MERCUR Kooperation – Project description

Composite collective excitations in correlated quantum materials

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Zusammenfassung (max. 15 Zeilen)

Zusammengesetzte kollektive Anregungen bestehen aus mindestens zwei bekannten kollektiven Anregungen in Festkörpersystemen; diese Kompositanregungen sind bisher kaum untersucht worden. Sie stellen jedoch interessante neuartige Quantenobjekte dar, die Energie und Information transportieren und insbesondere in Hybridstrukturen, die räumlich strukturiert aus mehreren Materialien bestehen, wichtig sind. Auch in Volumenmaterialien sind Kompositanregungen zentral, nämlich in der Nähe von Phasenübergängen und bei koexistierenden Ordnungsparametern. In dieser MERCUR-Kooperation soll das Gebiet der Kompositanregungen in Volumenmaterialien erschlossen werden. Dazu werden experimentelle Modellsysteme wie $NbSe_2$ und Fe(Se,S,Te) mit verschiedener chemischer Zusammensetzung hergestellt, charakterisiert und ihre Anregungen mit zeitaufgelöster Terahertz-Spektroskopie gemessen. Parallel wird der theoretische Rahmen für ein Verständnis der Kompositanregungen geschaffen, der auch Vorhersagen und Vorschläge für Experimente erlaubt. Supraleitende kollektive Moden wie die Higgs-, Leggett-, Baradasis-Schrieffer-Moden und ihr Wechselspiel mit Phononen und magnetischen Anregungen werden in linearer und nicht-linearer Antwort untersucht.

Current state of research and our preliminary works

The notion of collective excitations in many-body physics refers to objects which do not center around individual particles, but involve a cooperative, wave-like motion of many particles in the system simultaneously. This behavior is governed by the global interaction among the constituent particles; best known examples in solid state physics are phonons in a crystal lattice, spin waves or Goldstone excitations in a magnetically ordered systems, and Higgs (amplitude) excitations of a charged superfluid. The emergence of collective excitations and their space-time dynamics in correlated quantum materials with complex interplay of charge, spin, and lattice degrees of freedom (such as unconventional superconductors or, more recently, materials for quantum computation, and energy conversion) is a subject of growing interest in the scientific community, because it provides deep insight into the strength and spatial distribution of interactions and correlations in these systems [Guistino2020].

Collective behavior, in particular, lies at the heart of emergent phenomena in many-body systems with various structural, magnetic, and electronic instabilities and, eventually, phase transitions. Experimentally detecting and theoretically describing the interactions of the collective bosonic excitations with the fermionic quasiparticles, or the interactions among the bosonic excitations leads to understanding of a given many-body problem. Until recently, most of theoretical and experimental investigations of the dynamics of collective excitations in quantum materials have been focused on their charge, spin or vibrational origin. At the same time, in correlated quantum materials novel types of the so-called *composite collective excitations* form due to the complex entanglement of spin, charge, orbital as well as lattice degrees of freedom. These excitations present new challenges in their fundamental understanding and unique perspectives in using them for potential applications.

Contrary to the well-known example of the polariton, which is a hybrid state of a quantum of light (i.e. photon) with solid state excitations in a semiconductor, these novel types of *composite collective excitations* occur either in a homogeneous bulk quantum material or in heterostructures featuring different quantum materials. In the bulk, they occur due to near-degeneracy and competition of various symmetry-broken quantum states, such as the superconducting phase, and charge or spin density waves with accompanying structural instabilities. Although in heterostructures some progress has been made in creating and controlling those composite collective excitations, such as magnon polaron formation at the intersection of the magnon and phonon dispersions in a nanopatterned magnetic structure [Godejohann2020], or skyrmion-vortex topological defects in chiral magnet-superconductor heterostructure [Petrovic2021], much less is understood about the features of the composite collective excitations in bulk correlated quantum materials. Nevertheless, there are several recent experimental [Wu2017, Grasset2021] and theoretical [**P6**] indications of the existence of such composite collective excitations in iron-based superconductors due to a delicate interplay of superconducting, magnetic and structural (often dubbed 'nematic' to stress the electronic origin of the transition) instabilities, which need to be properly understood.

The overall goal of our MERCUR Kooperation is to experimentally investigate and to theoretically understand *composite collective excitations* in bulk quantum materials using unconventional superconductors as an example in and out of equilibrium. Our experimental tool in this endeavor is a broad range of experimental techniques, including high-resolution transport and thermodynamic probes, as well as time-resolved optical pump-probe spectroscopy and temperature dependent X-ray diffraction on femtosecond time scales. On the theory side, our aim is twofold. On the one hand, we intend to understand the experimental findings qualitatively and quantitatively on the corresponding energy (time) and spatial scale using modern theoretical tools. On the other hand, we want to predict non-equilibrium behavior of the *composite collective excitations* in regimes which are presently becoming accessible. A prominent example is fifth harmonic generation, which can be used to reveal the nature of the composite collective excitations by comparison to experimental results obtained in linear response and by third harmonic generation. This second route shall also enable us to suggest particularly interesting experiments for future investigations.

