PROGRAMME INSTITUTS ET INITIATIVES

Appel à projet – campagne 2021

Proposition de projet de recherche doctoral (PRD)

iMAT - Institut de Science des Matériaux

Intitulé du projet de recherche doctoral (PRD): Investigation of the crystal field in rare-earth titanate pyrochlores by resonant inelastic x-ray scattering

Directrice ou directeur de thèse porteuse ou porteur du projet (titulaire d'une HDR) :

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Unité de Recherche :
Intitulé : Laboratoire de Chimie Physique - Matière et Rayonnement
Code *(ex. UMR xxxx)* : UMR7614

École Doctorale de rattachement de l'équipe (future école doctorale de la doctorante ou du doctorant) : **ED388-ChimiePhysiqueChimieAnalytique Paris**

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1^e^ inscription et la quotité d'encadrement) : un doctorant inscrit en 2018, quotité d'encadrement 25%

Co-encadrante ou co-encadrant :

NOM : Juhin Prénom : Amélie
Titre : Chargé de Recherche ou HDR ☒
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Unité de Recherche :
Intitulé : Institut de Minéralogie, Physique des Matériaux et Cosmochimie
Code *(ex. UMR xxxx)* : UMR7590

École Doctorale de rattachement : **ED397-Physique Chimie des Matériaux**
Ou si ED non Alliance SU :

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1e inscription et la quotité d'encadrement) : une doctorante inscrite en 2020, quotité 100%

Co-encadrante ou co-encadrant :

NOM : Prénom :
Titre : Choisissez un élément : ou HDR ☐
e-mail :

Unité de Recherche :
Intitulé :
Code *(ex. UMR xxxx)* :

École Doctorale de rattachement : **Choisissez un élément :**
Ou si ED non Alliance SU :

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1e inscription et la quotité d'encadrement) :

Cotutelle internationale : ☒ Non ☐ Oui, précisez Pays et Université :

Selon vous, ce projet est-il susceptible d'intéresser une autre Initiative ou un autre Institut ?
☒ Non ☐ Oui, précisez Choisissez l'institut ou l'initiative :

Description du projet de recherche doctoral ***(en français ou en anglais) :***

Ce texte sera diffusé en ligne : il ne doit pas excéder 3 pages et est écrit en interligne simple.

Détailler le contexte, l'objectif scientifique, la justification de l'approche scientifique ainsi que l'adéquation à l'initiative/l'Institut.

Le cas échéant, préciser le rôle de chaque encadrant ainsi que les compétences scientifiques apportées. Indiquer les publications/productions des encadrants en lien avec le projet.
Préciser le profil d'étudiant(e) recherché.

Highly frustrated magnetic materials are sparking a considerable interest as candidates for exotic magnetic phases. Their understanding represents a major challenge in the field of materials science from both experimental and theoretical perspectives. A prime example are the pyrochlore titanates R2Ti2O7 where rare-earth R3+ ions and Ti4+ ions display a network of interpenetrating sub-lattices of corner-sharing tetrahedra. The magnetic frustration arises from inherent geometric considerations: the spins located at the corner of the tetrahedra cannot simultaneously satisfy the antiferromagnetic order. It was shown that the competition between interacting degrees of freedom might lead to enticing magnetic states in these materials. For R = Dy or Ho, at low temperatures, the spins on the R3+ sites feature a spin-ice state [see for instance A.M. Samarakoon et al., Nat. Comm. 11, 892 (2020)]. In this case two of the R3+ magnetic moments point into the tetrahedra and two moments point out of the tetrahedra. The attractiveness of spin-ice systems is strongly underlined by their potential as host candidates for topological excitations [L.D.C. Jaubert and P.C. W. Holdsworth, Nat. Phys. 5, 258 (2009)]. In contrast, the composition with R = Tb remains in a spin-liquid state even at lowest reachable temperatures [P. Bonville et al., Phys. Rev. B 84, 184409 (2011)]. Tb2Ti2O7 was recently shown to display electric dipole formation upon application of a magnetic field, thus establishing an appealing bridge towards multiferroicity [F. Jin et al., Phys. Rev. Lett. 124, 087601 (2020)]. A further member of the compound family, Yb2Ti2O7 received considerable attention as candidate for a model quantum spin ice [R. Applegate et al. Phys. Rev. Lett. 109, 097205 (2012)].

