansion is smaller than that observed experimentally.

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**I. INTRODUCTION**

The thermal expansion coefficients of a wide range of strongly correlated electron materials exhibit temperature and orientational dependencies that are distinctly different from simple metals and insulators [1]. Materials that have been studied included heavy fermion compounds [2], organic charge-transfer salts [3–6], iron pnictide superconductors [7,8], and  $\text{LiV}_2\text{O}_4$  [9]. The Grüneisen parameter  $\Gamma$ , which is proportional to the ratio of the thermal expansion to the specific heat, can be two orders of magnitude larger than the values of order unity found for elemental solids [2], and may diverge at a quantum critical point [10]. For organic charge-transfer salts, the thermal expansion coefficients show anomalies at the superconducting transition temperature [11], at the Fermi-liquid coherence temperature, at the Mott transition [12], and strong nonmonotonic temperature and orientational dependence [3]. Anomalies have been recently observed also in a spin-liquid candidate material,  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> [5]. For a proper understanding and interpretation of these experimental results it is important to elucidate the electronic (apart from the phononic) contribution to the thermal expansion, particularly since it may dominate at low temperatures. Related electronic effects are seen in lattice softening near the Mott transition via sound velocity measurements [13,14]. The electronic contribution can also lead to the critical behavior of the thermal expansion close to the metal-insulator transition [4,15].

Here we study the electronic contribution to the thermal expansion, including its directional dependence, by modeling the electrons with a Hubbard model on the anisotropic triangular lattice at half filling, an effective model Hamiltonian for several families of organic charge-transfer salts [16]. Our analysis requires a connection between the Hubbard model parameters ( $t$ ,  $t'$ ,  $U$ ) and structural parameters (lattice constants) that can be deduced from electronic structure calculations and bulk compressibilities for which we use experimental values. The origin of the thermal expansion in our approach is the thermal

excitations of electrons, which can be traced back to the temperature dependence of the electronic free energy and should be distinguished from usual textbook results, where the thermal expansion is related to thermally excited phonons in an anharmonic potential [17]. This potential is dictated also by electronic energy, but is taken as an electronic ground state energy and not allowed to vary with temperature.

**A. Summary of results**

Our main results concerning the electronic contribution to the thermal expansion  $\alpha$  are as follows. (i) At low temperatures strong correlations can increase the thermal expansion by as much as an order of magnitude. (ii) A nonmonotonic temperature dependence of  $\alpha$  is possible. (iii) Significant orientational dependence is possible, including the expansion having the opposite sign in different directions. (iv) In the metallic phase the crossover from a Fermi liquid to a bad metal may be reflected in a maximum in the temperature dependence of  $\alpha$ . (v) In the Mott insulating phase a maximum in the temperature dependence of  $\alpha$  can occur, at a temperature comparable to that at which a maximum also occurs in the specific heat and the magnetic susceptibility. (vi) All of the above results are sensitive to the proximity to the Mott metal-insulator transition and the amount of frustration, reflected in the parameter values ( $U/t$  and  $t'/t$ ) in the Hubbard model.

Although we can describe many of the unusual qualitative features of experimental data for organic charge-transfer salts, the overall magnitude of the thermal expansion coefficients that we calculate are up to an order of magnitude smaller than observed. This disagreement may arise from uncertainties in how uniaxial stress changes the Hubbard model parameters, and uncertainty in the compressibilities including not taking into account the effect of softening of the lattice associated with proximity to the Mott transition.

**B. Specific experimental results we focus on**

We briefly review some experimental results that our calculations are directly relevant to. We only consider thermal expansion within the conducting layers. Anomalies are also

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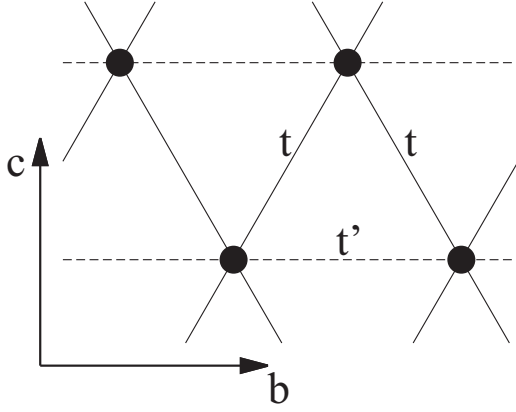


FIG. 1. Lattice and hopping integrals in the Hubbard model for  $\kappa$ -(BEDT-TTF) $_2$ X with  $X = \text{Cu}_2(\text{CN})_3$  and  $\text{Cu}(\text{NCS})_2$ . For  $X = \text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ , the crystal axes  $b$  and  $c$  should be replaced with  $c$  and  $a$ .

seen in the interlayer direction but are beyond the scope of this study. Figure 1 shows the relation between the anisotropic triangular lattice with the associated hoppings  $t$  and  $t'$ , and the intralayer crystal axes ( $b$  and  $c$ ) for  $\kappa$ -(BEDT-TTF) $_2$ X with anions  $X = \text{Cu}_2(\text{CN})_3$  and  $\text{Cu}(\text{NCS})_2$ . For  $X = \text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ , the crystal axes  $b$  and  $c$  should be replaced with  $c$  and  $a$ , respectively.

*Mott insulating phase of  $\kappa$ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$  (Fig. 1 in Ref. [5]).* For some temperature ranges thermal expansions in the  $b$  ( $t'$ ) and  $c$  ( $t$ ) directions have opposite signs. Thermal expansion is a nonmonotonic function of temperature.  $\alpha_b$  and  $\alpha_c$  have extremal values at about 60 and 30 K, respectively. For comparison, the magnetic susceptibility has a maximum at a temperature around 60 K [18].

*Metallic phase of undeuterated  $\kappa$ -(BEDT-TTF) $_2$ Cu [N(CN) $_2$ ]Br [Fig. 5(a) in Ref. [3]].* As the temperature decreases there is a crossover from a bad metal to a Fermi liquid [19].  $\alpha_a$  is a nonmonotonic function of temperature, with a large maximum around 35 K, which is comparable to the temperature at which there is a large change in slope of the resistivity versus temperature curve [20]. This is one measure of the coherence temperature associated with the crossover from the bad metal to the Fermi liquid [21].

*Mott transition in fully deuterated  $\kappa$ -(BEDT-TTF) $_2$ Cu [N(CN) $_2$ ]Br (Fig. 1 in Ref. [4] and Fig. 2 in Ref. [22]).* As the temperature decreases there is a crossover from a bad metal to a Fermi liquid to a Mott insulator (below 14 K).  $\alpha_c$  (direction of  $t'$ ) is much smaller than  $\alpha_a$  (direction of  $t$ ) and monotonically increases with temperature. In contrast,  $\alpha_a$  is a nonmonotonic function of temperature, with a large maximum around 30 K, which is comparable to the temperature at which the crossover from the bad metal to the Fermi liquid occurs. Also,  $\alpha_a$  is negative in the Mott insulating phase.

### C. Outline

The outline of the paper is as follows. In Sec. II we discuss how the thermal expansion is related to variations in the entropy through Maxwell relations from thermodynamics. In Sec. III the relevant Hubbard model is introduced

and it is shown how the temperature dependence of bond orders is related to the thermal expansion. We also discuss how the parameters in the Hubbard model depend on the lattice constants. Results of calculations of the bond orders using the finite-temperature Lanczos method are presented in Sec. IV. Comparisons are made between the calculated thermal expansion (for a range of parameter values) and specific experiments on organic charge-transfer salts. This is followed by a discussion of the remaining future challenges, while we summarize our main conclusions in Sec. V.