With the goal stated above we plan to interconnect experimental and theoretical approaches to investigate the composite collective states, their quantum dynamics and relaxation, and the interactions that mediate them. We will concentrate our study on two paradigmatic quantum materials. The first example will be layered $NbSe_2$, which displays a charge density wave transition at 33 K and a transition to a multiband conventional s-wave superconductor below $T_c = 7$ K. The presence of the coupling between the charge density wave excitations and the amplitude (Higgs) fluctuations of the superconducting order parameter has been detected within linear response Raman spectroscopy [Measson2014] where it was found that the Higgs mode couples linearly to the electromagnetic vector potential, which is not possible in usual superconductors without charge density wave. Hence this finding represents an important indication for the possible formation of composite collective modes.

$NbSe_2$ can thus be considered a platform material for observing *composite collective excitations* and will be our first "drosophila". Nevertheless, it is a conventional superconductor and has the drawback that it cannot be easily tuned by changing the chemical composition. In order to extend the range of our study to unconventional superconductivity, we will therefore also investigate the FeSe system and its isovalently substituted variants, where Se is partially replaced by either S or Te. This system – having been investigated intensely over the last few years – is an ideal platform for the study of unconventional superconductivity intertwined with exotic electronic order, which can be sensitively tuned via chemical or physical pressure [Watson2015, **Sprau2016, P1, P5**]. Namely, FeSe is one of the most prominent host systems for the so-called electronic nematic order, whose manifestation includes a tetragonal-to-orthorhombic structural transition at 90 K, and a superconducting transition at $T_c = 9$ K, most likely driven by orbitally selective magnetic fluctuations. Thus the Fe(Se,S,Te) system will be our second "drosophila". The comparison of $NbSe_2$ with FeSe will enable us to contrast also the interactions of soft acoustic with soft optical phonons related to the CDW and nematic transitions, respectively, with superconductivity and will therefore be highly insightful. Further, S or Te substitution of FeSe can suppress the nematic order gradually and has a complex effect on superconductivity (see Fig. 1). The behavior displayed in the phase diagram hints at a close entanglement of nematic and superconducting degrees of freedom. Very likely, these two competing phases display composite excitations formed from the generic excitations of the nematic and the superconducting phase as the system is tuned across a rich phase diagram.

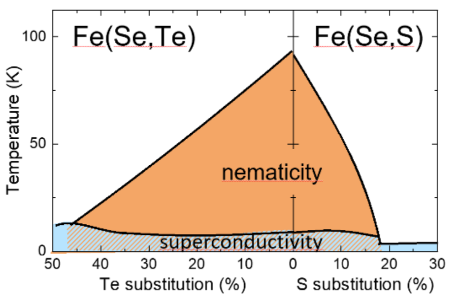

*Figure 1: Temperature-composition phase diagram of chemically substituted FeSe. [Mukasa2021, **Chibani2021**].*

Experimental approach to composite excitations

The two experiment PIs are newly appointed professors at Bochum (Böhmer) and Dortmund (Wang). They have accumulated experience on the study of strongly-correlated systems in various compounds featuring near-degenerate or intertwined orders, such as iron-based superconductors, using a wide range of experimental techniques ranging from sample growth, low-temperature transport, and high-resolution thermodynamic probes to various spectroscopies under tunable external conditions.

The Böhmer group has performed extensive research on intertwined and interacting collective ordering phenomena in the iron-based superconductors. For example, the group made diverse contributions to the study of FeSe. This includes the growth of single crystals of FeSe [**Böhmer2016**], up to a record high sulfur content, which formed the basis of numerous experimental results obtained for example via optical, NMR and Raman spectroscopy [**Chinotti2018, Wiecki2018, Chibani2021**]. In particular, the relation between different types of order (nematic, superconducting, magnetic) has been studied with chemical substitution and pressure as tuning parameters via transport [**Tanatar2016**], thermodynamic [**Böhmer2013**, **Böhmer2015I**] and diffraction [**P3, Böhmer2019**] techniques. The group has also prominently investigated nematicity in various iron-based systems via high-resolution thermal expansion and elastic modulus measurements [**P2, Böhmer2015II**], see Fig. 2, as well as elastotransport [**Wiecki2020, Wiecki2021**], which allows a unique view of the nematic order parameter and how it is intertwined with superconductivity. Notably, their intimate coupling results in a dramatic feedback effect of superconductivity on the nematic order parameter and the related soft elastic mode.

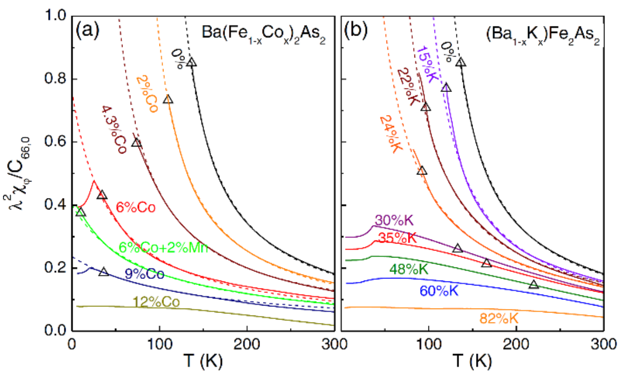

Figure 2: Nematic susceptibility of (a) electron- and (b) hole-doped $BaFe_2As_2$ iron-based superconductors inferred from shear-modulus measurements [**P2**].

