Thermally assisted ordering in Mott insulators

Hunter Sims,1 Eva Pavarini,2,3 and Erik Koch1,2,3

1Computational Materials Science, German Research School for Simulation Sciences, 52425 Jülich, Germany
2Institute for Advanced Simulation, Forschungszentrum Jülich, 52425 Jülich, Germany
3JARA High-Performance Computing, 52425 Jülich, Germany

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Ginzburg-Landau theory describes phase transitions as the competition between energy and entropy: The ordered phase has lower energy, while the disordered phase has larger entropy. When heating the system, ordering is reduced entropically until it vanishes at the critical temperature. This established picture implicitly assumes that the energy difference between ordered and disordered phase does not change with temperature. We show that for the Mott insulator KCuF₃ this assumption is strongly violated: thermal expansion energetically stabilizes the orbitally-ordered phase to such an extent that no phase transition is observed. This new mechanism explains not only the absence of a phase transition in KCuF₃ but even suggests the possibility of an inverted transition in closed-shell systems, where the ordered phase emerges only at high temperatures.

Mott insulators with orbital degrees of freedom often exhibit orbitally ordered phases [1]. There are two established explanations for this: (i) electron-phonon coupling induces cooperative Jahn-Teller distortions [2] that lead to orbital ordering or (ii) Kugel-Khomskii superexchange [3] gives rise to orbital order that leads to a cooperative lattice distortion. Since both mechanisms tend to result in the same type of ordering, identifying which one drives it is a ‘chicken-and-egg problem’ [4]. Even though they strongly differ, these two mechanisms have one fundamental aspect in common: Their hallmark is a conventional Ginzburg-Landau-type transition [3] between a low-temperature ordered structure and a symmetric high-temperature phase [3]. Here we show that this conventional picture overlooks a key aspect: Taking thermal expansion into account leads to a novel scenario, and to a third, unconventional, ordering mechanism. We find that, as consequence, the order is not necessarily destroyed by temperature. In fact, for the prototypical orbital-ordering perovskite KCuF₃ [3] we explain how thermal expansion favors the symmetry-broken phase with an order parameter that increases with temperature. The key feature of the new mechanism is the strong dependence of the energy gained by breaking the symmetry on the lattice constant, and ultimately, via thermal expansion, on temperature. We anticipate that this thermally-assisted ordering can operate even in closed-shell systems. This would result in an inverted Ginzburg-Landau transition, with symmetry-breaking above a critical temperature. These surprising conclusions are based on very general arguments. We thus expect that similar effects will play a key role in other ordering phenomena of totally different nature.

Following the seminal work of Kugel and Khomskii [2], the fluoride KCuF₃ is considered the prototype of an orbitally ordered material. Its structure [3], shown in Fig. 1, derives from a cubic perovskite with Cu in d⁹ configuration with one hole in the e₉ orbital surrounded by an octahedron of fluoride ions in a cage of potassium ions. The actual crystal shows a tetragonal compression, slightly lifting the e₉ degeneracy. The fluoride ions in the a-b plane move along the lines connecting the Cu ions such that long (ℓ) and short (s) bonds alternate in the x and y directions, leading to a cooperative Jahn-Teller distortion and a competing splitting of the e₉ orbital. The distortion pattern also alternates in the z direction, resulting in an antiferrodistortive orbital-ordering. The tetragonal distortion is parametrized by c/a√2 and the Jahn-Teller distortion by δ = (ℓ − s)/a√2.