## II. GENERAL THERMODYNAMIC CONSIDERATIONS

For simplicity and to elucidate the essential physics, we first discuss the isotropic case. Experiments are done at a constant temperature, pressure, and particle number (assuming the sample is not connected to electrical leads and the particle density is controlled by chemistry). Thus, the Gibbs free energy  $G(T, P, N_e)$  is a minimum and satisfies

$$dG = -SdT + VdP + \mu dN_e. \quad (1)$$

From this we can derive a Maxwell relation implying that the volume thermal expansion is given by

$$\alpha(T) \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = -\frac{1}{V} \left( \frac{\partial S}{\partial P} \right)_T. \quad (2)$$

In calculations it is, however, easier to vary the volume than pressure and so we rewrite this as

$$\alpha(T) = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial S}{\partial V} \right)_T = \kappa_T \left( \frac{\partial S}{\partial V} \right)_T, \quad (3)$$

where  $\kappa_T$  is the isothermal bulk compressibility. Given the expression above, it is natural to expect strong thermal expansion effects when the entropy is large (e.g., at the incoherence crossover) and sensitive to volume-dependent parameters in the system (e.g., close to the Mott transition).

As the volume changes so do the lattice constants and the parameters in an underlying electronic Hamiltonian, such as the hopping integral  $t$  in a Hubbard model. To evaluate (3) we use

$$\left( \frac{\partial S}{\partial V} \right)_{T, N_e} = \frac{\partial t}{\partial V} \left( \frac{\partial S}{\partial t} \right)_{T, N_e}, \quad (4)$$

leading to

$$\alpha(T) = \kappa_T \frac{\partial t}{\partial V} \left( \frac{\partial S}{\partial t} \right)_{T, N_e}. \quad (5)$$

This equation for volume thermal expansion is applicable for the isotropic case, while orientational dependence of the thermal expansion can be obtained in a similar manner by generalizing  $VdP$  to  $-\sum_i d\sigma_i V^0 l_i / l_i^0$ . Here  $i = x, y, z$ ,  $d\sigma_i$  is the change of uniaxial stress,  $l_i$  is the length in the  $i$  direction, while  $V^0$  and  $l_i^0$  are the reference volume and length. Thermal expansion in direction  $i$  is then, similarly as Eq. (4), given by

$$\alpha_i(T) = \frac{1}{E_i} \frac{l_i^0}{V^0} \frac{\partial t}{\partial l_i} \left( \frac{\partial S}{\partial t} \right)_{T, N_e} + \dots \quad (6)$$

Additional terms involve different electronic model parameters instead of  $t$ , e.g.,  $t'$  and  $U$ . This expression is valid for a small Poisson's ratio, which, together with a more detailed derivation in terms of the grand potential ( $\Omega = G - PV - \mu N_e$ ), is discussed in Appendix A. We take the value of the Young's modulus  $E_i$  from experiment and later comment on the effect of the Mott transition on it. We estimate  $\partial t/\partial l_i$  from band structure calculations and we calculate  $\partial S/\partial t$  numerically with the finite-temperature Lanczos method (FTLM) [23,24]. It follows from the third law of thermodynamics that  $\alpha_i(T) \rightarrow 0$  as  $T \rightarrow 0$ .

### III. HUBBARD MODEL

We model our system with two Hamiltonian terms,  $\hat{H} = \hat{H}_{\text{el}} + \hat{H}_{\text{other}}$ , where  $\hat{H}_{\text{el}}$  describes electrons in the highest occupied band and their contribution to the thermal expansion is our main interest. We decouple these electronic degrees of freedom from others such as phonons and electrons in lower filled bands, and denote their contribution with  $\hat{H}_{\text{other}}$ . With this we neglected the direct coupling of electrons and phonons, but we keep the dependence of  $\hat{H}_{\text{el}}$  on the lattice constants  $a_i$ , which is in the spirit of a Born-Oppenheimer approximation. A further discussion of the approximations used and the origin of our electronic contribution to the thermal expansion is given in Appendix B.

We model the electrons in the highest occupied band with the grand canonical Hubbard model on the anisotropic triangular lattice,

$$\begin{aligned} \hat{H}_{\text{el}} &= - \sum_{i,j,\sigma} t_{i,j} c_{i,\sigma}^\dagger c_{j,\sigma} + U \sum_i \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow} - \mu \sum_{i,\sigma} \hat{n}_{i,\sigma} \\ &= -t \hat{T}_1 - t' \hat{T}_2 + U \hat{D} - \mu \hat{N}_e. \end{aligned} \quad (7)$$

Here,  $t_{i,j} = t$  for nearest-neighbor bonds in two directions and  $t_{i,j} = t'$  for nearest-neighbor bonds in the third direction (compare Fig. 1). Electronic spin is denoted with  $\sigma$  ( $\uparrow$  or  $\downarrow$ ).  $\hat{T}_1$  and  $\hat{T}_2$  denote bond order operators corresponding to  $t$  and  $t'$  hopping, respectively, and  $\hat{D}$  is the double occupancy operator. The chemical potential  $\mu(T)$  is determined by the required half filling, i.e., that  $\langle \hat{N}_e \rangle = N_e = N$ , where  $N$  is the number of lattice sites.  $\langle \dots \rangle$  denotes the thermal average.

Following Eq. (6), we relate the thermal expansion to  $(\frac{\partial S}{\partial x})_{T, N_e}$ , where  $x = t, t', U$ . Using the Maxwell-type relations we can write

$$\left( \frac{\partial S}{\partial t} \right)_{T, N_e, t', U} = \left( \frac{\partial \langle \hat{T}_1 \rangle}{\partial T} \right)_{N_e, t, t', U}, \quad (8)$$

$$\left( \frac{\partial S}{\partial t'} \right)_{T, N_e, t, U} = \left( \frac{\partial \langle \hat{T}_2 \rangle}{\partial T} \right)_{N_e, t, t', U}, \quad (9)$$

$$\left( \frac{\partial S}{\partial U} \right)_{T, N_e, t, t'} = - \left( \frac{\partial \langle \hat{D} \rangle}{\partial T} \right)_{N_e, t, t', U}. \quad (10)$$

With the above equations we related the thermal expansion to the variation of entropy with the electronic model parameters ( $t$ ,  $t'$ , and  $U$ ) or analogously to the  $T$  dependence of bond orders ( $\langle \hat{T}_1 \rangle, \langle \hat{T}_2 \rangle$ ) or double occupancy ( $\langle \hat{D} \rangle$ ), again at a fixed particle number.

#### A. Dependence of the Hubbard model parameters on the lattice constants

The expression (6) for the thermal expansion requires knowledge of the dependence of the Hubbard model parameters ( $t$ ,  $t'$ , and  $U$ ) on the lattice constants. Estimates of this dependence can be obtained from electronic structure calculations via methods such as the extended Hückel or density functional theory (DFT). Calculations using the former with the experimental crystal structure for  $X = \text{Cu}_2(\text{CN})_3$  give the following (compare Fig. 8 in Ref. [25]):

$$t = t_0 \left[ 1 - 4.9 \left( \frac{c - c_0}{c_0} \right) \right], \quad (11)$$

$$t' = t'_0 \left[ 1 - 8.7 \left( \frac{b - b_0}{b_0} \right) \right], \quad (12)$$

$$U = U_0 \left[ 1 - 3.5 \left( \frac{b - b_0}{b_0} \right) - 2.8 \left( \frac{c - c_0}{c_0} \right) \right]. \quad (13)$$

Here,  $c$  and  $b$  are in-plane lattice constants (compare Fig. 1), while reference values at 1 bar pressure are denoted with  $c_0, b_0, t_0, t'_0$ , and  $U_0$ . In general, the Hubbard model parameters depend on all lattice constants and structural parameters (including angles) [26–30] and all should be considered, but for simplicity we keep only the dependencies given above. They were obtained [25] by assuming that squeezing only reduces the intermolecular distance along the direction of the uniaxial stress, but does not induce rotations of molecules.