The experiment group in Dortmund (Wang) has adopted the technique of terahertz spectroscopy to study quantum phenomena in various quantum many-body systems. The experimental technique is rapidly developing and has been shown to be a very powerful tool to study collective excitations in many-body systems. For instance, fractionalized magnetic excitations and many-body magnon bound states were revealed in low-dimensional quantum magnets by using this technique [**Wang2017, Wang2018, Wang2019**]. The Wang group has also investigated linear and nonlinear dynamics in *s*-

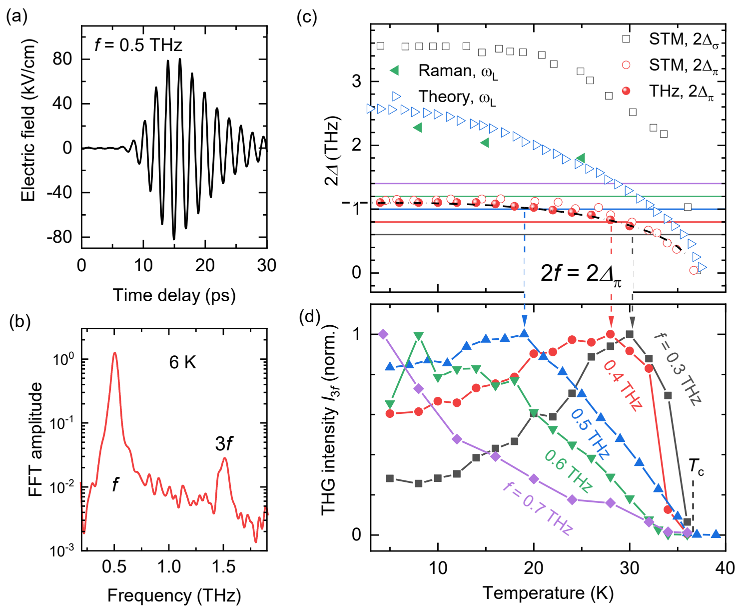

Figure 3: Third harmonic generation (THG) in MgB_2. (a) Electric field of 0.5 THz pump pulse in time domain. (b) Spectrum of the generated radiation from the sample at 6 K. (c) Temperature dependence of superconducting gaps for the σ and π bands (squares and circles) [Iavarone2002]. The horizontal solid lines indicate $2f$ for f = 0.3, 0.4, 0.5, 0.6, and 0.7 THz, respectively. (d) The corresponding normalized THG intensity I_{3f} as a function of temperature, measured through two band-pass filters of $3f$. The vertical dashed lines indicate the peak positions in the temperature-dependent curves, where the corresponding resonance condition $2f = 2\Delta_\pi$ is fulfilled simultaneously, [***Kovalev2020***].

and *d*-wave superconductors, such as iron-based superconductors [**P10,P11**], high-T_c cuprates [**P12**], and MgB_2 [**Kovalev2020**], with single-, two-, or multi-bands. In the linear response regime the superconducting gap and correlation effects can be sensitively probed [**P10,P11,P12**]. We can also reveal novel features, such as the Higgs amplitude mode, by optically driving a system out of equilibrium [**P12, Kovalev2020**]. In particular, nonlinear response (such as high-order harmonic generation) has been demonstrated to provide characteristic properties of the non-equilibrium states [**P12, Kovalev2020**]. As shown in Fig. 3, the temperature-dependent curves of the third harmonic generation in MgB_2 exhibits a band-selective resonance feature (see Fig. 3c,d) [**Kovalev2020**]: A resonance peak is only observed when the resonance condition $2f = 2\Delta_\pi$ is fulfilled for the π band. This points to an enhanced third harmonic generation due to the Higgs amplitude fluctuations of the π band in the dirty limit [Murotani2019, Haenel2021].

Theoretical approach to composite excitations

Correlated quantum materials and their collective excitations remain at the center of theoretical activities due to the fascinating variety of observed effects and the universality of the underlying theoretical ideas. Over the last years, the theory PIs (Eremin and Uhrig) have acquired significant expertise in studying collective excitations in correlated quantum materials using complementary theoretical methods.

The theory group in Dortmund (Uhrig) has clarified conceptual issues of pumped fermionic systems [**Kalthoff2018**, **Uhrig2019**] and has studied pumped *s*- and *d*-wave superconductors with one [**P8**, **Schwarz2020**] and two bands [**P9**] using the density matrix approach. Fig. 4 displays the characteristic frequencies of the Higgs and the Leggett (interband phase) mode in the latter case as a function of the relative interband coupling ν. Analogous calculations are planned in this Kooperation. Moreover, the group has a long-standing experience in nematic (orientational) order in strongly correlated Mott insulators [**P7**, **Stanek2011, Hafez2016**] and in signatures of the amplitude mode in ordered quantum antiferromagnets [**Powalski2015**]. The influence of small magnetic skyrmions on the topology of superconducting excitation has been studied recently [**Bedow2020**].