The mechanism driving the distortion δ and orbital-ordering has been the subject of intense controversy. As early as 1960, Kanamori noted that the structure of KCuF₃ could arise from the cooperative Jahn-Teller effect [2]. Later, Kugel and Khomskii showed that orbital

![Figure 1](https://example.com/figure1.png)

FIG. 1. (Color online) Crystal structure of KCuF₃. Inequivalent atoms inside the 14/mcm unit cell (thick black lines) are shown in color (Cu: brown, F: green, K: violet). The additional atoms in grey show the pseudocubic setting in which the network of corner sharing octahedra becomes apparent. The pseudocubic axes are defined as x = (a + b)/2, y = (−a + b)/2, and z = c/2. For clarity lattice distortions are exaggerated twofold.
order in KCuF$_3$ can originate from electronic superexchange even in the absence of distortions [3]. As one of the first applications of the density-functional theory plus U method (DFT+U) [8], Liechtenstein et al. found that a Hubbard $U$ is necessary to stabilize the distorted structure and concluded that an electronic Kugel-Khomskii mechanism drives the transition. In the same year Towler et al. found that Hartree-Fock also gives reasonable agreement with experiment, despite the complete lack of correlations [9]. Eventually, the question was settled by density-functional theory plus dynamical mean-field theory (DFT+DMFT) calculations, which showed that Kugel-Khomskii superexchange alone can only account for orbital order below $T_{KK} \approx 350$ K [10], while experimentally it persists to much higher temperatures [2]. In fact, the transition to the undistorted high-temperature phase has never been seen experimentally, and the analysis of the crystal structure up to 900 K showed that, contrary to conventional wisdom, the distortion increases with temperature instead of vanishing above some critical value [11]. Applying hydrostatic pressure dramatically reduces the distortion as the lattice constant decreases [12], while expanding the lattice by chemical pressure, substituting K by Rb [13] or NH$_4$ [14], results in an increase of the distortion parameter $\delta$ following the same trend as in thermally expanded KCuF$_3$. All this points to the lattice constant as the key player in determining the size of the distortion (see Fig. 2).

To understand the role of the lattice, we have performed DFT+U calculations for KCuF$_3$ with the experimental lattice constants at different temperatures. Calculations were performed using the Vienna \textit{ab-initio} Simulation Package (VASP) [15] within the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof [16] to density functional theory using the projector augmented-wave (PAW) [17] pseudopotentials of Kresse and Joubert [18]. We apply onsite Coulomb interactions on the Cu 3$d$ orbitals through the “$+U$” correction of Liechtenstein et al. [8] with double-counting corrections in the fully localized limit.

It is known that DFT+U describes structural properties remarkably well [19]. We find that also the energy gained by moving the fluorine ions agrees with both experimental estimates [20] and calculations explicitly including many-body effects [21, 22]. Moreover, extracting the frequency of the $A_{1g}$ mode, we find excellent agreement with Raman data [23]. Our results are fairly independent of the model parameters $U$ and $J$, as long as they are large enough to open a gap. The main effect of increasing $U$ is to slightly increase the effective radius of the cation [24]. Fig. 3 shows the energy gained by distorting the lattice for the experimental unit cell parameters at increasing temperatures [11, 25] calculated using the established values $U = 7$ eV and $J = 0.9$ eV [3]. We find that the distortion $\delta$ increases with lattice constant in good agreement with the experimental values (see Fig. 2).

While our calculations reproduce the observed increase of the distortion very well, neither of the established theoretical mechanisms can explain it: The orbital superexchange coupling decreases with distance so that the Kugel-Khomskii mechanism weakens as the lattice expands [3]. The Jahn-Teller mechanism could in principle explain a distortion that increases with volume. Writing the energy gained by displacing the fluorine ions by $\Delta = (\ell - s)/2 = a \delta/\sqrt{2}$ from their symmetric position as $E_{JT}(\Delta) = -g \Delta + C \Delta^2/2$, where $g$ gives the split-
The complete failure of the established distortion mechanisms calls for a change of perspective. Instead of focussing on the displacement from the high-symmetry position, we consider the Cu–F distance. The shortest distance \( s \) should be given by when the ions touch. In fact, for KCuF\(_3\) it is practically independent of temperature \([11]\) so that the increase of \( \Delta \) is simply a consequence of thermal expansion. The same is true when applying pressure \([12]\), substituting K by Rb \([13]\), or NH\(_3\) \([14]\). We can make this picture quantitative by plotting the energy curves of Fig. 3 as a function of the Cu–F distance \( s \) (see Fig. 4): pushing the ions closer together than the optimal distance results in a strong repulsion — a Born-Mayer potential \([26]\).