The actual dependence of the Hubbard  $U$  on the structure is subtle. In a crystal such as sodium or nickel oxide,  $U$  would simply be associated with a single atomic orbital and would not vary with lattice constant and stress, provided screening is neglected. Screening could introduce some dependence. However, for  $(\text{BEDT-TTF})_2X$  crystals, things are more complicated because  $U$  is not the Coulomb repulsion between two electrons in an orbital localized on a single molecule but rather on a molecular orbital on a dimer of BEDT-TTF molecules and the dimer geometry will vary with uniaxial stress. Furthermore, the estimate given in expression (13) is based on the assumption that  $U$  is solely given by the intradimer hopping integral  $2t_{b1}$ . However, that is only in the limit  $t_{b1} \ll \hat{U}_0$ , where  $\hat{U}_0$  is the Coulomb repulsion associated with a single BEDT-TTF molecule. Although this assumption is actually unrealistic [16], Eq. (13) is useful as an estimate, particularly because it is an upper bound for the dependence. Furthermore, we will see below that the  $U$  dependence of the entropy is much smaller than that of the  $t$  and  $t'$  dependence (compare Figs. 3 and 4) and so it turns out to make a relatively insignificant contribution to the thermal expansion. Hence, the above concerns are not particularly important.

The thermal expansion in the direction of the  $c$  axis can therefore be calculated from Eqs. (6), (8), and (11), related to the bond order ( $\hat{T}_1$ ), to give

$$\alpha_c = \frac{1}{E_c} \frac{c_0}{N V_{\text{luc}}} \frac{\partial t}{\partial c} \frac{\partial \langle \hat{T}_1 \rangle}{\partial T}, \quad (14)$$

where  $E_c$  is the Young's modulus in the  $c$  direction, and we have neglected the contribution from the double occupancy.  $V_{\text{luc}}$  denotes the volume of one unit cell. In a similar way, the

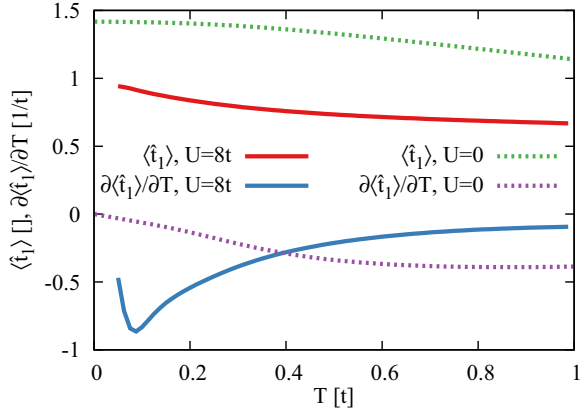


FIG. 2. (Color online) Strong correlations significantly enhance the electronic contribution to the thermal expansion through the temperature dependence of the bond order. This is demonstrated by comparing  $\partial \langle \hat{t}_1 \rangle / \partial T$  at low  $T$  for  $U = 8t$  with the noninteracting  $U = 0$  result.  $\langle \hat{t}_1 \rangle = \langle \hat{T}_1 \rangle / N$  is the average kinetic energy in certain directions. At low temperatures the enhancement is by an order of magnitude. The plotted quantity is related to the thermal expansion via Eq. (14) and to the stress dependence of entropy  $s = S/N$  via a Maxwell relation  $\partial \langle \hat{t}_1 \rangle / \partial T = \partial s / \partial t$ , Eq. (8). In addition, strong correlations also produce a strong nonmonotonic temperature dependence. Results are for  $t' = 0.8t$  and  $U = 8t$ , corresponding to the system in the Mott insulating phase [24].

main contribution to  $\alpha_b$  is given by the  $t'$  dependence on  $b$  according to Eq. (12) and the temperature derivative of  $\langle \hat{T}_2 \rangle$ ,

$$\alpha_b = \frac{1}{E_b} \frac{b_0}{NV_{\text{luc}}} \frac{\partial t'}{\partial b} \frac{\partial \langle \hat{T}_2 \rangle}{\partial T}. \quad (15)$$

These are the expressions we use below to calculate the thermal expansion. We stress that, by neglecting the double occupancy contribution or change of entropy with  $U$  and keeping only the kinetic energy terms, we are not solely dealing with band effects, since strong correlations at larger values of  $U$  also significantly enhance the kinetic terms as shown, e.g., in Fig. 2.

#### IV. RESULTS

In the following we discuss several numerical results obtained on  $N = 16$  sites by the finite-temperature Lanczos method (FTLM) [23], which was previously successfully used to determine a range of thermodynamic quantities for the same Hubbard model [24]. In particular, it was shown that one could describe the Mott metal-insulator transition and the crossover from a Fermi liquid to a bad metal.

##### A. Dependence of the entropy on Hubbard model parameters

In Fig. 2 we show the  $T$  derivative of  $\langle \hat{t}_1 \rangle = \langle \hat{T}_1 \rangle / N$ , namely,  $(1/N)(\partial \langle \hat{T}_1 \rangle / \partial T)_{t,t',U,N_e}$ , in the insulating phase ( $U = 8t$ ,  $t' = 0.8t$  [24]) and compare it to the result for noninteracting fermions ( $U = 0$ ). The strong difference shows that correlations can increase the electronic contribution to the thermal expansion by as much as an order of magnitude at low temperatures, and produce a nonmonotonic temperature dependence.

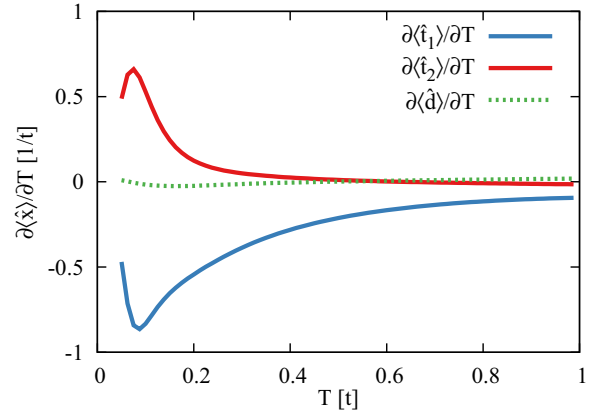


FIG. 3. (Color online) Strongly anisotropic temperature dependence of the bond orders  $\langle \hat{T}_1 \rangle$  and  $\langle \hat{T}_2 \rangle$ . Due to strong correlations and frustration, a small anisotropy (i.e., deviation from the isotropy of the triangular lattice) with  $t' = 0.8t$  leads to strongly anisotropic electronic contributions to the thermal expansion. This is seen by comparing  $\partial \langle \hat{t}_1 \rangle / \partial T = \partial s / \partial t$  and  $\partial \langle \hat{t}_2 \rangle / \partial T = \partial s / \partial t'$ , which are large and have opposite sign at low  $T$ . For the isotropic case ( $t' = t$ ) they have essentially the same  $T$  dependence, with only a factor of 2 difference coming from a number of bonds associated with the corresponding hopping. The double occupancy  $\langle \hat{d} \rangle = \langle \hat{D} \rangle / N$  shows a much weaker  $T$  dependence. Results are for the insulating phase with  $t' = 0.8t$  and  $U = 8t$  [24].

