Hidden-orders of uranium compounds

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Abstract

Hidden order is often discussed in strongly correlated electron systems. In many cases, it shows no magnetic responses, so that the order parameter is electric, but accompanies few lattice distortion. In the Jahn-Teller cases, the ordered state gains its energy by changing inter-site mixing strengths, leading a larger structural distortion with lowering symmetry. On the contrary, in strongly correlated electron systems, the strong intra-site Coulomb energy causes the the symmetry lowering. It is not necessary to bring the lattice distortion for lowering local site symmetry. In fact, lower symmetry of electronic state than the symmetry of the crystal structure can be found for UTe_2, UGe_2 similarly for URu_2Si_2.

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1 Introduction

The second order phase transition indicates lowering the symmetry of the system. In magnetic ordered states, the time reversal symmetry is broken. If the low temperature phase is not magnetic, the space symmetry is lowered. The change of the electronic state is often accompanied by lattice distortion, which can be usually detected by such as X-ray scattering measurement. When the distortion is very small, or cannot be detected within the range of experimental accuracy, such the ordering is called “hidden-order”.

Lattice distortion brings an increase in the energy of the lattice system, so that the electronic system should get much larger energy gains for the phase transition. Interatomic distances needs to change, in order to modify intersite mixing energy. Such changes usually brings lowering the symmetry of atomic arrangement, except the first order isostructural transition. The question arises whether it is possible that the electronic symmetry is lowered with the lattice symmetry unchanged.

Non-magnetic crystal structure belongs to one of 230 space groups [1]. The symmetry at an atom site belongs to one of 32 crystallographic point groups, which can be found as

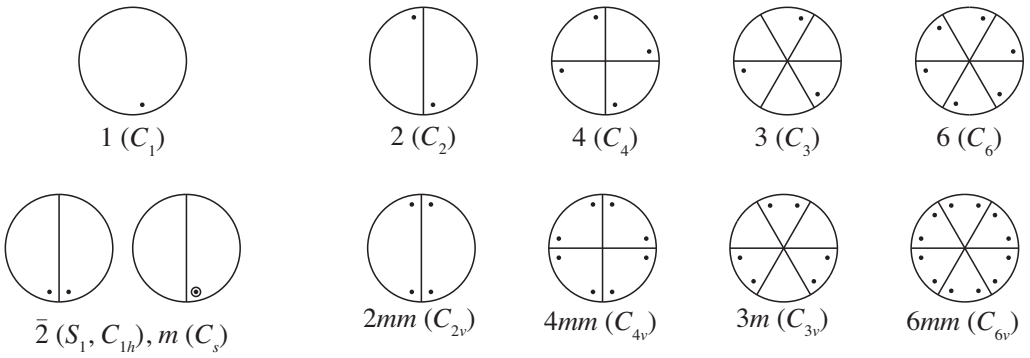

Figure 1: Stereograms for10 pyroelectric point groups. No symmetry operations lies on 1 (C_1), so that three position parameters (x, y, z) are needed, for the site with this symmetry. $\bar{2}$ (or m: two stereograms are the same from different view points) has the mirror plane, so that two position parameters are needed. The other 8 pyroelectric point groups needs one position parameter. The other 22 point groups, not shown here, are the fixed-point groups, where only one point does not move by all symmetry operations, so no parameter is needed to fix the atom position.

"site symmetry" with "multiplicity" and "Wyckoff letter", in the literature [1]. Among 32 crystallographic point groups, 10 pyroelectric point groups, shown in Fig. 1, need the value for a parameter to fix the atom position, because more than one point remain unmoved by any symmetry operations in pyroelectric point groups. A number of parameters is three for the point group 1 (C_1), two for $\bar{2}$ (S_1, C_{1h}) or m (C_s), one for the other pyroelectric point groups (in this paper, we call them "axial symmetry groups"). For the other 22 point groups, an atom position is uniquely determined, as there is only one fixed point by all symmetry operations. In this paper, such the point groups are called "fixed point groups".

