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Emergent phenomena in actinides: Multipolar order, correlation effects, and unconventional superconductivity

Phénomènes émergents dans les actinides : ordre multipolaire, effets de corrélation et supraconductivité non conventionnelle

Foreword

The actinide series is formed by the fourteen chemical elements with atomic number Z from 90 to 103, thorium through lawrencium. Except for the heaviest one, they are f-block elements, the 5f electronic shell being progressively filled with increasing Z.

Electrons in the open 5f shell, drawn tightly together by the huge electric charge of the nucleus, are in average close to each other, so that their mutual Coulomb repulsion is particularly strong. This fact has important consequences on the physical properties of actinide materials, as the correlated electron behaviour resulting from the strong interaction favours a tendency to localization, with a subsequent formation of large magnetic moments. However, hybridization with conduction electrons or with the electronic states of neighbouring atoms favours an opposite tendency towards itinerancy. This competition results in wobbly narrow-band 5f states that can be driven toward either localization or itinerancy by small perturbations. The complexity of actinides is largely due to this instability. Hybridization effects are also responsible for the appearance of fluctuations, damping of the magnetic dynamics, stabilization of heavy-Fermi-liquid ground states, or unconventional superconductivity. Moreover, when quantum fluctuations become large enough, magnetism melts and new kind of order may develop, unveiling new physics beyond the “standard” Landau–Fermi liquid theory [1].

A second source of complexity in actinide materials is related to relativistic effects, especially those associated with the electromagnetic interaction between the spin of the electron and the magnetic field arising from the electron’s orbital motion around the nucleus. Strong spin–orbit coupling and the presence of unquenched orbital degrees of freedom give rise to a rich variety of phenomena involving dipole and higher-order electromagnetic multipole interactions. These interactions influence the dynamics of the system and may also drive exotic phase transitions with *hidden* (non-dipolar) order parameters. Fluctuations of multipolar-order parameters, on the other hand, can provide the mediating bosons in exotic superconductors or lead to the emergence of novel heavy-fermion states [2].

This dossier of *Comptes rendus Physique*, devoted to exotic emergent phenomena exhibited by actinide compounds, opens with an article from Rebecca Flint and Piers Coleman describing how the realization of two-channel Kondo physics in heavy-fermion materials can lead to exotic symmetry-breaking order. They use their theory to propose original solutions for the long-standing problem of the hidden-order nature in URu_2Si_2 [3], and for the mechanism leading to unconventional superconductivity in $NpPd_5Al_2$ [4]. The former problem has inspired many different theoretical models, often contradicting each other, but a quantitative description of the full body of experimental evidence is not yet available. Below a $T_{HO} =$ 17.5 K, URu_2Si_2 exhibits a phase transition involving a large fraction of the spin entropy but, despite extensive investigations, the microscopic nature of the order parameter has not yet been identified. This hidden-order phase shows several unusual properties, one of which is the Ising-like behaviour of itinerant electrons. *The hastatic order*, proposed by Flint and Coleman to describe the ground state of URu_2Si_2, explains this behaviour by considering conduction electrons hybridized with a non-Kramers doublet (non-protected by time-reversal symmetry) through a mechanism that breaks both single and double time-reversal. The hybridization operator, mixing half-integer and integer spin states, carries itself a half-integer spin and transforms like a spinor. If these spinors select a direction in spin space because of the development of Kondo coherence, both time-reversal and spin-rotation symmetries are broken and hastatic order sets in. On the other hand, if a Kramers doublet interacts with one hole-like and one electron-like channel, the two-channel Kondo effect breaks charge conjugation symmetry to form a composite pair superconductor, where the localized spin screened by two conduction electrons is “part of the fabric” of the composite pairs. Such a mechanism is proposed to explain superconductivity in $NpPd_5Al_2$. The article by Flint and Coleman is an example of the role played by actinides in exploring new frontiers of physics. Maybe, it will be

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discovered that after all the hidden order in URu_2Si_2 is not hastatic, or that composite pairing does not occur in $NpPd_5Al_2$, but most probably the new theoretical ideas stimulated by the exotic behaviour of these compounds will find application in some other context.