In Fig. 3 we show that an anisotropy value of  $t'/t = 0.8$  leads to strong anisotropy of the bond orders and their  $T$  derivative relevant for thermal expansion. This probably originates in strong frustration for the isotropic case with a large low  $T$  entropy, and therefore small changes in the anisotropy can lead to a strong change of bond orders which in the insulating phase is associated with spin correlations. In Fig. 3 we also show the  $T$  derivative of double occupancy which has smaller values than for bond orders. By the Maxwell relation in Eq. (10), our results in Fig. 3 are qualitatively consistent with the  $U$  variation of  $S$  shown in Fig. 4 of Ref. [24]. This relation of the entropy and negative values of  $(\partial \langle \hat{D} \rangle / \partial T)_{t,t',N_e}$  at low  $T$  was recently evoked [31,32] as a possible mechanism for adiabatic cooling in optical lattices.

In Fig. 4 we show results for a metallic case ( $t' = 0.8t$ ,  $U = 6t$  [24]) for which a Fermi-liquid-like behavior is expected at low  $T$ , leading to a linear-in- $T$  thermal expansion coefficient below the coherence temperature  $T_{\text{coh}}$ , above which a crossover to a bad metallic phase appears [33]. Such a linear-in- $T$  dependence originates in  $\alpha \propto -\partial S / \partial x$  (with  $x = t$ ,  $t'$ , or  $U$ ) and a linear-in- $T$  entropy  $S$ . Such a dependence of entropy and its variation with  $U$  is shown in Fig. 4 in Ref. [24]. Based on these considerations we include in Figs. 4 and 6 a linear extrapolation of the FTLM results to zero temperature.

##### B. Thermal expansion coefficients

We now present the results of calculations that can be compared to experimental data for the thermal expansion of specific organic charge-transfer salts. We used Eqs. (14) and (15) together with the following estimates for the parameter

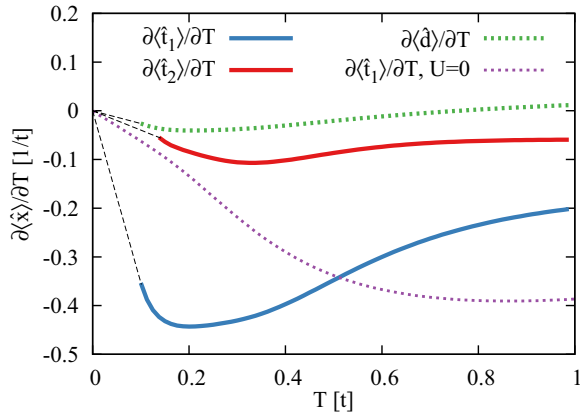


FIG. 4. (Color online) In the metallic phase ( $t' = 0.8t$ ,  $U = 6t$  [24]) the temperature dependence of the bond orders is strongly anisotropic and nonmonotonic. At low temperatures, a linear dependence is expected for a Fermi liquid, extrapolating to zero, in accordance with the third law of thermodynamics. This is shown by the dashed lines. The linearity ceases above the coherence temperature  $T_{\text{coh}}$ , where there is a crossover to a bad metal and where a maximum magnitude of the thermal expansion is observed. At low temperatures ( $T \simeq 0.1t$ ),  $\partial\langle\hat{t}_1\rangle/\partial T = \partial s/\partial t$  can be an order of magnitude larger than for the noninteracting ( $U = 0$ ) system.

values:  $V_{\text{1uc}} = 800 \times 10^{-30} \text{ m}^3$  from Fig. 5 in Ref. [30], and the temperature scale is determined by  $t = 50 \text{ meV}$  [24], estimated from density functional theory (DFT)-based calculations [29,30,34]. Estimates for the Young's modulus from x-ray determination of the crystal structure under uniaxial stress are  $1/E_c = (1/c_0)(dc/d\sigma_c) = 6.9 \times 10^{-11} \text{ Pa}^{-1}$  and  $1/E_b = (1/b_0)(db/d\sigma_b) = 5 \times 10^{-11} \text{ Pa}^{-1}$  from Table 1 in Ref. [28] for  $\alpha$ -(BEDT-TTF) $_2$ NH $_4$ Hg(SCN) $_4$ . Comparable values for isotropic pressure in  $\kappa$ -(BEDT-TTF) $_2$ Cu(NCS) $_2$  are given in Ref. [35]. We also use Eqs. (11) and (12) for estimates of  $\partial t/\partial c$  and  $\partial t'/\partial b$ .

In Fig. 5 we show an estimate of the thermal expansion coefficients for the insulating phase and parameters ( $t' = 0.8t$ ,  $U = 8t$ ) that correspond to  $\kappa$ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$ , and can be compared to experimental data shown in Fig. 1 of Ref. [5]. The calculated magnitude of about  $5 \times 10^{-6}/\text{K}$  at 50 K is approximately one fifth of the measured value. We discuss possible explanations for this discrepancy later. As in experiment, we observe a strong anisotropy with a maximum around 50 K, but the sign of the anisotropy is opposite to the experimental one at such  $T$ . Interestingly, a similar  $T$  dependence with the right absolute values is experimentally observed as a very low  $T$  ( $\sim 6 \text{ K}$ ) anomaly (see Fig. 2 in Ref. [5]), but for agreement our  $T$  scale would need to be reduced by a factor of 10, suggesting that this involves different physics beyond our calculations, such as a transition into some type of spin-liquid phase.

Our results in Fig. 5 have significantly different  $T$  dependencies for the thermal expansion coefficients in the  $c$  ( $t$ ) and  $b$  ( $t'$ ) directions due to anisotropy in the bond orders shown in Fig. 3, originating in the anisotropy  $t' = 0.8t$ , and since similar variation of the corresponding lattice constants  $b$  and  $c$  changes  $t$  and  $t'$  differently [Eqs. (11) and (12)]. Low temperature experimental results shown in Fig. 1 of Ref. [5] show a strong

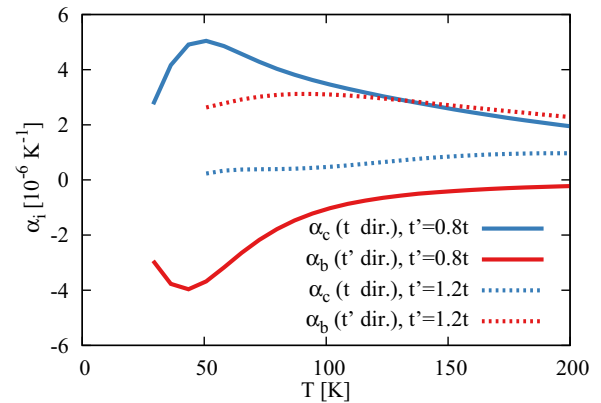


FIG. 5. (Color online) Temperature dependence of the thermal expansion in the Mott insulating phase. Note the nonmonotonic behavior and the large anisotropy. Indeed, in the  $b$  direction, thermal contraction rather than expansion occurs. The maximum magnitude occurs at approximately the same temperature as that for which the specific heat and magnetic susceptibility are a maximum (compare Fig. S1 of Ref. [24]). The solid curves ( $t' = 0.8t$  and  $U = 8t$ ) can be compared to experimental results for  $\kappa$ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$  shown in Fig. 1 in Ref. [5]. The results are quite sensitive to the parameter values and proximity to the Mott transition. This is seen by comparing the dashed curves ( $t' = 1.2t$ ). The parameter values used are described in the text.