In the second order phase transition, let us consider the sub-groups belonging to the same crystal system as in the higher temperature phase. There are seven crystal systems, which are classified by unit cell parameters, so that it is easily detected when the crystal system changes. The maximal sub-groups of the space groups are listed in [1]. If the symmetry of the crystal structure is lowered, either the symmetry of the atom positions is reduced or the number of equivalent atomic positions is reduced. If the number of equivalent atom positions is reduced, it is easy to be detected by experiments such as X-rays diffraction. Even if the site symmetry of the atoms is lowered, it cannot be found by non-resonant X-rays diffraction, unless the number of parameters for the atom site increases. If the number of the parameters does not change for all atom sites in the crystal, lowering symmetry of the electric state cannot be observed. The existence of such subgroups was discussed for a heavy fermion superconductor URu_2Si_2 [2], and will be discussed for UTe_2 and UGe_2 in the following sections.

2 Uranium on 2*mm* symmetry

Let us consider the case that the symmetry of uranium site is 2mm (C_{2v}) (see Fig. 1). UTe_2 is well known as a heavy fermion superconductor [3, 4]. The crystal structure of UTe_2 belongs to the space group $Immm$ (D_h^{25}, #71), and the site of uranium is 4i $mm2$ [5, 6]. UGe_2 also undergoes superconductivity in magnetic phase under pressure [7]. The crystal structure of UGe_2belongs to the space group $Cmmm$ (D_{2h}^{19}, #65), and the site of uranium is 4i $m2m$ [8]. Although C_2 rotation axis is along the c axis in UTe_2, along the y axis in UGe_2, respectively, the each point group is 2mm (C_{2v}), so that there is one parameter for the Wyckoff position.

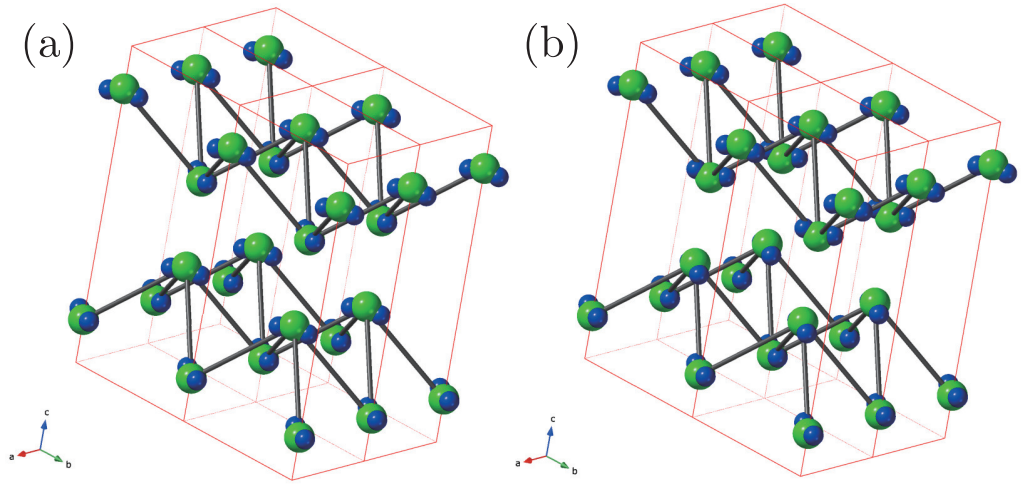

Figure 2: The schematic electric charge distribution of UTe_2 in hidden ordered states; (a) $I222$ (D_2^8, #23) and (b) $Pnnn$ (D_{2h}^2, #48). Green spheres show U atoms, and blue parts indicate the charge distribution of valence electrons of U ions. The nearest U atoms (dimer) form an electric octupole xyz, which is ferroic arrangement in (a), antiferroic arrangement in (b). Note that the center of the gray bar connecting two uranium atoms in (b) is the space inversion center of the symmetry, while space inversion is broken in (a).

There are two maximal subgroups of $2mm$ (C_{2v}), i.e., 2 (C_2) and m (C_s), which is equivalent to $\bar{2}$ (S_1 or C_{1h}). (See Fig. 1) 2 (C_2) is axial symmetry, so that one parameter remains for the Wyckoff position, while m (C_s) is plane symmetry with two parameters for the Wyckoff position. We could not learn the lost of the mirror symmetry on uranium site. However, we should investigate the change of symmetry on the site of the other atoms.

