Bound state of $4f$-excitation and magnetic resonance in unconventional superconductors

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We analyze the influence of unconventional superconductivity on crystalline electric field (CEF) excitations of rare earth ions in novel superconductors. We show that resonant magnetic excitations of the conduction electrons that have been observed in these systems below $T_e$ may result in the formation of the bound state in the $4f$-electron susceptibility. This occurs at energies well below the CEF excitation energy. The effect is discussed as a function of temperature and the strength of the coupling between the $4f$ and $d$-electrons. We argue that these effects may be present in the layered cuprates and ferropnictides which contain rare-earth ions.

The influence of the crystalline electric field (CEF) splitting of rare-earth impurities on the various thermodynamic properties in metals is well known[1]. It is also known that CEF split rare earth impurities in a conventional $s$-wave superconductor influence the superconducting transition temperature quite differently than non-CEF split magnetic ions described by the Abrikosov-Gor’kov theory. There is also a feedback of conduction non-CEF split magnetic ions described by the Abrikosov-Gor’kov theory. There is also a feedback of conduction non-CEF split magnetic ions described by the Abrikosov-Gor’kov theory. There is also a feedback of conduction non-CEF split magnetic ions described by the Abrikosov-Gor’kov theory. There is also a feedback of conduction non-CEF split magnetic ions described by the Abrikosov-Gor’kov theory.

In this letter we analyze the effect of such a resonance below the superconducting transition temperature on CEF excitations of the $4f$ states. We show that the formation of a resonance may cause striking anomalies in the CEF excitation spectrum. Depending on the strength of the coupling between the $4f$ and $d$-electrons, the resonance may cause the formation of the bound state (an additional pole) in the $4f$-electron susceptibility. We argue that these effects may exist in the electron- and hole-doped cuprates containing rare-earth ions. In addition we also address the anomalous features of the CEF excitations which have been reported in the CeFeAsO$_{0.84}$F$_{0.16}$ superconductor[11]. In the latter case, measurements of the intrinsic linewidth and the peak position of the lowest excited mode at 18.7meV show a clear anomaly at $T_e$ and an unusual temperature dependence in the superconducting state.

The presence of rare-earth ions with $4f$ electrons in a metallic matrix with $d$-electrons forming the conduction band can be described by the model Hamiltonian

$$H = \sum_{i,\gamma} \varepsilon_{\gamma} |i\gamma\rangle \langle i\gamma| + \sum_{k,\sigma} \varepsilon_k d^\dagger_{k\sigma} d_{k\sigma} + U \sum_{i,m} n_{i\uparrow} n_{i\downarrow}. \quad (1)$$

Here, $|i\gamma\rangle$ denotes a CEF eigenstate $\gamma$ of the incomplete $4f$-shell at lattice site $i$, and $d^\dagger_{k\sigma}$ creates an electron in the conduction band with wave vector $k$ and spin $\sigma$. The energies of the CEF eigenstates are defined by $\varepsilon_\gamma$. Furthermore, $\varepsilon_k = t_k - \mu$ is the dispersion of the conduction

The situation is different in unconventional high-$T_c$ superconductors like the layered cuprates or ferropnictides which may contain rare-earth elements. Firstly, in these systems the superconducting gaps are often comparable and even larger than $\Delta_{CEF}$. This allows to study in detail the feedback effect of superconductivity on CEF excitations. For example, partially successful attempts have been made to analyze the symmetry of the superconducting gap in layered cuprates by looking at the CEF linewidth as a function of temperature with $\Delta_{CEF} \ll 2\Delta_0$[2]. A much more dramatic effect on CEF excitations is the strong change in the conducting electrons spin susceptibility below $T_e$ and its consequence for the $4f$ response. In unconventional superconductors this change may result in a resonance peak. This is a quite general phenomenon. It has been observed by inelastic neutron scattering (INS) [1, 2] near the antiferromagnetic wave vector $Q=(\pi, \pi)$ in a number of systems like high-$T_c$ cuprates[4], UPd$_2$Al$_3$[7], CeCoIn$_5$[8], CeCu$_2$Si$_2$[9], and recently also in ferropnictides[5]. It depends sensitively on the type of unconventional Cooper-pairing and may also be used to eliminate certain forms of pairing when a resonance is observed[10].