difference in the  $T$  dependence between the  $b$  and  $c$  directions, suggesting that, if they originate from the electronic degrees of freedom, the proper electronic model should have a notable  $t$ - $t'$  asymmetry, or that the dependence of  $t$  and  $t'$  on the lattice constants  $c$  and  $b$  is strongly asymmetric. The anisotropy  $\alpha_c - \alpha_b$  in our results shown in Fig. 5 has the opposite sign to experiment. Taking  $t' \sim 1.2t > t$  changes the sign of our  $\alpha_c - \alpha_b$  results, making the comparison to experiment better. The change in the sign of the thermal expansion by increasing  $t'$  above the isotropic point ( $t' = t$ ) originates in moving away from maximal frustration (and therefore maximal entropy). This also involves moving away from the isotropic point for which the temperature dependence of both  $\langle\hat{T}_1\rangle$  and  $\langle\hat{T}_2\rangle$  is essentially the same (apart from a factor of 2) due to symmetry (compare Fig. 3).

In Fig. 6 we show our estimate of the electronic contribution to the thermal expansion for the metallic phase of organic charge-transfer salts. Similar to the experimental data, our results show a maximum at  $T \sim 60 \text{ K}$  and suggest that the experimentally observed anomalies (see Fig. 5 in Ref. [3]) could have an electronic origin. On the other hand, in Fig. 6 we observe a larger anisotropy ( $\alpha_c - \alpha_b$ ) for  $t' = 0.4t$  than for  $t' = 0.6t$ , which is in agreement with the experimentally observed larger ( $\alpha_a - \alpha_c$ ) for  $\kappa$ -(H $_8$ -ET) $_2$ Cu[N(CN) $_2$ ]Br ( $\kappa$ -Br) shown in Fig. 5(a) in Ref. [3] than ( $\alpha_c - \alpha_b$ ) for  $\kappa$ -(D $_8$ -ET) $_2$ Cu(NCS) $_2$  ( $\kappa$ -NCS) shown in Fig. 5(b) in Ref. [3]. We note that in  $\kappa$ -(H $_8$ -ET) $_2$ Cu[N(CN) $_2$ ]Br, it is estimated that  $t' \sim 0.4t$ , while in  $\kappa$ -(D $_8$ -ET) $_2$ Cu(NCS) $_2$ ,  $t' \sim 0.6t$  [29].

### C. Sign of the hopping integrals

We note that for comparison with the organics in Figs. 5 and 6 we used positive  $t$  and  $t'$  for the Hubbard model defined

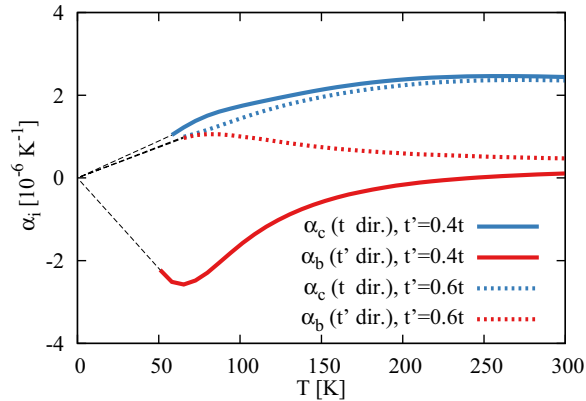


FIG. 6. (Color online) Temperature dependence of the thermal expansion in the metallic phase ( $U = 4t$ ). These results can be compared to Figs. 5(a) and 5(b) in Ref. [3], with the  $t' = 0.4t$  results being more relevant for Fig. 5(a) ( $\kappa$ -Br) and the  $t' = 0.6t$  results being more relevant for Fig. 5(b) ( $\kappa$ -NCS). The dashed lines are linear extrapolations to zero temperature, as expected for a Fermi liquid. Note that  $t' = 0.4t$  is closer to the Mott insulating phase than  $t' = 0.6t$  (compare Fig. 3 in Ref. [24]). Our  $\alpha_c$  ( $\alpha_b$ ) should be compared to the experimental data shown as solid squares (open circles) in Fig. 5 in Ref. [3]. Our calculated values are about five to ten times smaller than the measured values. As in experiment, we observe for  $T \sim 60$  K a larger anisotropy ( $\alpha_c - \alpha_b$ ) for  $t' = 0.4t$  than for  $t' = 0.6t$  with the right sign for  $t' = 0.4t$ . We observe a maximum magnitude at  $T \sim T_{\text{coh}} \sim 60$  K, suggesting that the experimental anomalies at  $T \sim 50$  K could have an electronic origin, although the observed increase (decrease) of  $\alpha_c$  for  $\kappa$ -Br ( $\kappa$ -NCS) at such a temperature is inconsistent with our results. We use the same parameter values and approximations as for Fig. 5.

by Eq. (7), while with respect to our definition, DFT-based calculations suggest they are both negative [29]. This is not a problem, since changing the signs of both  $t$  and  $t'$  corresponds at half filling to a particle-hole transformation and leads to the same result due to a double sign change, e.g.,  $\partial\langle\hat{T}_1\rangle/\partial T \rightarrow -\partial\langle\hat{T}_1\rangle/\partial T$  and  $\partial t/\partial c \rightarrow -\partial t/\partial c$ . On the other hand, Refs. [34,36] suggest negative  $t'/t$ , which could affect the results, but actually also  $t'/t \rightarrow -t'/t$  corresponds to a particle-hole transformation with an additional  $k$ -space shift of  $(\pi, \pi)$  (considering the equivalent square lattice with one diagonal hopping  $t'$ ). This again does not change the results for thermal expansion. On the other hand, such particle-hole transformations are important for the sign of the thermopower [37].

#### D. Future challenges

We now discuss several possible improvements to our theoretical description that we leave as future challenges. First, it is clear from the discussion of Eq. (6) and furthermore from the discussion of anisotropic effects in Appendix A and Eq. (A6) therein that for anisotropic materials, such as the organics, the stiffness tensor  $C_{ijkl}$  can be strongly anisotropic with several important elastic constants that are not known at a moment, but may be experimentally accessible. For example, adding Poisson's ratios to known Young's moduli and extracting also other elastic constants would allow for

a full tensor description. This is not just of interest for the study of thermal expansion, but also on its own, since the stiffness tensor also has notable electronic contributions. These have been already observed as lattice softening, e.g., via sound velocity [13,14], which becomes substantial (up to 50%) close to the metal-insulator transition (MIT), and in addition suggests critical behavior at the end of the first-order line, leading to a diverging  $\partial^2\Omega/\partial t^2$  related to  $\partial^2\Omega/\partial l_i^2$  [see Eq. (A5)]. One should, however, keep in mind that the MIT is experimentally observed to be weakly first order in the organics [38], but its order (and character of insulating phase) in a Hubbard model at half filling is still controversial [39–43]. In our analysis we do not include these lattice softening effects (reduced Young's modulus) close to the metal-insulator transition, but their inclusion would increase our  $\alpha_i$  by roughly a factor of 2, making the electronic contribution to  $\alpha_i$  larger and more important, and would improve the comparison to experiment (see in particular the discussion of Fig. 6).