In UTe_2, two tellurium sites are $4j$ ($mm2$) and $4h$ ($m2m$) in $Immm$ (D_h^{25}, #71). The number of parameters in Wyckoff position on tellurium sites are unchanged, when the mirror symmetry is lost. The corresponding maximal subgroup is $I222$ (D_2^8,#23). However, there is one more possible subspace group. Body centering translation can be replaced by glide reflection, so that $Pnnn$ (D_{2h}^2, #48) provides the same site symmetry for each atom. In fact, the number of each atom in the primitive unit cell becomes doubled in $Pnnn$ (D_{2h}^2, #48), but it remains crystallographically equivalent. As the arrangement of atoms (crystal structure) is unchanged, the electric symmetry of $I222$ (D_2^8,#23) or $Pnnn$ (D_{2h}^2, #48) for UTe_2 is not distinguished from $Immm$ (D_h^{25}, #71), as shown in Fig. 2. Although the detailed neutron diffraction measurement and the careful analysis have been carried out [6], a resonant X-ray scattering measurement or similar measurement is necessary to unveil the real hidden ordered state.

In UGe_2, there are three germanium sites, i.e., $2b$ mmm, $2d$ mmm, and $4i$ $m2m$. When $4j$ $m2m$ on the uranium site becomes lowered to .2., the site symmetry mmm and $m2m$ of germanium sites becomes 222 and .2., respectively. mmm and 222 are both fixed point groups, then the positions are unchanged, $C222$ (D_2^6, #21) of UGe_2 is not distinguished from $Cmmm$ (D_{2h}^{19}, #65). In this case, C-centered translation is replaced by the proper glide reflection, the electric symmetry belonging to $Pban$ (D_{2h}^4, #50) is also the possible hidden ordered states.

The above consideration of the hidden ordered states has been applied to URu_2Si_2 [2, 9]. In the case of URu_2Si_2, uranium and ruthenium sites remain a fixed point group, Si

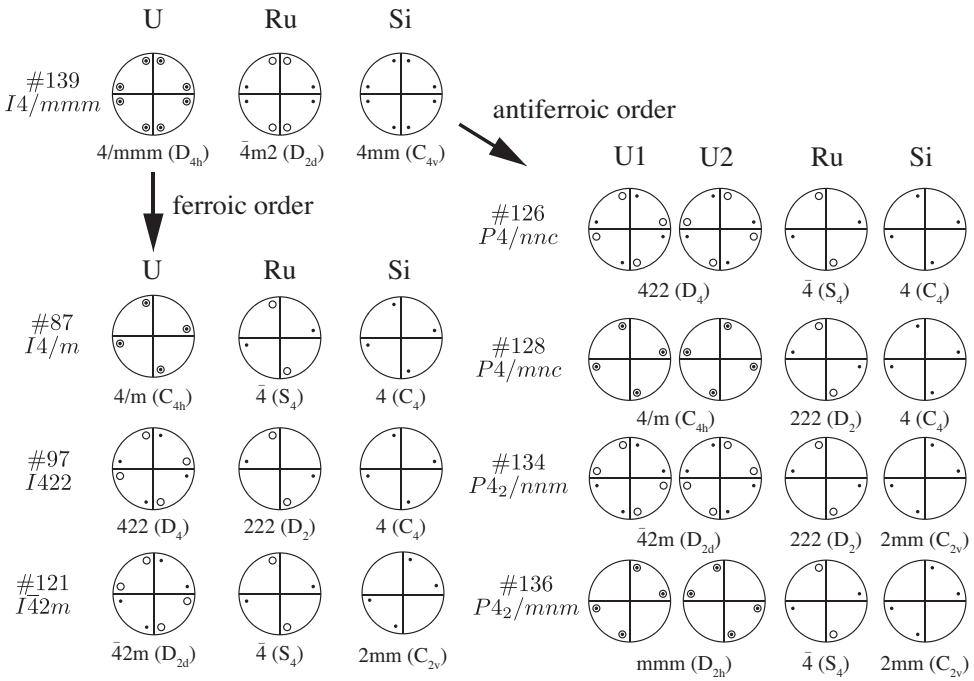

Figure 3: Possible subgroups for electric symmetry within the same crystal structure, and point groups of site symmetry for URu_2Si_2. All atoms are on the same site symmetry with typical stereogram, but two stereograms are shown for uranium sites in the anti-ferro case. U and Rh remains in the fixed point groups, and Si axial symmetry group.