This suggests a straightforward model: we describe \( E(\Delta) \) using a Born-Mayer repulsion energy \( E_{\text{BM}} = A \exp(-r_{\text{Cu-F}}/\rho) \), the Ewald energy \( E_{\text{Ewald}} \) of the periodic arrangement of ions, and a term \( E_{\text{CF}} = \Gamma - \sqrt{2} - \langle g\Delta \rangle^2 \) describing the crystal-field splitting of the \( e_g \) level due to the tetragonal compression and the displacement \( \Delta \). Since the ionic charges are practically independent of the lattice constant, as are the Born-Mayer coefficients \( A \) and \( \rho \), the couplings \( \Gamma \) and \( g \) are the only parameters that depend on the lattice constant. As expected, the crystal-field splitting scales as \( 1/a^4 \), while the change in Ewald energy can be approximated by \( -E_{\text{Ewald}}\Delta^2/2 \), where \( E_{\text{Ewald}} \) scales as \( 1/a^3 \). The resulting expression

\[
E_{\text{ionJT}}(\Delta) = \Gamma - \sqrt{2} - (g\Delta)^2 - E_{\text{Ewald}}\Delta^2/2 + 2Be^{-\alpha/\sqrt{2\rho}}(\cosh(\Delta/\rho) - 1)
\]

gives not only excellent fits to the DFT+U energies for KCuF\(_3\) as shown by the curves in Figs. 3 and 4 with the parameters given in Table I but also should describe strongly ionic Jahn-Teller-active compounds in general.

We can now explain the anomalous behavior seen in KCuF\(_3\). To simplify the discussion we neglect for the moment the tetragonal splitting, setting \( \Gamma = 0 \). The Cu\(^{2+}\) cation is fairly small, i.e., \( \rho \ll a/2\sqrt{2} \), so that the frequency about the undistorted position, \( \omega_{A_1g}^2 = \frac{d^2E(\Delta)/d\Delta^2}{\Delta=0} = 2Be^{-\alpha/\sqrt{2\rho}}/\rho^2 - E_{\text{Ewald}} \), is quite low. In a simple Jahn-Teller picture this would imply a very large distortion \( \Delta_{\text{JT}} \), that would bring Cu and F extremely close to each other. In reality, however, the ions repel strongly at short distance. Since this Born-Mayer repulsion increases exponentially, the distortion will be stopped at a Cu–F distance \( s_{\text{min}} \) that is practically independent of the lattice constant. The observed linear increase of the distortion with the lattice constant \( \Delta_{\text{min}}(a) \approx a/2\sqrt{2} - s_{\text{min}} \) is thus simply the consequence of a constant \( s_{\text{min}} \) (see the line in Fig. 2). At the same time the energy gained from the distortion increases with \( \Delta_{\text{min}} \). The large thermal expansion \( \alpha(T) \) thus stabilizes the distortion in KCuF\(_3\), explaining the absence of a transition to the undistorted structure. We note that in our model the frequency \( \omega_{A_1g} \) differs from the frequency of the \( A_1g \) Raman mode, which is given by the expansion about the minimum: \( \omega_{A_1g}^2 = \frac{d^2E(\Delta)/d\Delta^2}{\Delta=\Delta_{\text{min}}} \). The difference is due to the Born-Mayer potential, which makes the \( A_1g \)-mode quite anharmonic, in agreement with experiment \([23]\). The scenario of fixed \( s_{\text{min}} \) is not limited to KCuF\(_3\). In fact, Table 5 of Ref. [15] lists the short Cu–F distances \( s \) of thirteen materials of widely varying

| \( T \) (K) | \( a \) (\( \AA \)) | \( c \) (\( \AA \)) | \( \Gamma \) (eV) | \( g \) (eV/\( \AA \)) | \( E_{\text{Ewald}} \) (eV/\( \AA^2 \)) |
|---|---|---|---|---|---|
| 10 | 5.835 | 7.828 | 0.0620 | 2.195 | 20.059 |
| 300 | 5.852 | 7.841 | 0.0640 | 2.173 | 19.877 |
| 600 | 5.903 | 7.897 | 0.0677 | 2.112 | 19.342 |
| 900 | 5.950 | 7.954 | 0.0698 | 2.060 | 18.883 |