Another challenge is to obtain the dependence of the Hubbard model parameters ( $t$ ,  $t'$ , and  $U$ ) on all lattice constants  $a_i$  and on all structural parameters, including the angles and orientation of molecules. These dependencies are not easy to obtain, and the simple Eqs. (11)–(13) could be greatly improved with more elaborate DFT calculations or studies such as in Refs. [26,27]. In particular, Fig. 2 in Ref. [27] shows that in various salts the different angle between ET molecules is directly connected to the lattice constants, which suggests that this angle is an important structural parameter and that it possibly varies also with temperature and applied stress. Therefore, DFT calculations, which would, in addition to intermolecular spacing, relax also the angles between molecules, could be valuable and present a future challenge. DFT could connect the changes in the  $H_{el}$  parameters to the changes in the structural parameters with the complete tensor. This would further facilitate the full tensor description of the electronic contribution to the thermal expansion and elastic constants.

For reasons of simplicity we considered the simplest possible Hubbard model. A further challenge is the inclusion of additional, possibly relevant, interactions and parameters in the microscopic model  $H_{el}$  [Eq. (7)]. The first candidates would be the nearest-neighbor repulsion  $\tilde{V}$ , which could have a substantial value and effect the electronic properties as discussed in Ref. [34], and dimerization  $\delta$  of the hopping parameters ( $t - \delta, t + \delta, t - \delta, \dots$ ) in a particular direction, which seems to play an important role in thermopower [20,37]. Other terms that might be considered are multiple bands (so the system is at quarter filling) and the electron-phonon couplings such as those considered by Mazumdar and collaborators [44]. We have also assumed that the thermal expansion is dominated by the contribution from itinerant electrons and that these are described by the Hubbard model. Relating the Hubbard model to the total energy of the system as described by density functional theory is subtle. Specifically, we have neglected any role played by the core electrons and the correlations associated with them. A full treatment of them would require calculations based on density functional theory and approximations such as local density approximation plus dynamical mean field theory (LDA+DMFT) [45].

## V. CONCLUSIONS

We have shown how the electronic contribution to the thermal expansion is related to the electronic degrees of freedom via the parameters ( $t$ ,  $t'$ , and  $U$ ) in a Hubbard model and temperature derivatives of known quantities (bond orders and double occupancy). The values of thermal expansion coefficients are further governed by the relation of model parameters to the lattice (structural) constants and by elasticity constants.

The electronic contribution to the thermal expansion is large, with a strong orientational and nonmonotonic temperature dependence. Furthermore, we showed that correlations strongly increase the electronic contribution, and by estimating it for organic charge-transfer salts, we showed that it can provide a qualitative understanding of experimental data for temperatures below 100 K. In particular, contrary to suggestions in Ref. [3], the anomalies around 50 K may not be lattice anomalies or structural phase transitions. Rather, they could originate from the electronic contribution, and be due to the bad metal–Fermi liquid crossover.

It should be pointed out that phononic contributions to the thermal expansion may also play an important role at low  $T$ , and we sketch some possible future steps in this direction in Appendix B. A relevant role of phonons is suggested by the large phononic contribution to specific heat (see Refs. [46,47] and the Supplemental Material of Ref. [24]) and in turn to entropy relevant for thermal expansion [Eq. (3)]. Therefore, the study of lattice vibrations (e.g., anharmonic effects, orientational dependence, or the Grüneisen parameter [17]) and the estimates of their contribution to the thermal expansion or stiffness tensor may aid our understanding.

## ACKNOWLEDGMENTS

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## APPENDIX A: ANISOTROPIC THERMAL EXPANSION

Here we discuss thermal expansion in terms of a grand potential  $\Omega$ , due to its simple connection to the electronic Hamiltonian

$$\exp(-\beta\Omega) = \text{Tr}[\exp(-\beta\hat{H}_{\text{el}})], \quad (\text{A1})$$

and its straightforward calculation within FTLM [23]. Thermal expansion coefficients are given by

$$\alpha_i \equiv \frac{1}{l_i} \left( \frac{\partial l_i}{\partial T} \right)_{P, N_e}, \quad (\text{A2})$$

where  $l_i$  is a length of a sample in the  $i$  ( $= x, y, \text{ or } z$ ) direction and can be exchanged also by a lattice constant  $a_i$ , and where we have denoted that experiments are done at a constant pressure ( $P$ ) and fixed electron number ( $N_e$ ). Since we are interested also in an orientational ( $i$ ) dependence, we first need to generalize the standard mechanical work  $-PdV$  to  $V^0 \sum_{i,j} \sigma_{ij} d\varepsilon_{ij}$ , with  $V^0$  being a reference volume,

while  $\sigma_{ij}$  and  $\varepsilon_{ij}$  are stress and strain tensors, respectively. However, we simplify our analysis by considering just normal stress and no shear deformations, taking only diagonal terms.  $\sigma_{ii} = \sigma_i$  is the uniaxial stress which equals  $-P$  for isotropic pressure and  $\varepsilon_{ii} = dl_i/l_i^0$ , with  $l_i^0$  denoting the reference length. With this we can write the mechanical work as  $\sum_i \sigma_i V^0 dl_i/l_i^0$ . This brings us to  $\Omega = \Omega(T, l_i, \mu)$  and  $d\Omega = -SdT + \sum_i \sigma_i V^0 dl_i/l_i^0 - N_e d\mu$ , where for a fixed  $N_e$  one needs to adjust the chemical potential,  $\mu = \mu(T, l_i, N_e)$ . From  $\Omega$  one can obtain the equation of state, which for usual work ( $-PdV$ ) reads  $-P = (\partial\Omega/\partial V)_{T, \mu}$ , but with our generalized work the three equations of state (for  $i = x, y, z$ ) are

$$\sigma_i = \frac{l_i^0}{V^0} \left( \frac{\partial \Omega}{\partial l_i} \right)_{T, l_{j \neq i}, \mu}. \quad (\text{A3})$$

Taking the full derivative of the equation of state for fixed  $N_e$  in the case of usual work ( $-PdV$ ), one obtains a differential equation of state  $-dP = [\frac{\partial}{\partial T} (\frac{\partial \Omega}{\partial V})_{T, \mu}]_{V, N_e} dT + [\frac{\partial}{\partial V} (\frac{\partial \Omega}{\partial V})_{T, \mu}]_{T, N_e} dV$ , which, when compared to  $dV/V = \alpha dT - \kappa_T dP$ , gives the expression for isothermal bulk compressibility  $\kappa_T^{-1} = V [\frac{\partial}{\partial V} (\frac{\partial \Omega}{\partial V})_{T, \mu}]_{T, N_e}$  and volume thermal expansion  $\alpha = -\kappa_T [\frac{\partial}{\partial T} (\frac{\partial \Omega}{\partial V})_{T, \mu}]_{V, N_e}$  in terms of  $\Omega$ . Similarly taking full differentials of Eq. (A3) leads to differential equations of state,

$$d\sigma_i = \frac{l_i^0}{V^0} \left[ \frac{\partial}{\partial T} \left( \frac{\partial \Omega}{\partial l_i} \right)_{T, l_{k \neq i}, \mu} \right]_{l_j, N_e} dT + \sum_j C_{ij} \frac{dl_j}{l_j^0}, \quad (\text{A4})$$

$$C_{ij} = \frac{l_i^0 l_j^0}{V^0} \left[ \frac{\partial}{\partial l_j} \left( \frac{\partial \Omega}{\partial l_i} \right)_{T, l_{k \neq i}, \mu} \right]_{T, l_{k \neq j}, N_e}. \quad (\text{A5})$$

From Eq. (A4) it is clear that a small change of strain  $dl_j/l_j^0 = \varepsilon_j$  leads to a small change of stress  $d\sigma_i = \tilde{\sigma}_i$ , which is, at constant temperature ( $dT = 0$ ), related by  $\tilde{\sigma}_i = C_{ij} \varepsilon_j$  or with the expanded indices  $\tilde{\sigma}_{ii} = C_{iijj} \varepsilon_{jj}$ , namely, by Hooke's law. Now we recognize  $C_{ij}$  or  $C_{iijj}$  as a stiffness tensor, which depends on the material's elastic constants, and has replaced  $\kappa_T^{-1}$ . The symmetry of  $C_{ij}$  is discussed in Appendix D.