The ground state of the magnetically frustrated rare-earth sublattice depends on the interplay between the spin-exchange interaction and the single-ion anisotropy. Therefore the precise knowledge of the crystal electric field (CEF) acting on the R3+ is an essential ingredient for the understanding of magnetic behaviour. A rather straightforward way for gathering information on CEF is optical absorption [e.g. B.Z. Malkin et al., Phys. Rev. B 70, 075112 (2004) for Yb2Ti2O7]. In this case, optical spectroscopy grants access to the energies of spin-conserving ff orbital excitations. However, optical data turn out to be scarce and the extracted CEF parameters are subject to reconsideration by recent studies. A powerful alternative arises from inelastic neutron scattering (INS) studies. The latter probes CEF excitations with remarkable meV resolution and generally covers excited states within the first hundreds meV from the ground state [A. Bertin et al., J. Phys.: Condens. Matter 24 256003 (2012); M. Ruminy et al. Phys. Rev. B 94, 024430 (2016)]. Therefore, the INS data mainly deliver information on CEF states arising from the same atomic spectral term. We note however that INS is not restricted to spin-conserving transitions, excitations with $\Delta(S_z) = 1$ being allowed.

While the CEF characterization represents the bottleneck for the modeling of magnetic behavior, the information available through INS data display clear inconsistencies. For instance, the CEF energy levels issued by A. Bertin et al. and M. Rumny et al. show sizable discrepancies. These eventually arise from the limited number of ff states probed within the first 100 meV above the ground state, despite very high energy resolution. The magnitude of the CEF splittings is known to increase for higher-lying ff excited states. We therefore target to settle the debate by working out a reliable CEF description based on the examination of ff states situated at several eV above the ground state.

The objective of the present project is to cope with recent instrumental and theoretical developments to open a novel approach to resolve the CEF in R2Ti2O7 compounds. Our goal is to probe CEF excitations with resonant inelastic x-ray scattering (RIXS) at the N4,5 resonances of rare-earth ions. The latter correspond to 4d-4f electronic transitions and are reached with photon energies encompassing 150 to 200 eV for second half of the lanthanide series. The measurements will be interpreted in terms of model Hamiltonian calculations using the versatile frame provided by Quanty (for more information see quanty.org).

Over the last 15 years, RIXS evolved into a major spectroscopic approach for the exploration of strongly correlated materials [L.J.P. Ament et al., Rev. Mod. Phys. 83, 705 (2011)]. This development took roots with the advances in availability of 3rd generation synchrotron light sources and relies on substantial instrumental developments. The team at LCP-MR is an important actor in the field. In collaboration with colleagues at SOLEIL Synchrotron, we developed the AERHA spectrometer for RIXS studies with soft x-rays [S.G. Chiuzbaian et al., Rev. Sci. Instrum. 85, 043108 (2014)]. AERHA is a permanent end-station on the SEXTANTS beamline; it is open to the French and the international community through biannual calls for proposals. It is worth mentioning that AERHA is worldwide one of the very few instruments covering the energies of rare-earth N4,5 resonances. Its combined energy resolution of 50 meV is outstanding for this energy range.

At the N4,5 edges, the RIXS scattering process consists of two dipole-allowed transitions [4d10, 4fn] -> [4d9 4f(n+1)] -> [4d10, 4fn] involving the creation and decay of a virtual core-hole state [L.J.P. Ament et al., Rev. Mod. Phys. 83, 705 (2011); S.G. Chiuzbaian, Springer Proc. in Phys. 151, 185-210 (2013)]. By examining the energy transferred to the sample it becomes possible to probe the energy of orbital, magnetic and vibrational excitations. In centrosymmetric systems, the access to orbital excitations relies on the parity change imposed by the dipole-allowed transitions; the final states have the same parity as the ground state. For the measurement of magnetic excitations as well as for an orbital excitation with a change of multiplicity, it is important to note that the spin-orbit interaction in the intermediate 4d states removes the goodness of the spin quantum number, thus opening the scattering channels to final states with changes in spin multiplicity and spin projections. For resonances situated in this soft x-ray region, the overall scattering cross-section is very low and sufficient resolution in general means using small instrumental acceptance. The AERHA spectrometer was specially designed for optimal trade-off between energy resolution and instrumental transmission. The RIXS measurements will be performed at room temperature and at 25 K. The access to lower temperatures provides a mean to shed light on the spectroscopic contrast arising from the thermal population on low-lying CEF states. Large single-crystal samples (few millimetres) are provided by Dr. Haidong Zhou (Univ. Tennessee, Knoxville, USA).

