Eliashberg theory of superconductivity and inelastic rare-earth impurity scattering in the filled skutterudite La$_{1-x}$Pr$_x$Os$_4$Sb$_{12}$

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We study the influence of inelastic rare-earth impurity scattering on electron-phonon-mediated superconductivity and mass renormalization in (La$_{1-x}$Pr$_x$)Os$_4$Sb$_{12}$ compounds. Solving the strong-coupling Eliashberg equations we find that the dominant quadrupolar component of the inelastic scattering on Pr impurities yields an enhancement of the superconducting transition temperature $T_c$ in LaOs$_4$Sb$_{12}$ and increases monotonically as a function of Pr concentration. The calculated results are in good agreement with the experimentally observed $T_c(x)$ dependence. Our analysis suggests that phonons and quadrupolar excitations cause an attractive electron interaction which results in the formation of Cooper pairs and singlet superconductivity in PrOs$_4$Sb$_{12}$.

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The Pr-based filled-skutterudite compounds have attracted much attention because of their exotic properties like metal-insulator transition or unusual heavy-fermion behavior. This also concerns recently discovered PrOs$_4$Sb$_{12}$, the first Pr-based heavy-fermion superconductor with $T_c=1.85$ K which possesses many exotic properties compared to that of the Ce- and U-based superconductors. The heavy-electron mass has been confirmed by the large specific heat jump $\Delta C/T_c \sim 500$ mJ/(K$^2$mol) at $T_c$ (see Ref. 4) and by de Haas–van Alphen (dHvA) measurements. The ground state in the crystalline electric field (CEF) for Pr$^{3+}$ ion is a $I^+_1$, singlet, which is separated by the first excited state, a $I^+_4$ triplet by a gap of $\Delta_{CEF} \sim 8$ K. Because of the small $\Delta_{CEF}$, the relation between the quadrupole fluctuations associated with the $I^+_2$ state and the superconductivity has been recently the focus of intense discussions.

At present, the Cooper-pairing mechanism and the corresponding symmetry of the superconducting gap in PrOs$_4$Sb$_{12}$ is still under debate. For example, initial studies of the thermal conductivity in a rotated magnetic field have suggested the presence of two distinct SC phases. Similarly, the London penetration depth has indicated a possible nodal structure of the superconducting gap. On the contrary, a number of experimental techniques such as nuclear-quadrupole-resonance (NQR), scanning tunneling microscopy (STM), muon spin relaxation ($\mu$SR), thermal conductivity, and specific heat measurements are in agreement with a fully developed isotropic s-wave-like superconducting gap at the Fermi surface (FS). Another interesting experimental observation by means of the dHvA effect was that PrOs$_4$Sb$_{12}$ has a very similar FS topology as the conventional s-wave superconductor LaOs$_4$Sb$_{12}$ (Ref. 5) ($T_c=0.74$ K) which hints at a relatively weak hybridization of the conduction band with Pr$^{3+}4f^2$ electrons. Furthermore, it has been found that in the alloy compound La$_{1-x}$Pr$_x$Os$_4$Sb$_{12}$ the superconducting transition temperature changes smoothly upon changing x. These observations raise doubts about the unconventional nature of the Cooper pairing in PrOs$_4$Sb$_{12}$. But the enhancement of $T_c$ and the effective quasiparticle mass in this compound with respect to that of LaOs$_4$Sb$_{12}$ have to be understood.

It is well known that scattering by magnetic impurities suppresses conventional s-wave superconductivity by destroying Cooper pairs in a singlet state. This situation, however, can change in the case of paramagnetic non-Kramers rare-earth impurities. For example, it has been shown previously that for superconductors containing an impurity with crystal-field-split energy levels the inelastic charge scattering of conduction electrons from the aspherical part of the $4f$ charge distribution may yield an increase of $T_c$. However, in most of the cases the usual magnetic exchange interaction is dominant, thus suppressing $T_c$. In this Rapid Communication, we solve the nonlinear Eliashberg equations for electron-phonon-mediated Cooper pairing including inelastic scattering on Pr impurities. We find that a dominant quadrupolar scattering introduced by the Pr ions is responsible for an increase of $T_c$ in La$_{1-x}$Pr$_x$Os$_4$Sb$_{12}$ as a function of Pr concentration.