The thermal expansion coefficients can now be expressed as

$$\alpha_i = \sum_j (C^{-1})_{i,j} \frac{-l_j^0}{V^0} \left[ \frac{\partial}{\partial T} \left( \frac{\partial \Omega}{\partial l_j} \right)_{T, l_{k \neq j}, \mu} \right]_{l_k, N_e}, \quad (\text{A6})$$

and, for clarity, we further simplify our calculation by assuming that Poisson's ratio is small, which makes  $C^{-1}$  diagonal,  $(C^{-1})_{i,j} = (1/E_i) \delta_{ij}$ , with  $E_i$  being the Young's modulus in the  $i$  direction.

Similarly one can show that the  $l_i$  and  $T$  derivatives of  $\Omega$  in Eq. (A6) can be replaced with the  $l_i$  derivative of entropy  $S$  (see Appendix C for more details),

$$\alpha_i = \frac{1}{E_i} \frac{l_i^0}{V^0} \left( \frac{\partial S}{\partial l_i} \right)_{T, l_{k \neq i}, N_e}. \quad (\text{A7})$$

Furthermore, since  $E_i > 0$ , the sign of  $\alpha_i$  is determined by the entropy derivative and therefore whether the change of  $l_i$  [or, in turn, some electronic model parameter—see

Eqs. (12) and (11)] increases or decreases the entropy. For maximally frustrated systems, the low- $T$  entropy is expected to be maximal, and therefore the sign of  $\alpha_i$  can help to determine whether one is with a certain parameter above or below the maximal frustration.

## APPENDIX B: DISCUSSION OF ADIABATIC APPROXIMATION AND ANHARMONICITY

Here we discuss our approach in terms of different adiabatic approximations. This allows us to comment in more detail on our approximations, different contributions, and possible future improvements. In particular, we discuss the effect of phonon anharmonicity and distinguish it from our approach.

In the usual Born-Oppenheimer approach one first solves the electronic part of the Hamiltonian for fixed ions (or nuclei) and then solves the ionic part, for which the electronic energy enters as the potential energy for ions. Here we allow for thermal excitations of electrons and therefore generalize the electronic energy to finite  $T$ . The total Hamiltonian can be written as  $H_{\text{tot}} = H_{\text{el}} + T_{\text{ion}} + V_{\text{ion-ion}}$ , where  $H_{\text{el}}$  describes electrons in the ionic potential and therefore depends on electronic coordinates  $r$  and also on the coordinates of ions,  $R$ .  $T_{\text{ion}}$  and  $V_{\text{ion-ion}}$  are the ionic kinetic and potential energies, respectively, both depending on  $R$ . We simply denote all the electronic (ionic) coordinates with  $r$  ( $R$ ). Solutions to the electronic part for fixed ions satisfy  $H_{\text{el}}|\psi_i^{\text{el}}(r, R)\rangle = E_i^{\text{el}}|\psi_i^{\text{el}}(r, R)\rangle$  and  $i$  goes over ground and also excited states. The total wave function of electrons and ions then can be expanded over sets of  $|\psi_i^{\text{el}}(r, R)\rangle|\psi_j^{\text{ion}}(R)\rangle$ , where  $|\psi_j^{\text{ion}}(R)\rangle$  denotes some basis states for the ions' positions. At finite  $T$ , we calculate the total grand potential  $\Omega_{\text{tot}} = \text{Tr}\{\exp[-\beta(H_{\text{tot}})]\}$  instead of the ground state energy,

$$e^{-\beta\Omega_{\text{tot}}} = \sum_{i,j} \langle \psi_j^{\text{ion}} | \langle \psi_i^{\text{el}} | e^{-\beta(H_{\text{el}} + T_{\text{ion}} + V_{\text{ion-ion}})} | \psi_i^{\text{el}} \rangle | \psi_j^{\text{ion}} \rangle. \quad (\text{B1})$$

Within the adiabatic Born-Oppenheimer approximation [48] we neglect the effect of the ions' kinetic energy on the electronic states,  $T_{\text{ion}}|\psi_i^{\text{el}}\rangle \sim 0$ , and by using commutation of  $H_{\text{el}}$  with  $V_{\text{ion-ion}}$  we can write

$$e^{-\beta\Omega_{\text{tot}}} = \sum_{i,j} \langle \psi_j^{\text{ion}} | e^{-\beta(E_i^{\text{el}} + T_{\text{ion}} + V_{\text{ion-ion}})} | \psi_j^{\text{ion}} \rangle. \quad (\text{B2})$$

By further identifying the electronic grand potential  $e^{-\beta\Omega_{\text{el}}} = \sum_i e^{-\beta E_i^{\text{el}}}$  we can calculate  $\Omega_{\text{tot}}$  as

$$e^{-\beta\Omega_{\text{tot}}} = \sum_j \langle \psi_j^{\text{ion}} | e^{-\beta(\Omega_{\text{el}} + T_{\text{ion}} + V_{\text{ion-ion}})} | \psi_j^{\text{ion}} \rangle. \quad (\text{B3})$$

With this we find that the ground state electronic energy  $E_0^{\text{el}}$  plays a potential energy role in the usual Born-Oppenheimer approximation at  $T = 0$ , and can now, at finite  $T$ , be generalized with  $\Omega_{\text{el}}$ , which depends on  $R$ , but also on  $T$ . This  $T$  dependence is important for the thermal expansion.

If we further neglect the kinetic energy of ions or their vibrations, which can be a reasonable approximation in some regimes, e.g., low  $T$ , the ions will take the positions in which the combined potential ( $\Omega_{\text{el}} + V_{\text{ion-ion}}$ ) is minimal. For finite external pressure ( $P$ ) the ions are actually close to these

positions, given by the equation of state,

$$-P = \frac{\partial\Omega_{\text{el}}}{\partial V} + \frac{\partial V_{\text{ion-ion}}}{\partial V}. \quad (\text{B4})$$

The electronic contribution to the thermal expansion then comes from the  $T$  dependence of  $\Omega_{\text{el}}$  and our result is related to the  $T$  dependence of  $\partial\Omega_{\text{el}}/\partial V$ , in particular,  $\partial^2\Omega_{\text{el}}/(\partial V\partial T)$  [cf. Eq. (A4) and corresponding text]. Furthermore, here one recognizes  $\partial^2\Omega_{\text{el}}/\partial V^2$  as the electronic part of the ion's potential harmonicity, which is reflected in  $\kappa_T$  or Young's modulus. It has been demonstrated [14] that the anomalies and their  $T$  dependencies in the sound velocity close to the Mott metal-insulator transition can be explained with just this electronic contribution, which gives firm support to the presented approach. Its  $T$  dependence also contributes to thermal expansion, but is due to the higher-order derivative with respect to  $V$  and therefore is even more involved and nontrivial than the one considered in this work.