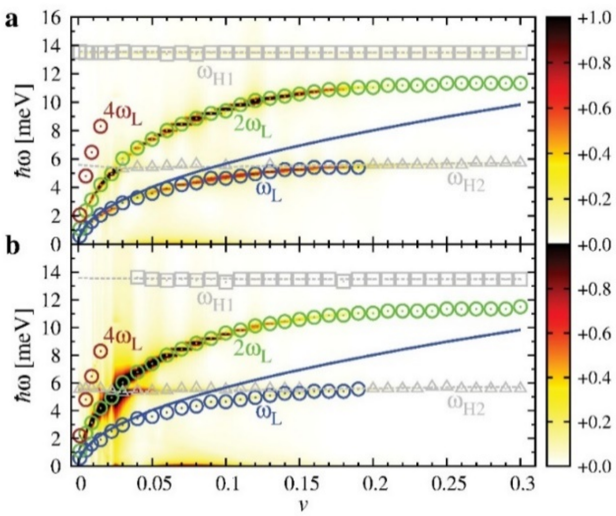

*Figure 4: Spectral features resulting from the Higgs mode in band 1 (H1) and band 2 (H2) and the interband Leggett mode (L) vs. the interband coupling ν, from Ref. [**P9**].*

The theory group in Bochum (Eremin) has studied recently the phase diagram in and out of equilibrium in multiband unconventional superconductors with the main emphasis on the various aspects of the competition between different quantum phases and their collective excitations [**P4,Böker2019,Böker2020,P5,P6**] including nematicity and superconductivity, driven by the non-

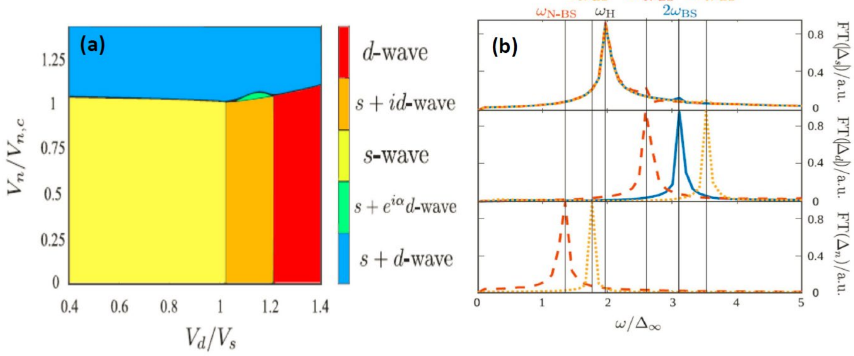

Fig. 5 (a) Superconducting zero temperature phase diagram of the interacting model, see Ref. ***[P6]****, featuring a competition between the electronic nematic order, and the s-wave and the d-wave superconducting orders, respectively. (b) Collective modes in the s-wave superconducting ground state with Higgs mode and the composite nematic Bardasis-Schrieffer mode.*

phononic mechanism. In particular, in Ref. [**P6**] the signatures of collective modes with competing nematic and *s*- and *d*-wave superconducting orders were considered. In the rotationally symmetric state, see Fig. 5, it was shown that the Bardasis-Schrieffer mode, corresponding to the subdominant pairing, hybridizes with the nematic collective mode and merges into a single composite collective mode, with the mixing vanishing only close to the phase boundaries. The group also studied heterostructures featuring chiral magnets in proximity to a superconductor **[Dahir2019, Dahir2020]** including coupled topologically robust magnetic skyrmions.

Own publications (according to the DFG standard, we only list 3 own publications for every PI; other publications by the PIs are listed in the Reference and marked in bold.)

[**P1**] **Anna E. Böhmer** and Andreas Kreisel, *Nematicity, magnetism and superconductivity in FeSe,* Journal of Physics: Condensed Matter **30**, 023001 (2017) (invited Topical Review)

[**P2**] **A. E. Böhmer**, P. Burger, F. Hardy, T. Wolf, P. Schweiss, R. Fromknecht, M. Reinecker, W. Schranz, and C. Meingast, *Nematic susceptibility of hole-doped and electron-doped BaFe2As2 iron-based superconductors from shear modulus measurements*, Phys. Rev. Lett. **112**, 047001 (2014)

[**P3**] K. Kothapalli*, **A. E. Böhmer***, W. T. Jayasekara, B. G. Ueland, P. Das, A. Sapkota, V. Taufour, Y. Xiao, E. E. Alp, S. L. Bud'ko, P. C. Canfield, A. Kreyssig and A. I. Goldman, *Strong cooperative coupling of pressure-induced magnetic order and nematicity in FeSe,* Nature Communications **7**, 12728 (2016)

[**P4**] M.A. Müller, P.A. Volkov, I. Paul, and **I.M. Eremin**, *Collective modes in pumped unconventional superconductors with competing ground states*, Phys. Rev. B **100**, 140501(R) (2019)

[**P5**] L.C. Rhodes, J. Böker, M.A. Müller, M. Eschrig and **I.M. Eremin**, *Non-local d_{xy} nematicity and the missing electron pocket in FeSe*, npj Quantum Mater. 6, 45 (2021)