In this letter we analyze the effect of such a resonance below the superconducting transition temperature on CEF excitations of the $4f$ states. We show that the formation of a resonance may cause striking anomalies in the CEF excitation spectrum. Depending on the strength of the coupling between the $4f$ and $d$-electrons, the resonance may cause the formation of the bound state (an additional pole) in the $4f$-electron susceptibility. We argue that these effects may exist in the electron- and hole-doped cuprates containing rare-earth ions. In addition we also address the anomalous features of the CEF excitations which have been reported in the CeFeAsO$_{0.84}$F$_{0.16}$ superconductor[11]. In the latter case, measurements of the intrinsic linewidth and the peak position of the lowest excited mode at 18.7meV show a clear anomaly at $T_e$ and an unusual temperature dependence in the superconducting state.
band with $\mu$ being the chemical potential. Correlations of the $d$-electrons are due to an on-site electron repulsion $U$. The coupling term between the conduction and $4f$-electrons at site $i$ is given by

$$H_I = -I_{cz}(g_J - 1) \sum_i s_i J_i = -I_0 \sum_i s_i J_i,$$

i.e. by the exchange interaction between itinerant $d$-spins ($s_i$) and localized $4f$-electrons determined by Hund’s rule with a total angular momentum, $J$. The behavior of the conduction electron susceptibility in the superconducting state is treated within the random phase approximation (RPA), i.e.,

$$\chi^{(d)}_{RPA}(q, \omega) = \frac{\chi^{(d)}_0(q, \omega)}{1 - U\chi^{(d)}_0(q, \omega)},$$

where $\chi^{(d)}_0(q, \omega)$ is the non-interacting electron susceptibility in the superconducting state. For large momenta $q$ and low frequencies, $\text{Im}\chi^{(d)}_0(q, \omega)$ is zero. It can exhibit a discontinuous jump at the onset frequency of the particle-hole continuum $\Omega_c = \min(|\Delta_k| + |\Delta_{k+q}|)$ where both $k$ and $k+q$ lie on the Fermi surface. Note, however, that the discontinuity in $\text{Im}\chi^{(d)}_0(q, \omega)$ occurs only if $\text{sgn}(\Delta_k) = -\text{sgn}(\Delta_{k+q})$ which is not possible for an isotropic s-wave order parameter! A discontinuity in $\text{Im}\chi^{(d)}_0(q, \omega)$ leads to a logarithmic singularity in $\text{Re}\chi^{(d)}_0(q, \omega)$. As a result, the resonance conditions (i) $U\text{Re}\chi^{(d)}_0(q, \omega) = 1$ and (ii) $\text{Im}\chi^{(d)}_0(q, \omega) = 0$ can both be fulfilled at $\omega_{\text{res}} < \Omega_c$ for any value of $U > 0$. This results in a resonance peak below $T_c$ in form of a spin exciton. For finite quasiparticle damping $\Gamma$, condition (i) can only be satisfied if $U > 0$ exceeds a critical value, while condition (ii) is replaced by $U\text{Im}\chi^{(d)}_0(q, \omega) < 1$.