We have performed a series of feasibility measurements and achieved propitious results. In case of Yb2Ti2O7 the data provide the first measurement of CEF excitations with RIXS for a rare-earth ion. The complementary of our approach is manifold. RIXS provides a way to probe ff excitations accompanied by $\Delta S_z = 0$, 1 or 2 and therefore gives insight to a broader type of transitions. The current detector sizes cover energy losses up to about 10 eV.

In contrast to optical or INS measurements, this represents the unique perspective of probing higher-lying excited states. For instance, our preliminary results on Tb2Ti2O7 indicate that the intensities of ff transitions situated above 2 eV are rather poorly described by the CEF parametrization available in the literature. As such, RIXS measurements impose tight boundary conditions for the description of the crystal field and therefore call for a state-of-the-art theoretical approach.

The theoretical expertise provided by the partner team at IMPMC represents a cornerstone of the current project. The N4,5 RIXS spectra will be simulated in the framework of Ligand Field Multiplet (LFM) theory using the Quanty program. LFM is a multi-electronic, semi-empirical approach that is well suited to calculate N4,4 RIXS spectra, since they involve transitions between localized electronic states with sizeable multielectronic effects (spin-orbit coupling, electron-electron repulsions and electron-hole interaction). CEF effects are described via a parametrized crystal field Hamiltonian which takes into account the local environment of the absorbing atom. Crystal Field parameters are then determined from the theoretical spectra yielding the best agreement to the experimental ones. Note that the IMPMC partner has a long standing experience with LFM theory applied to the calculation of various core level spectroscopies (Elnaggar et al. in H. Bulou, L. Joly, F. Scheurer (Eds), Mittelwihr 2018 lecture book, ISBN 978-3-030-64622-6, Elnaggar et al. Phys Rev Let 123, 207201 (2019), Vercamer et al. Phys Rev B 94, 245115 (2016), and works in collaboration with the developpers of the Quanty code (several international schools organized jointly).

The inclusion of CEF effects for the simulation of x-ray scattering spectra of rare-earth ions bears inherent complexity, only few examples being available [A. Amorese et al., Phys. Rev. B 93, 165134 (2016), M. Sundermann et al., Phys. Rev. Lett. 120, 016402 (2018)]. Our approach involves setting up new strategies for the scrutiny of large CEF parameters space.

The description of the CEF on the rare-earth sites in R2Ti2O7, in a joint experimental and theoretical study, will benchmark existing descriptions of these frustrated magnetic systems and fertilize the development of new perspectives.

Our project brings together two expert teams at Sorbonne Université with long-standing expertise in the study of strongly correlated materials. We collaborated in the past [J. Feng et al., J. Appl. Phys 122, 194101 (2017)] and are militating to establish a local network with theoretical and experimental competences in RIXS. The benefits of our collaboration will constitute a basis for further investigations of topical materials which are situated in the center of the iMAT initiative.

The PhD candidate, with a Master degree in chemical physics, physics or related fields, is expected to demonstrate experience in the operation of experimental setups, as well as interest in data analysis and spectra simulations. We fully advocate for equal participation in science for women.

Merci d’enregistrer votre fichier au format PDF et de le nommer :
«ACRONYME de l’initiative/institut – AAP 2021 – NOM Porteur.euse Projet »

Fichier envoyer simultanément par e-mail à l’ED de rattachement et au programme :
cd_instituts_et_initiatives@listes.upmc.fr avant le 20 février.