The three following articles deal with a different class of phenomena, related to multipolar interaction and order. Actually, the first example of hidden order in actinides was the one manifested by NpO_2. In the 1950s, a phase transition was observed to occur at 25 K in this apparently simple oxide. It took almost 50 years to assess that the primary order parameter in this transition is a rank-5 magnetic multipole, a *triakontadipole*, accompanied by the order of electric quadrupoles and forming a non-collinear (3-**k**) ordered structure that preserves the cubic symmetry of the system [5]. A similar arrangement is observed also in the ordered phase of UO_2, but in that case the primary-order parameter is the magnetic dipole, which drives the ordering of electric quadrupoles and induces an internal distortion of the oxygen sublattice [6]. In uranium dioxide, quadrupolar interactions mediated by phonons (Jahn–Teller) and superexchange mechanisms strongly influence the microscopic lattice dynamics. Collective excitations of the quadrupolar ordered structure take the form of quadrupolar waves, representing a propagating pattern of charge densities in the form of a modulation of the quadrupole moments [7,8]. The article by Russel Walstedt, Yo Tokunaga, and Shin Kambe offers a brief review of the ground-state properties of actinide dioxide, with a special focus on the role played by NMR experiments in elucidating the quadrupole and magnetic multipole order. Paolo Santini's article describes the complex lattice dynamics of UO_2. Quadrupolar waves are not easily detected and had previously remained an elusive entity. The breakthrough in UO_2 was obtained by resorting to an artful experimental approach based on inelastic neutron scattering techniques. By measuring how a neutron beam is slowed down and deflected by a uranium dioxide crystal, experiments were able to probe the quadrupole dynamics by observing the uranium atomic spins in the act of "surfing" on quadrupolar waves. The signatures of quadrupolar waves are however subtle, and a combination of theory and experiment was crucial to the understanding of the phenomenology. The experiments on the oxides stimulated a theoretical attempt to describe the effects of multipolar interactions by first-principles methods, and the results of this attempt are described in the paper by Nicola Magnani, Michi-To Suzuki, and Peter Oppeneer.

Multipole fluctuations of itinerant 5f electrons are invoked in the article by Hiroaki Ikeda et al. to explain the hidden-order phase of URu_2Si_2. In this case, the hidden-order parameter is identified with rank-5 magnetic multipoles, as suggested by the divergent behaviour of the corresponding multipole susceptibility. The paper reviews recent progress in first-principle theoretical calculations allowing one to account for multipole correlations and magnetic anisotropy in itinerant heavy-fermion systems. Again, maybe triakontadipoles are not the order parameter in URu_2Si_2. Nevertheless, the achieved theoretical development represents an important contribution to the understanding of heavy-fermion systems.

The remainder of the dossier is dedicated to superconductivity in actinide materials. First, Jean-Christophe Griveau and Éric Colineau present a detailed review of the main features of superconducting compounds containing transuranium elements. The most prominent example of this class of materials is $PuCoGa_5$ [9], exhibiting a critical temperature $T_c = 18.5$ K, which is astonishingly high for a heavy-fermion compound (T_c in heavy-fermion systems is usually in the 1–2-kelvin range). The nature of the bosons mediating the formation of Cooper pairs and the symmetry of the superconducting order parameter in these compounds are still matters of debate. What is clear is that the conventional BCS theory and a simple mechanism based on electron–phonon coupling are not adequate to describe the properties of these materials. Yoshichika Ōnuki et al. review in their article the Fermi surface properties of selected heavy-fermion superconductors, and address the ferromagnetic pressure-induced superconductivity in UGe_2. Superconductivity in the presence of ferromagnetic order and the role of spin fluctuations and Fermi surface instabilities is reviewed by Dai Aoki et al., with emphasis on UGe_2, URhGe, and UCoGe. An article by Alexander Shick and Jindrich Kolorenc concludes the issue. This article describes electronic structure calculations combining the local density approximation approach with an exact diagonalization of the Anderson impurity model. The results show that in δ-Pu and $PuCoGa_5$ the 5f-local magnetic moment is compensated by a moment formed in the surrounding cloud of conduction electrons, leading to a singlet ground state for the Anderson impurity. This could have important consequences for the superconductivity in $PuCoGa_5$, suggesting that the unconventional d-wave symmetry superconducting state could be mediated by valence fluctuations, rather than antiferromagnetic ones [10].

The progress achieved in the field of actinide physics has been driven by a strict combination between theory and experiments. The latter have been crucial to unveil curious phenomena in transuranium compounds, and have been possible only thanks to the existence of specialized facilities equipped for performing experiments on radioactive materials under extreme conditions.

We hope that the range of these articles will stimulate the interest of the readers in actinide materials, a treasure box of fascinating physical phenomena that challenge and motivate fundamental scientific theory at large.

Avant-propos

La série des actinides est composée des quatorze éléments de numéro atomique Z compris entre 90 (thorium) et 103 (lawrencium). À l'exception de ce dernier, les actinides appartiennent au bloc f, leur couche électronique 5f se remplissant progressivement quand Z augmente.

À cause de l'énorme charge du noyau, les électrons 5f forment une couche compacte, restant en moyenne assez proches les uns des autres, de sorte que la répulsion coulombienne entre eux est considérable. Ceci influence profondément les propriétés des matériaux à base d'actinides, car le comportement des électrons corrélés résultant de cette forte interaction favorise une tendance à la localisation et à la formation d'un moment magnétique élevé. Cependant, l'hybridation avec les