Typically a CEF splits the Hund’s rule $J$-multiplet of the incomplete $4f$-shell with different CEF levels. For Ce$^{3+}$ ions these levels are either three Kramers doublets or a doublet and a quartet, depending on the symmetry of the CEF. We assume for simplicity a two level system (TLS) only consisting of two doublets. The splitting is $\Delta_{CEF}$ and the susceptibility of this TLS is $u_\alpha(\omega) = |m_\alpha|^2 \frac{2\Delta_{CEF}}{(\omega^2 - \omega_0^2)^2} \sum_{ij} |(i|J_\alpha|j)|^2 \tanh(\beta\Delta_{CEF}/2)$. For the sake of simplicity we further assume $|m_z| \ll |m_x|$ and $|m_x| = |m_y| = |m_\perp| = m_0$. The $4f$-electron susceptibility within RPA approximation is given by

$$\chi^{(d)}(q, \omega) = \frac{u_\alpha(q, \omega)}{1 - I_0^2 u_\alpha(q, \omega)\chi^{(d)}_{RPA}(q, \omega)}.$$

The position of the pole and its damping by the imaginary part of $\chi^{(d)}$ can be probed by INS. It is determined by

$$\Delta_{CEF}^2 - \omega_0^2 - 2\Delta_{CEF} I_0^2 |m_\perp|^2 \left[\chi^{(d)}_{RPA}(q, \omega)\right] = 0,$$

FIG. 1: (a) Graphical illustration of the solution of Eq. (5). The dotted curve refers to the function $\Delta_{CEF}^2 - \omega^2$ with $\Delta_{CEF} = 2\Delta_0$ (black) and $\Delta_{CEF} = 1.5\Delta_0$ (grey), while $2\Delta_{CEF} I_0^2 \chi^{(d)}_{RPA}(q, \omega)$ is shown for the normal (dashed curve) and the superconducting (solid curve) state assuming $I_0 \approx \Delta$. (b) Calculated imaginary part of $\chi^{(d)}(q, \omega)$ at $T = T_c$ (dashed curve) and in the superconducting state ($T = 0.1T_c$) (solid curve). The dispersion parameters and Coulomb repulsion for the electron gas on a square lattice have been used [13].

$$\Gamma_q = 2I_0^2 \Delta_{CEF}|m_\perp|^2 \left[\chi^{(d)}_{RPA}(q, \omega)\right]^{\nu}.$$
where \( z_r \) is residue of the resonance peak in the \( d \) spin susceptibility.

In Fig.2(b) we show the total structure of the imaginary part of the \( f \)-electron spin susceptibility as function of frequency at the antiferromagnetic wave vector, \( \mathbf{Q} \). Due to appearance of the resonance mode in the conduction electron susceptibility the CEF excitations acquire an additional pole below the superconducting transition temperature at energies well below \( 2\Delta_0 \) with a small linewidth. In addition a second pole is found at a frequency which is higher than the renormalized \( \Delta_{CEF} \) in the normal state. At the same time damping induced by \( \text{Im} \chi_{RPA}^{(d)} \) is still larger than it is in the normal state value as a consequence of discontinuous jump of \( \text{Im} \chi_0 \) at \( 2\Delta_0 \) induced by the requirement \( \Delta_k = -\Delta_{k+\mathbf{Q}} \). Therefore, CEF excitations behave completely opposite as in conventional superconductors. It is also interesting to note that in case \( \Delta_{CEF} \) becomes smaller than \( 2\Delta_0 \) the position of the bound state shifts to lower energies (see Fig.2(a)). Moreover, at certain value of the \( \Delta_{CEF} < 1.5\Delta_0 \) one finds a single pole as a result of the coupling between \( d \)- and \( f \)-susceptibilities representing the renormalized CEF excitations. Furthermore, the second pole related to the bound state no longer exists. In Fig.2(a) we show the temperature evolution of the CEF excitations below the superconducting transition temperature. Here we assume a tight-binding energy dispersion for the electron-doped cuprates and a \( d \)-wave symmetry for the superconducting gap, \( i.e. \Delta_k = \Delta_k - \Delta_{k+\mathbf{Q}} \). Using a temperature dependence for the superconducting gap that resembles the solution obtained for the Eliashberg strong-coupling equations \( \Delta_k(T) = \Delta_k \tanh \left( 1.76 \sqrt{\frac{T_c}{T}} - 1 \right) \),

we analyze the CEF excitations below the superconducting transition temperature. Close to \( T_c \), \( i.e. \), in the range \( 0.8T_c < T < T_c \), the splitting of the CEF excitations due to formation of the magnetic resonance is not well resolved and it looks as if the CEF level gets damped anomalously strong. With lowering temperature, \( i.e. \), \( T \approx 0.8T_c \), both peaks become well separated. At even lower temperatures both peaks are clearly separated in energy and the lower mode is much narrower.