[**P6**] M.A. Müller, P.A. Volkov, I. Paul, and **I.M. Eremin**, *Interplay between nematicity and Bardasis-Schrieffer modes in the short-time dynamics of unconventional superconductors*, Phys. Rev. B 103, 024519 (2021)

[**P7**] **G.S. Uhrig**, M. Holt, J. Oitmaa, O.P. Sushkov, and R.R.P. Singh, *Pnictides as frustrated quantum antiferromagnets close to a quantum phase transition*, Phys. Rev. B **79**, 092416 (2009)

[**P8**] H. Krull, D. Manske, **G.S. Uhrig**, and A.P. Schnyder, *Signatures of nonadiabatic BCS state dynamics in pump-probe conductivity*, Phys. Rev. B **90**, 014515 (2014)

[**P9**] H. Krull, N. Bittner, D. Manske, **G.S. Uhrig**, and A.P. Schnyder, *Coupling of Higgs and Leggett modes in nonequilibrium superconductors*, Nature Communications **7**, 11921 (2016)

[**P10**] **Zhe Wang**, M. Schmidt, J. Fischer, V. Tsurkan, M. Greger, D. Vollhardt, A. Loidl, J. Deisenhofer*, Orbital-selective metal-insulator transition and gap formation above Tc in superconducting* $Rb_{1-x}Fe_{2-y}Se_2$, Nature Communications **5**, 3202 (2014)

[**P11**] **Zhe Wang**, V. Tsurkan, M. Schmidt, A. Loidl, and J. Deisenhofer, *Tuning orbital-selective correlations in the superconducting* $Rb_{0.75}Fe_{1.6}Se_{2-z}S_z$, Phys. Rev. B **93**, 104522 (2016)

[**P12**] H. Chu, M.-J. Kim, K. Katsumi, S. Kovalev, R. D. Dawson, L. Schwarz, N. Yoshikawa, G. Kim, D. Putzky, Z. Z. Li, H. Raffy, S. Germanskiy, J.-C. Deinert, N. Awari, I. Ilyakov, B. Green, M. Chen, M. Bawatna, G. Christiani, G. Logvenov, Y. Gallais, A. V. Boris, B. Keimer, A. Schnyder, D. Manske, M. Gensch, **Zhe Wang**, R. Shimano, and S. Kaiser, *Phase-resolved Higgs response in superconducting cuprates*, Nature Communications **11**, 1793 (2020)

Goals and working program

The main goal of our joint experimental and theoretical initiative is to understand collective excitations in bulk materials at equilibrium and away from equilibrium so that pump-probe setups are covered with the temporal evolution from the initial equilibrium state to states far from equilibrium on a scale of picoseconds and beyond. The relevant quantities are the order parameters, i.e., the density of Cooper pairs or particle-hole pairs associated with the corresponding nematic, spin or charge density wave order, and the density of (unpaired) quasiparticles. The challenge is to identify, to measure, to describe, and to understand the relevant couplings which drive the dynamics of collective excitations. Key interactions are (i) the electron-electron interaction, (ii) the electron-phonon interaction, and (iii) the interaction between electrons and collective spin and charge fluctuations.

Specifically, we aim at a detailed experimental and theoretical analysis of the *collective composite excitations* where several degrees of freedom are actively involved such as charge density waves, soft phonons and superconductivity with sign-preserving (*s*++) order parameter in $NbSe_2$ and nematicity, spin density wave, and sign-changing (*s*+-) superconductivity in $FeSe_{1-x}Te_x$ and $FeSe_{1-x}S_x$.

Before we detail our working schedule and milestones, we shall emphasize here that all four PhD projects (one per PI) described in the following will be continued after the MERCUR funding period ensuring a proper completion of the PhDs.

1. Synthesis and characterization of single crystals (1^{st} – 12^{th} months)

We (Böhmer group) will prepare single crystals of FeSe, Fe(Se,S), and Fe(Se,Te) by using vapor growth techniques. Samples will be fully characterized in-house, including their chemical composition with energy-dispersive X-ray spectroscopy and structural investigations with powder X-ray diffraction. We will optimize the growth conditions to achieve homogenous composition and highly reproducible properties to obtain a reliable basis for the physical investigations.

We will also prepare $NbSe_2$ single crystals using reported chemical vapor transport techniques, carefully characterizing their crystallographic phase as different variants can be stable. The charge-density wave transition at 33 K and superconductivity will be characterized using the available suite of low-temperature transport and thermodynamic measurements, as well as diffraction techniques. The project will be complemented by a novel material component. Recent reports of intercalated $Fe_{1/3}NbS_2$ and $Cr_{1/3}NbS_2$, which turn out to be antiferromagnets, motivate us to try similar intercalations of $NbSe_2$. These materials may lead to a new platform for the study of the interplay of phonons, superconductivity and magnetism in follow-up projects.

Milestones: Synthesis of high-quality FeSe, Fe(Se,S), and Fe(Se,Te) single crystals. Synthesis of high-quality $NbSe_2$ single crystals and intercalated $NbSe_2$.