an axial symmetry group. As discussed in [2], the space group $I4/mmm$ (D_{4h}^{17}, #139) has 8 IIa type maximal non-isomorphic subgroups (In [2], only k-subgroups are investigated). In the 4 subgroups any atoms U, Ru, and Si are not necessarily moved. The glide reflection keeps the three kinds of atoms in their crystallographic equivalent positions, instead of the body centered translation (1/2, 1/2, 1/2). Each subgroup corresponds anti-ferro electric multipole ordering. Including ferro electric ordering case, the site symmetry of ordered states are illustrated in Fig. 3. Among them, most promising subgroups is $P4/nnc$ (D_{4h}^{4}, #126), which demonstrates electric anti-ferro dotriacontapole ordering [9].

3 Discussion

What is emphasized in this paper is that electrons can take a lower symmetry than the symmetry of the crystal structure (symmetry of atom positions). A clear phase transition has been observed from the specific heat in URu_2Si_2, while there is in fact no such indication in UTe_2 and UGe_2. However, the transition might not have been reported, such as the transition temperature is high enough. Any lattice distortion lowers the transition temperature, but no distortion is needed in this case.

The hidden order discussed in this paper is that the mirror symmetry at the atomic position is lost and the electric charge distribution is tilted from the crystal axis. It can be expected that such a change is possible only for electrons with large angular momentum degrees of freedom, such as the $5f$ electron of uranium.

Recently, it is reported that URhSn, belonging to the space group of $P\bar{6}2m$ (D_{3h}^{3}, #189), undergoes two phase transitions, with 16K and 54K [10]. The ground state is ferromagnetic,

while the high temperature (54K) transition is non-magnetic with q = 0, where the primitive unit cell is unchanged [11]. 3-hold rotational symmetry remains keeping uranium atoms in crystallographically equivalent positions. But the site symmetry for uranium, $3g$ $2mm$ can lower to 2.., like in UTe_2, UGe_2. The corresponding space group is $P321$ (D_3^2, #150). The electric charge distribution on uranium site is tilted along the x axis in the ordered state, and such charge distribution recently observed by resonant X-ray scattering. Sn-NMR measurement indicating the lost of the mirror plane on tin (Sn) [12], also suggests $P321$ (D_3^2, #150). However, in this case, one new parameter appears, because one of two rhodium sites changes from fixed point group ($2c$ $\bar{6}$.. in #189) to axial symmetry group ($2d$ 3.. in #150). The parameter has not yet been determined, as it is expected to be very small.

There are two possible hidden ordered subgroups both for UTe_2 and UGe_2. The space groups are $I222$ and $Pnnn$ for UTe_2 and $C222$ and $Pban$ for UGe_2. Both cases are originally symmorphic space groups with space inversion symmetry, but the space inversion symmetry is lost in the former, and the latter is a non-symmorphic space group. To investigate the symmetry of superconducting state, it is very important to identify the symmetry of the normal state. Let us recall that the space groups of other uranium heavy fermion superconductors UBe_{13} ($Fm\bar{3}c$, O_h^6, #226)) [13], UPt_3 ($P6_3mmc$, D_{6h}^4, #194) [14], URhGe ($Pnma$, D_{2h}^{16}, #62) [15] , and UCoGe (the same as URhGe) [16] are non-symmorphic. $Pnnn$ for UTe_2 and $Pban$ UGe_2 provide a common background for heavy fermion superconductivity, as well as $P4/nnc$ for URu_2Si_2.

To obtain the electronic structure of such the hidden ordered states, it is necessary to take into account strong correlation effect. Conventional calculations with a local density approximation (LDA) obtain the electronic structure in the same symmetry as the lattice, as it is mean field approximation.

Recently, research on the Fermi surfaces on UTe_2 has been progressing from the observation of quantum oscillations [17]. A GGA+U calculation or an LDA calculations for $ThTe_2$ seem to predict safely the observed Fermi surfaces. The further investigation is desired to make the situation clear.