In the second case when the coupling between conduction electrons and \( 4f \)-electrons is weak, the effect of unconventional superconductivity on the CEF excitations still differs substantially from that of conventional superconductors. In particular, for \( I_0 < \Delta_0 \) there is no additional peak in \( \text{Im} \chi \) below \( T_c \). This is due to relatively small value of \( I_0 \chi_{RPA}^{(d)}(\mathbf{Q},\omega) \). This is also the case if the damping of the magnetic resonance in \( \chi^{(d)} \) is relatively strong. In other words, even though \( \chi^{(d)} \) is strongly frequency dependent at low energies the coupling is not large enough to produce a second pole in the \( f \)-electron susceptibility. Nonetheless, the effect of the resonance in the former is present in this frequency range. Because the overall conduction electrons response of the unconventional superconductor is larger than its normal state counterpart, the CEF excitations below \( T_c \) will experience larger damping due to \( \text{Im} \chi_{RPA}^{(d)}(\mathbf{Q},\omega) \approx 2\Delta_0 \) which is enhanced in the superconducting state. Similarly \( \text{Im} \chi_{RPA}^{(d)}(\mathbf{Q},\omega) \) is lower than its normal state value but, more important, it changes sign above \( \omega_r \) (see Fig.2(a)). As a result the CEF excitation simultaneously becomes more damped and also shifts towards higher frequencies. We show the evolution of the CEF excitation in Fig.2(b) as a function of temperature where below this effect is clearly visible as a function of temperature.

The description above is correct under the assumption that there is a well-defined resonant excitation in the conduction electron susceptibility at the two-dimensional antiferromagnetic wave vector, \( \mathbf{Q} \). This implies that for all points of the Fermi surface the condition \( \Delta_k = -\Delta_{k+\mathbf{Q}} \) is satisfied. It has been shown previously, that this condition is realized particularly well in quasi-two-dimensional systems such as hole- and electron-doped cuprates as well as in the novel iron-based superconductors and also in other heavy-fermion systems like CeCoIn\(_5\).

It has been found recently that lowest CEF excitations of Ce ions located at around \( 2\Delta \) shows an anomalous behavior in the superconducting state of CeFeAs\(_{1-x}\)F\(_x\), see Ref. 11. In particular, the lowest CEF excitations shifts slightly towards higher energies and acquire an additional damping below \( T_c \). Assuming the extended \( s \)-wave symmetry of the superconducting gap that most likely is realized in ferropnictide superconductors

\[
(\Delta_k = \Delta_k \tanh \left( 1.76 \sqrt{\frac{T_c}{T}} - 1 \right) \)
\]