2. Development of time-resolved terahertz pump-probe techniques (1^{st} – 12^{th} months)

We (Wang group) will build up various time-resolved terahertz pump-probe spectroscopic techniques based on femtosecond amplifier laser systems. These techniques will be specifically designed and optimized for our proposed study of composite excitations in quantum materials, particularly on those prepared by the Böhmer group. This mainly includes (but is not limited to) terahertz-pump terahertz-probe spectroscopy, terahertz-pump optical-probe spectroscopy, and terahertz harmonic generation spectroscopy. These optical techniques will be equipped with cryogenic conditions to study the phases with charge density wave, nematicity, and superconductivity with intertwined orders (see e.g. Fig. 1).

Milestone: Buildup of time-resolved terahertz pump probe techniques for low-temperature experiments.

3. Experimental exploration of intertwined order parameters (7^{th} – 24^{th} months)

Based on the experimental progress of the first six months, we will be well prepared for the measurements of physical properties with various experimental techniques (Böhmer and Wang). The experimental studies will be fueled by theoretical predictions of the theory groups (Eremin and Uhrig) and will undoubtedly also raise new questions for the theory groups to address.

3.1. Probe of equilibrium states

We (Böhmer group) will search for experimental signatures of the expected intimate coupling of nematic degrees of freedom of Fe(Se,S) and Fe(Se,Te) with superconductivity using a broad range of experimental equilibrium techniques, including anisotropic magneto-transport, high-resolution thermal expansivity and measurements of the elastic Young modulus. The nematic order parameter will be probed microscopically via diffraction. The intimate coupling of the two ordering phenomena typically manifests in a dramatic response of the nematic order parameter (or corresponding elastic modulus) to the onset of superconductivity, or in a pronounced two-fold symmetry of the superconducting state. It is the prerequisite for well-developed composite collective excitations and will be an important baseline for their understanding. Towards the end of the project, we will also address the spin-density wave state in iron-based superconductors based on the results obtained by the theory groups.

The physical properties of $NbSe_2$ will be characterized using low-temperature transport and thermodynamic probes. We will further characterize the charge-density wave microscopically via X-ray diffraction and search for signatures of the interplay of superconductivity with the charge-density wave in these equilibrium properties. Understanding these signatures will be essential for subsequent investigations of the nonequilibrium state by spectroscopic techniques (Wang group).

Milestone: Signatures of the coupling of superconductivity with nematic order and a charge-density wave in physical equilibrium properties.

3.2. Probe of nonequilibrium states

As introduced above, by driving the systems out of equilibrium, one can detect exotic collective and composite excitations (such as Higgs amplitude modes, Leggett modes, and Bardasis-Schrieffer modes), which are not necessarily detectable in equilibrium state. We (Wang group) will use terahertz-pump optical-reflectivity-probe (e.g. 800 nm) spectroscopy to investigate the nematic and superconducting phases in Fe(Se,S) and Fe(Se,Te). This technique allows the study of a third-order susceptibility. In particular, a probe signal proportional to the square of the pump electric field (the so-called terahertz Kerr effect) is expected to reflect the Higgs amplitude fluctuations of the superconducting phase as demonstrated, e.g., in the cuprate superconductor $Bi_2Sr_2CaCu_2O_{8+x}$ [Katsumi2020]. By tuning the polarization of the pump and/or probe pulses, we can reveal the symmetry-dependent properties, therefore this technique is also suitable for the study of the nematic phase. In the composite phase, we expect this technique to provide signatures for the Bardasis-Schrieffer mode theoretically predicted by the Eremin group (see Fig. 5).

Milestone: Symmetry-dependent nonlinear response in the iron-based superconductors (Higgs mode, Bardasis-Schrieffer mode)

We (Wang group) will also use the terahertz-pump terahertz-probe technique to study two- or multi-band superconductors [$NbSe_2$, Fe(Se,S), and Fe(Se,Te)] grown and characterized by the Böhmer group. As shown in Fig. 4 (Uhrig group), novel collective excitations (Leggett modes) can emerge due to interband interactions. Signatures of the Leggett mode can possibly be detected in the nonequilibrium state driven by terahertz fields as recently demonstrated in the two-band compound MgB_2 [Giorgianni2019]. Our experimental results will be understood together with the theory groups (Eremin and Uhrig). Furthermore, we will perform terahertz higher-order harmonic generation measurements, such as the fifth-order harmonics, in order to possibly reveal new physical properties which are not contained for instance in the third-order response of the multiband superconductors or in the composite phase (Eremin group). For the magnetic systems, e.g. $Fe_{1/3}NbSe_2$ (Böhmer group), we can use the terahertz-pump Kerr-rotation-probe to study the interplay between magnetic and structural properties.

Milestone: Leggett mode and high-order harmonic generation in multiband superconductors.

Theoretically we want to understand the role of collective excitations and their interplay upon forming composite collective excitations in bulk materials. The first goal is to reach a qualitative understanding of the behavior of these novel quantum objects. Second, we aim at a quantitative description of experimental results of the Böhmer and Wang groups. Third, we intend to suggest experimental tests which can verify theoretical predictions and thereby guide future research into promising directions, helping to elucidate the relevant physics of composite collective excitations. Two technical starting points will be chosen.