Textbooks usually relate thermal expansion to the anharmonicity of the ionic potential, since thermally excited ionic vibrations in an anharmonic potential lead to displaced average ionic positions. In our case the electronic contribution to the anharmonicity is given by  $\partial^3\Omega_{\text{el}}/\partial V^3$  and is therefore a higher-order effect, highly nontrivial, and, in addition, has  $T$  dependence. We stress that this anharmonic origin of thermal expansion should be distinguished from our results related to the change of the equilibrium positions of the ions with  $T$ , simply because the electronic energy (and in turn the ionic potential) is  $T$  dependent. Textbooks usually neglect any  $T$  dependence of the electronic degrees of freedom.

Now we are in a position to discuss several possible improvements. The most natural next step would be to consider just the phononic contribution to the thermal expansion in which the electrons would not be thermally excited and the thermal expansion would then be given only by thermally excited phonons in an anharmonic potential. However, the ionic potential and its anharmonicity would be given also by the electronic ground state energy  $E_0^{\text{el}}$  depending on  $R$  or  $V$ . Its calculation for strongly correlated electrons is highly nontrivial. The next possible step would then be to have both electrons and phonons thermally excited, but still within the adiabatic approximation. However, the most comprehensive description would emerge by going beyond the adiabatic approximation and allowing for the coupling between electrons and phonons (vibrations), which is a difficult task mainly because the Hilbert space drastically increases and correlations do not allow for any simple reduction. How important and relevant any of these improvement are is hard to judge at this point without an explicit evaluation and therefore remain a future challenge.

## APPENDIX C: RELATION OF THERMAL EXPANSION TO ENTROPY VIA GRAND POTENTIAL

Here we show that the  $T$  and  $l_i$  derivative of  $\Omega$ , one at fixed  $N_e$  and the other at fixed  $\mu$ , appearing in Eq. (A6) for thermal expansion can be expressed as the  $l_i$  derivative of entropy.



Such a relation can be shown with the use of the Helmholtz free energy  $F$ , but here we show it by using  $\Omega$ :

$$\left[ \frac{\partial}{\partial T} \left( \frac{\partial \Omega}{\partial l_i} \right)_{T, l_{k \neq i}, \mu} \right]_{l_k, N_e} = \left( \frac{\partial^2 \Omega}{\partial T \partial l_i} \right)_{l_{k \neq i}, \mu} + \left( \frac{\partial^2 \Omega}{\partial \mu \partial l_i} \right)_{T, l_{k \neq i}} \left( \frac{\partial \mu}{\partial T} \right)_{l_k, N_e}, \quad (\text{C1})$$

$$- \left( \frac{\partial S}{\partial l_i} \right)_{T, l_{k \neq i}, N_e} = \left( \frac{\partial^2 \Omega}{\partial l_i \partial T} \right)_{l_{k \neq i}, \mu} + \left( \frac{\partial^2 \Omega}{\partial \mu \partial T} \right)_{l_k} \left( \frac{\partial \mu}{\partial l_i} \right)_{T, l_{k \neq i}, N_e}. \quad (\text{C2})$$

Since  $-N_e = (\partial \Omega / \partial \mu)_{T, l_i}$ , we can write

$$\left[ \frac{\partial}{\partial l_i} \left( \frac{\partial \Omega}{\partial \mu} \right)_{T, l_k} \right]_{T, l_{k \neq i}, N_e} = 0 = \left( \frac{\partial^2 \Omega}{\partial \mu \partial l_i} \right)_{T, l_{k \neq i}} + \left( \frac{\partial^2 \Omega}{\partial \mu^2} \right)_{T, l_k} \left( \frac{\partial \mu}{\partial l_i} \right)_{T, l_{k \neq i}, N_e}, \quad (\text{C3})$$

$$\left[ \frac{\partial}{\partial T} \left( \frac{\partial \Omega}{\partial \mu} \right)_{T, l_k} \right]_{l_k, N_e} = 0 = \left( \frac{\partial^2 \Omega}{\partial \mu \partial T} \right)_{l_k} + \left( \frac{\partial^2 \Omega}{\partial \mu^2} \right)_{T, l_k} \left( \frac{\partial \mu}{\partial T} \right)_{l_k, N_e}. \quad (\text{C4})$$

Using Eqs. (C3) and (C4) in Eqs. (C1) and (C2) makes it clear that both expressions [Eqs. (C1) and (C2)] are equal, and therefore  $\alpha_i$  in Eq. (A6) can be connected to the derivative of entropy.

#### APPENDIX D: SYMMETRY OF $C_{ij}$

By symmetry  $C_{ij}$  should equal  $C_{ji}$ , which is not directly seen from Eq. (A5) since, for example, the  $i$  derivative of  $\Omega$  is taken at fixed  $\mu$ , while the  $j$  derivative is taken at fixed  $N_e$ . Here, we show, for example, that  $C_{xy}$  given with Eq. (A5) obeys the symmetry. Keeping in mind that  $\Omega = \Omega(T, l_i, \mu)$  and for fixed  $N_e$ ,  $\mu = \mu(T, l_i, N_e)$ , we can write out the first term,

$$\left[ \frac{\partial}{\partial l_y} \left( \frac{\partial \Omega}{\partial l_x} \right)_{T, l_{k \neq x}, \mu} \right]_{T, l_{k \neq y}, N_e} = \left( \frac{\partial^2 \Omega}{\partial l_y \partial l_x} \right)_{T, l_{k \neq x}, \mu} + \left( \frac{\partial^2 \Omega}{\partial l_x \partial \mu} \right)_{T, l_{k \neq x}} \left( \frac{\partial \mu}{\partial l_y} \right)_{T, l_{k \neq y}, N_e}. \quad (\text{D1})$$

By using  $-N_e = (\partial \Omega / \partial \mu)_{T, l_i}$ , one obtains

$$\left[ \frac{\partial}{\partial l_x} \left( \frac{\partial \Omega}{\partial \mu} \right)_{T, l_i} \right]_{T, l_{k \neq x}, N_e} = 0 = \left( \frac{\partial^2 \Omega}{\partial l_x \partial \mu} \right)_{T, l_{k \neq x}} + \left( \frac{\partial^2 \Omega}{\partial \mu^2} \right)_{T, l_i} \left( \frac{\partial \mu}{\partial l_x} \right)_{T, l_{k \neq x}, N_e}. \quad (\text{D2})$$

Using this relation in Eq. (D1) and then further in Eq. (A5), one gets

$$C_{xy} = \frac{l_x l_y}{V} \left[ \left( \frac{\partial^2 \Omega}{\partial l_x \partial l_y} \right)_{T, l_{k \neq x}, \mu} - \left( \frac{\partial^2 \Omega}{\partial \mu^2} \right)_{T, l_i} \left( \frac{\partial \mu}{\partial l_x} \right)_{T, l_{k \neq x}, N_e} \left( \frac{\partial \mu}{\partial l_y} \right)_{T, l_{k \neq y}, N_e} \right]. \quad (\text{D3})$$

From this it is obvious that  $C_{xy} = C_{yx}$  and the symmetry is obeyed.

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