In $4f$ electron systems, such hidden ordered states can be realized, as well. Recent discovered unconventional superconductor $CeRh_2As_2$ [18] crystalizes in $CaBe_2Ge_2$-type structure [19], which belongs to $P4/nmm$ (D_{4h}^7, #129). In the crystal structure, two kinds of the electric multipole ordering within the same crystal structure are possible: anti-ferro quadrupolar ordering ($P\bar{4}2_1m$, D_{2d}^3, #113) and ferro hexadecapole ordering ($P4/n$, C_{4h}^3, #85). Both are non-symmorphic, and the former one ($P\bar{4}2_1m$) is non-centrosymmetric. Either hidden ordered state might correspond to the ordered state below T_o. The property of the multiphase superconductivity in $CeRh_2As_2$ may reflect the symmetry of hidden ordered states.

Interestingly, the hidden ordered state has been proposed for α-Ce [20]. Solid Ce is well known to show several phases in temperatures and pressures. Among them, α-Ce and γ-Ce are both face centered cubic structure ($Fm\bar{3}m$, O_h^5, #225). While γ-Ce is stable at room temperature and ambient pressure, it transforms to α-Ce at 0.8 GPa. [21] This so-called isostructural phase transition from γ to α phase is accompanied by a 16% volume collapse. It is claimed that α-Ce is a triple-$\boldsymbol{q}$ antiferro quadrupolar ordered statesα-Ce [20]. From γ to α transition in Ce, the crystal structure is unchanged, while the electronic space group is lowered from $Fm\bar{3}m$ to $Pa\bar{3}$ (T_h^6, #205), as shown in Fig.4. The phase transition changes to crossover under applied pressure. It implies that quadrupole moment in Ce fluctuates in high temperature, then gradually freezes in low temperature.

Let us consider about UTe_2 again. Although there is no report for the clear phase transition, fluctuating quadrupole moment in U ions in high temperature could form an octupole by two U, then freeze in low temperature. The octupoles can freeze in two ways; ferroic $Immm$ or antiferroic $Pnnn$. Two phases are able to coexist; one of them shows superconductivity and

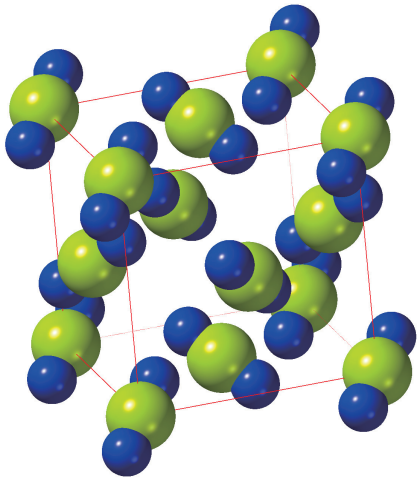

Figure 4: The schematic electric charge distribution of α-Ce. The crystal structure is FCC ($Fm\bar{3}m$, O_h^5, #225), represented by green spheres, while the electric symmetry is $Pa\bar{3}$ (a triple-$\boldsymbol{q}$ antiferro quadrupolar ordered state). The quadrupole is represented by blue parts. The site symmetry of Ce is $m\bar{3}m$ in $Fm\bar{3}m$ and $\bar{3}$ in $Pa\bar{3}$.

the other not. It is naturally understood that the residual specific heat may appears even in a superconducting sample [3], then reduces almost zero in a high quality superconducting sample [17]. The symmetry lowering can be detected in a high quality superconducting sample ($Pnnn$) by resonant X-ray measurements.

4 Conclusion

In this paper, it is pointed out that C_2 rotation degrees of freedom for the electric charges of uranium site of UTe_2 and UGe_2, do not violate the symmetry of the crystal structure. Depending on the combination of the local charge with lower symmetry, the obtained space group either breaks the space inversion symmetry or become non-symmorphic.

Although, no clear phase transition corresponding to the hidden order has been found in UTe_2 and UGe_2, a similar hidden order has been studied in URu_2Si_2. In URhSn, a phase transition where the electric charge of uranium is tilted from the crystallographic axes is observed. The large angular momentum degrees of freedom of $5f$ electrons may cause various physical properties in uranium compounds. Especially, the physical property of UTe_2 might be affected by lower symmetry electric state within the same crystal structure. With considering violation of the inversion symmetry at uranium site in many uranium compounds, the role of $6d$ electrons is important.

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