TABLE I. Model parameters for \( E_{\text{ionJT}}(\Delta) \) that fit the DFT+U curves calculated for KCuF\(_3\) with experimental lattice constants at different temperatures (Figs. 3 and 4). \( \Gamma \) increases with the tetragonal distortion, while \( g \) decreases with \( a \). The Born-Mayer parameters \( B = 9.88 \) eV and \( \rho = 0.2186 \) \( \AA \) are independent of the lattice constants. This is also true for the charges of the ions entering the Ewald energy: \( Z_{\text{Cu}} = 1.86e = 2Z_K = -2Z_F \).
structure and composition with Jahn-Teller-active CuF₆ octahedra. They all differ by less than 2%.

For larger cations, ω₀ will be harder, leading to smaller distortions and a more Jahn-Teller-like picture. There is, however, a crucial difference: ω₀ softens dramatically with the expansion of the lattice, leading to a robust distortion even as the temperature increases. Remarkably, this is what is actually observed in the tetragonal phase of another fluoride, KCrF₃, up to the volume-collapse transition at 973 K \cite{22}. The persistence of the distortion with increasing temperature is expected for all strongly ionic Jahn-Teller-active compounds with significant thermal expansion coefficients. This thermally assisted ordering mechanism should be particularly useful for engineering materials, where we want the symmetry-broken phase to survive to high temperatures \cite{28}. Moreover, it suggests an intriguing scenario: When a exceeds the critical value \(a_c = \rho^22\sqrt{\ln(2B/\rho^2C_{\text{Ewald}}(a_c))}\) the frequency \(\omega_0\) becomes imaginary so that even a system with a non Jahn-Teller-active cation would start to distort. When \(a_c\) is crossed in thermal expansion such a system could show an \textit{inverted} Ginzburg-Landau transition from a high-symmetry phase at low temperatures to an ordered high-temperature structure. Ideal candidates are compounds with large lattice constant and small B-site cation as shown in Fig. 5. While it might be difficult to find a material where \(a_c\) can be reached by thermal expansion alone, it is conceivable to additionally increase the lattice constant by strain \cite{29} or negative pressure \cite{30} to just beyond the critical value, so that this unusual pressure transition can be reached.

It turns out, then, that Ginzburg-Landau theory is oversimplified in that it assumes a temperature-independent electronic Hamiltonian. We have identified a striking example which highlights the failure of this standard model of symmetry breaking: in the Mott insulator KCuF₃ orbital-ordering is \textit{stabilized} by thermal expansion. In fact, this is just an instance of a more general principle: When the effective Hamiltonian describing symmetry breaking has a significant temperature dependence, we can expect to observe more exotic phenomena than predicted by Ginzburg-Landau theory.

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\[\text{FIG. 5. (Color online) Dependence of the calculated elastic constant } m\omega_0^2 \text{ for the distortion about } \Delta = 0 \text{ on the lattice parameter } a. \text{ For the open-shell systems the values are calculated by DFT+U with } U = 7 \text{ eV and } J = 0.9 \text{ eV for KCrF}_3 \text{ and RbCuF}_3, \text{ and } U = 6 \text{ eV and } J = 0.9 \text{ eV for KCrF}_3, \text{ while the closed shell CsZnF}_3 \text{ is already gapped without a Hubbard } U. \text{ Large filled circles indicate the experimental lattice constant at room temperature, open circles the DFT+U or DFT relaxed lattice constant, which are between 1–2% larger than the experimental values. For all compounds the elastic constant changes sign when the lattice constant gets large enough. The larger the cation, the larger the critical lattice constant } a_c. \text{ For the smallest, Zn, the relaxed structure is tantalizingly close to the value required for an inverted Ginzburg-Landau transition.} \]
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