4. Density-matrix formalism and pseudo-spin approach

We (Uhrig group) employ the time-dependent solutions as obtained in the preliminary studies of pump experiments where the induced dynamics is probed in the temporal evolution of the order parameters and the electric currents [**P8, P9**]. The coupling of the electromagnetic field is achieved in the continuum limit by minimal coupling. Alternatively, in lattice models, the vector potential is coupled via the Peierls substitution (Eremin and Uhrig group). Subsequently, the density-matrix formalism is used which amounts up to time-dependent mean-field theory and which can be mapped to the dynamics of Anderson pseudo-spins [Yuzbashyan2005] if all involved expectation values are diagonal in momentum. These approaches are well-justified for the short-time dynamics after the pumping when scattering processes have not yet kicked in decisively in accordance with experimental findings [Matsunaga2013].

4.1 Single-band systems close to instabilities (1st – 6th month)

We start with a single band *s*-wave superconductor (SC) supplemented by an interaction favoring the formation of a charge density wave (CDW). Tuning the parameters such that the system is in the SC phase, but close to the CDW transition, the interplay of the two corresponding collective excitations will be investigated and compared to previous studies [Moor2014, Sentef2017]. Vice-versa we choose parameters implying a CDW phase, but close to the SC, and study the interplay of the collective excitations and the formation of composite excitations.

Milestone: Dynamics of the order parameter in the single-band SC-CDW system.

4.2 Two-band systems close to a charge density wave (7th – 12th month)

Subsequently, we will extend the model by passing from a single band to a two-band model in order to approach the physical situation in $NbSe_2$ so that this brings theory close to the experimental studies of the first platform system. This will allow us to compare with experimental results from the groups of Böhmer and Wang and with the theoretical results from the Eremin group. In the comparison with the latter, important conceptual issues will be addressed: how strong is the back-action of the fermionic system onto the electromagnetic fields? The Meißner-Ochsenfeld effect clearly suggests the relevance of this back-action.

Milestone: Dynamics of the order parameter in the two-band SC-CDW system.

4.3 Single band system close to a spin density wave (13th – 18th month)

A second extension is to stick to a single-band model, but to turn to a spin density wave (SDW) instead of a CDW. This requires to take special features into account such as spin conservation and the occurrence of massless Goldstone bosons (magnons) since the continuous spin symmetry is spontaneously broken. Hence, it can be advantageous to introduce the Goldstone bosons a priori avoiding to describe them as pairs of fermionic particles and holes. This will lead us to spin-fermion models [Abanov2003]. The magnetic part can be chosen to reproduce the physics of the J_1-J_2-model on the square lattice [**P7,Stanek2011**] which displays magnetic nematicity by singling out one out of two equivalent spatial directions in its columnar phase. In the vicinity of the critical temperature of the spin ordering a Schwinger boson representation of the spin degrees of freedom is advantageous. Complementarily, the Eremin group will employ an itinerant description in which the SDW is described by particle-hole pairing at the corresponding wavevector **Q** and the spin excitations (spin structure factor) are computed within the generalized random phase approximation (RPA) technique.

Milestone: Dynamics of the order parameter in the single band SC-SDW system.

4.4 Two-band or multi-band system close to a spin density wave (18th – 24th month)

Eventually, we pass to a multi-band model in order to approach the physics of the unconventional superconductors related to Fe(Se,Te,S). With the understanding and experience collected in 4.3 we will be able to connect to the experimental results of the Böhmer and Wang group as well as with the theoretical results, obtained previously [Dzero2015] and by the Eremin group.

Milestone: Dynamics of the order parameter in a multi-band SC-SDW system.

5. Effective Langrangian in terms of the collective fields using gauge-invariant formalism

The second theoretical approach pursued in Bochum (Eremin) starts from the corresponding Lagrangian, describing the interacting electrons coupled to an electromagnetic (EM) field. Its advantage is that in contrast to the pseudospin representation, this formalism is gauge-invariant, which allows us to especially treat the phase fluctuations of the charged superfluid and to include the long-range Coulomb interaction. The non-interacting part of the Lagrangian is obtained as usual within tight-binding approximation and describes the multiband Fermi surface topology and the low-energy band structure of either the iron-based superconductor like Fe(Se,Te) or Fe(Se,S), or the $NbSe_2$ (Böhmer group). The interaction part includes the relevant electron-electron and the electron-phonon couplings. By performing the Hubbard-Stratonovich transformations for the fields in the particle-particle (Cooper-pairing) and particle-hole (spin/charge density wave and nematicity) channels, respectively, and integrating out the fermionic degrees of freedom, we will obtain the effective action in terms of the corresponding collective fields which describe the low-energy dynamics of the system of interest coupled to the external electromagnetic field, similar to our previous analysis **[Müller2021]**. Following the standard procedure, we will split the action into mean-field and fluctuation parts where in the mean-field part the trace is evaluated with space and time-independent order parameters, and the fluctuation part is the difference between the mean-field action and the full action. It will be expanded in powers of the fluctuations around a homogeneous solution specifically studying the coupling of different collective modes and their dispersions. The composite collective excitations form when the dispersions of the two collective modes are expected to hybridize and we will analyze the possible interplay of CDW and multiband superconductivity in $NbSe_2$ and of SDW, nematicity, and unconventional superconductivity in the iron-based superconductors.