the unusual behavior can be well understood. In particular, if the coupling between the conduction electrons and Ce ions is relatively weak
(I_0 < \Delta_0) the effect of the unconventional superconductivity on the CEF excitations does not result in the appearance of an additional pole in \text{Im}\chi_f, since the coupling is too weak. However, because of the sign change of the superconducting gap for the electron and the hole Fermi surfaces connected by \text{Q}_{AF}, \text{Im}\chi^{(d)}_{RPA} enhances in the superconducting state at energies \omega > \omega_r. Simultaneously, the real part of \chi_f changes sign and becomes negative for \omega > \omega_r which leads to the negative shift of \Delta_{CEF} below T_c, \text{i.e.} it shifts to higher energies below T_c (see Fig.2(b)). In order to compare our results to the experimental data we show in Fig.3 the calculated shift of the lowest frequency of the CEF excitations as well as their damping (half width at half maximum) in the superconducting state normalized to their values at T_c. We adopt the parameters used previously for calculations of the itinerant magnetic excitations in ferropnictides\textsuperscript{12}. We further assume the coupling of the itinerant 3d electrons to the 4f-shell \textit{I} = 4.3\text{meV} < \Delta. In the superconducting state, due to the extended s-wave symmetry of the superconducting gap the itinerant interband RPA spin susceptibility between electron and hole Fermi surface pockets centered around the \Gamma and M points of the BZ, respectively, shows the characteristic enhancement at energies smaller than 2\Delta\textsuperscript{12,21}. Due to weak coupling to the 4f-shell this does not yield a second pole in the Im\chi_f but results in the anomalous damping of the CEF excitations and a shift of the characteristic frequency, \omega_q towards higher energies. We find that this behavior qualitatively and also to large extent quantitatively agrees with the experimental data on CeFeAsO\textsubscript{0.84}O\textsubscript{0.16}\textsuperscript{11}.

The other systems where similar effects can realize but with strong coupling between the conduction and 4f-electrons are layered cuprates with rare-earth ions or heavy-fermion superconductor CeCoIn\textsubscript{5}. For example, in the electron-doped cuprate system Nd\textsubscript{2−x}Ce\textsubscript{x}CuO\textsubscript{4}, the splitting between the ground and the first CEF excited levels of the 4f multiplet for Nd\textsuperscript{3+} ions is about \Delta_{CEF} \approx 20\text{meV}\textsuperscript{12} which is comparable to the energy of 2\Delta of the superconducting gap in the same system\textsuperscript{13}. At the same time, the situation with the position of the feedback spin resonance due to the \textit{d}_{x^2−y^2}-wave symmetry of the superconducting gap in the electron-doped cuprates is far from being well understood. For example, original has been reported in Pr\textsubscript{0.85}La\textsubscript{0.12}CuO\textsubscript{4−δ} and Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4} at the energies of about 12\text{meV} and 10\text{meV}, respectively\textsuperscript{16,17}. Recently, this conclusion has been challenged by another group\textsuperscript{18} where the feedback of superconductivity in Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4} has been found at much smaller energies around 4.5\text{meV} and 6.4\text{meV}. In Fig.4(b) we show the calculations for \text{Im}\chi_f assuming a tight-binding energy dispersion for the 3d-electrons\textsuperscript{13}, the coupling constant \textit{I}_0 = \Delta_0 and \Delta_{CEF} = 2\Delta_0. One finds that in this case the f-electron susceptibility shows two peaks below \textit{T}_c with the lower one at the energy smaller than \omega_r and the upper one slightly above the renormalized \Delta_{CEF} in the normal state. In order to see whether the lower peak found recently\textsuperscript{18} is indeed related to the feedback effect of the unconventional superconducting order parameter on the CEF excitations further studies are necessary. A hallmark of this would be the large contribution of the incomplete 4f-shell to the d-electron susceptibility spin resonance. In addition, below \textit{T}_c the CEF excitations should possess larger damping in the superconducting state than in the normal state and show slight shift towards higher energies.

In conclusion, we find that the feedback of unconventional superconductivity on the CEF excitations may results in two characteristic features. If the coupling between the CEF excitations and conduction d-electrons is large (\textit{I}_0 \sim \Delta), the resonant excitations in the conducting electrons susceptibility centered at \omega_r yield an additional bound state in the f-electron susceptibility at energies \omega_1 \leq \omega_r. At the same time, the CEF excitations shifts towards higher energies and acquire an additional damping below \textit{T}_c. If the coupling between the d-electrons and CEF excitations is weak, \textit{i.e.} \textit{I}_0 < \Delta the additional pole does not occur and the only effect of the unconventional superconductivity is the anomalous damping of the CEF excitations and their slight upward shift below \textit{T}_c. We argue that both these effects may be present in different layered cuprates and ferropnictides, respectively.

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