5.1 Phase-amplitude modes and pair density wave (PDW) in a multiband CDW superconductor (1^{st} – 7^{th} months)

One of the most important questions in the CDW superconductor is a potential formation of the pair density wave (PDW), which is the Cooper-pair density with a finite momentum of the CDW. The PDW may appear as a byproduct (composite nature) of the SC order parameter and the CDW order. However, it can also acquire its own dynamics due to residual interactions in this channel, independent of CDW and SC order. We plan to investigate the collective modes associated with the PDW as well as the coupling of the amplitude (Higgs mode) and phase-related (plasmon and Leggett) modes mediated via CDW order.

Milestone: Coupled dynamics of the multiband CDW superconductor displaying a PDW

5.2. Third and fifth harmonics generated current (8^{th} – 14^{th} months)

In the next step, we will derive the third and the fifth harmonic generated currents and analyze the signatures of various modes in the experimentally relevant physical observable, see Wang group. For that we will differentiate the effective action with respect to the vector potential and obtain the perpendicular and the parallel component of the third (THG) and the fifth harmonic generated (FHG) current and its polarization dependence. We expect that due to the richness of the collective modes their contribution to the THG and FHG can be selectively enhanced in the corresponding harmonic, which allows for the straightforward experimental identification of the corresponding modes.

Milestone: Analytic expression for the THG and FHG currents and its numerical evaluation

5.3. Composite collective modes in a nematic superconductor with SDW fluctuations (15^{th} – 24^{th} months)

In FeSe doped with Se or Te the nematicity coexists with the *s*+- superconducting state. It was shown by the Bochum group previously that in such a case the subdominant Cooper-pairing fluctuations in the *d*-wave channel couple to the nematic fluctuations yielding the so-called composite Bardasis-Schrieffer nematic mode [**P6**]. However, to make a detailed comparison to experiments of the Wang and Böhmer groups it is required also to include fluctuations in the SDW channel due to the presence of this phase under pressure and to consider the smallness of the Fermi energy. Therefore, we will study how the composite collective excitations are influenced by the presence of the SDW fluctuations and by the renormalization of the chemical potential. Furthermore, following the gauge invariant approach, outlined above, we will compute the THG and FHG in such a case.

Milestone: Coupled dynamics of the multiband nematic superconductor with small Fermi energies and SDW fluctuations

Strategic perspectives

Our MERCUR Kooperation will help to weave the research network in the UAR tighter and tighter. The common activities will constitute a core for broader collaborations in quantum material synthesis and their experimental and theoretical studies. In particular, the two newly appointed professors (Böhmer and Wang) will be integrated very quickly in the UAR community, providing the necessary foundation for future joint applications.

While our MERCUR Kooperation focuses on composite excitations in bulk materials we intend to extend this fascinating field to hybrid structures where composite excitations are expected to appear at the interfaces. The possibility to tailor the design of such structures will provide a massive degree of control on the physical properties of the final device. Hence, we will apply as medium-term follow-up of this MERCUR Kooperation for a DFG Research Unit with an expanded consortium of UAR colleagues for which we have already won Ilya Akimov (TUDO), Uwe Bovensiepen (UDE) and Alexey Scherbakov (TUDO) for their expertise in further systems including interfaces and nanostructured systems and their manipulation. Further PIs will be searched for among female and young researchers. This will further substantiate the emerging field of composite excitations providing a basis for the long-term perspective of a DFG-CRC in the UAR as successor of the existing ICRC/TRR 160 at the TUDO.

Our MERCUR Kooperation will enhance the national and international visibility of the UAR by its tangible research projects. While in Germany KIT (Karlsruhe) and MPI-FKF (Stuttgart) are the other research centres studying collective excitations in unconventional superconductors using complementary experimental and theoretical techniques, there are multiple groups in the USA (Stanford, Rutgers Universities and Ames and Argonne National Labs), Canada (Vancouver), United Kingdom (St Andrews, Oxford Universities) as well as China (Beijing, Shanghai, and Nanjing universities) and Japan (universities of Tokyo and Kyoto) with whom we have established research contacts. Composite collective excitations represent a promising unique route since they can serve as carriers of energy and information quanta with a high degree of control by structural design. The Excellence Initiative on Materials planned at the RUB will benefit from our initiative by opening up a new research direction in complex correlated materials. Positive effects for the Ruhr Research Centre “Future Energy Materials and Systems” can also be conceived.

Internationalization: Our joint research enhances the attractiveness of the UAR for international students and young researchers. We apply for funding to organize an international workshop once first results of our project will have been found and made available to the scientific community. For this workshop, we intend to invite speakers mainly from abroad to make (i) our results internationally visible and (ii) to profit from the understanding and insights of international colleagues. Particularly for our young collaborators (PhD students and postdocs) this workshop will provide a unique opportunity for networking. We including our PhD students and postdocs will also present our results in internationally visible conferences and workshops, and contribute to international collaborations.

Transfer to society, politics, and economy: A better understanding of excitations in conventional and unconventional superconductivity is generally advantageous. It may contribute in conceiving novel devices or help to transport energy with less dissipation, hence in a sustainable way. Nevertheless, our research is fundamental in nature and we currently do not know specifically how it may be applied in the future.

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