Before solving the nonlinear version of the Eliashberg equations let us illustrate the results of Ref. 18 where the influence of inelastic scattering by rare-earth impurities on the superconducting transition temperature $T_{c0}$ without impurities has been studied for both exchange and quadrupolar scattering. In particular, for impurities with two singlet levels separated by an energy $\Delta_{CEF}$ the analog of the Abrikosov-Gor’kov relation for the change of $T_c$ as a function of the total impurity scattering rate $\tau^{-1}$ for the s-wave superconductor is given by

$$-\frac{8}{\pi} T_c \tau^M_{12} \ln \frac{T_c}{T_{c0}} = 1 + \frac{\tanh x}{x} - \frac{1}{x} - A(x) + B(x),$$

$$-\frac{8}{\pi} T_c \tau^Q_{12} \ln \frac{T_c}{T_{c0}} = 1 - \frac{\tanh x}{x} - \frac{1}{x} - A(x),$$

Here, $1/\tau^M_{12}$ and $1/\tau^Q_{12}$ are the magnetic and quadrupolar scattering rate, respectively, and $x=\Delta_{CEF}/k_B T_{c0}$. Furthermore, $A(x)$ and $B(x)$ are the combinations of digamma functions and are smooth functions of $x$. In Figs. 1(a) and 1(b) we show the behavior of $T_c/T_{c0}$ as a function of $\Delta_{CEF}/k_B T_{c0}$ for the quadrupolar (charge) and exchange (magnetic) scattering,
FIG. 1. Calculated values of the superconducting transition temperatures as a function of $\Delta_{CEF}/T_c$ for inelastic quadrupolar (a) and magnetic (b) scattering by impurities with two singlet levels using Eqs. (1).

respectively. Assuming equal matrix elements for both scatterings ($\Gamma_{12}^T=T_{12}^{T\sigma}=T_{12}^{T\sigma}=1$) we find very different behavior. For quadrupolar scattering $T_c$ increases with respect to $T_c$ with a pronounced maximum around $\Delta_{CEF}/k_BT_c=10$, the magnetic scattering results in a complete suppression of $T_c$ at small $\Delta_{CEF}$ and gives a moderate reduction at larger $\Delta_c$ values. Overall one finds that for similar scattering amplitudes the magnetic exchange scattering dominates and $T_c$ decreases.

Let us consider more specifically Pr$^{3+}$ impurities in La$_{1-x}$Pr$_x$Os$_4$Sb$_{12}$ compounds. As mentioned above the CEF level scheme is composed of a $\Gamma_1$ singlet ground state, a $\Gamma_4$ triplet first excited state with $\Delta_{CEF}=8\text{ K}$ and the associated excited states located at much larger energies above $\sim 100\text{ K}$. Furthermore, due to $T_c$ crystal group symmetry, the $\Gamma_4$ level is of the form $[\Gamma_4^{(2)}(m)=\Gamma_3(m)\pm d\Gamma_2(m)]$, where $m=+,\ldots,0$. Here, $\Gamma_3$ and $\Gamma_4$ are the wave functions for the cubic $O_h$ symmetry and $d$ is a parameter that describes the mixture of the two states and is estimated to be equal 0.26. Since scattering between $\Gamma_1$ and $\Gamma_3$ is quadrupolar, the dominant scattering between $\Gamma_1$ and $\Gamma_4$ will be quadrupolar as well. Furthermore, from Fig. 1(a) we see that the enhancement of $T_c$ is largest for $\Delta_{CEF}=8\text{ K}$. Keeping in mind that the higher excited states lie at energies $\gtrsim 100\text{ K}$ the magnetic pair-breaking scattering from these levels will play only a minor role in affecting $T_c$. This suggests that Pr$^{3+}$ ions in La$_{1-x}$Pr$_x$Os$_4$Sb$_{12}$ yield a strong Cooper-pair enhancement as compared with LaOs$_4$Sb$_{12}$. At the same time, the Pr$^{3+}$ ions in La$_{1-x}$Pr$_x$Os$_4$Sb$_{12}$ can be treated as independent impurities at low enough doping. At large Pr concentrations the RKKY interaction between the 4$f^2$ ions results in the formation of $O_{xy}$-type quadrupolar exciton bands as confirmed experimentally. The latter can be treated as low-energy bosonic excitations which contribute in addition to phonons to the Cooper pairing. But one should notice that the exciton dispersion is relatively weak—i.e., about 10% of $\Delta_{CEF}$.

Using the generalized Holstein-Primakoff (HP) method, the low-energy Hamiltonian describing the magnetic and quadrupolar interaction between conduction electrons and the CEF-split energy levels of Pr$^{3+}$ is given by

$$H = \sum_{\mathbf{q},\sigma} \omega_{\mathbf{q}} \beta_{\mathbf{q},\sigma}^\dagger \beta_{\mathbf{q},\sigma} - \frac{g_L}{I_c} \sum_{\mathbf{k},\sigma,\sigma'} n_{\mathbf{k},\sigma} \lambda_{\sigma\sigma'}^M \hat{J}_{\mathbf{k},\sigma} \hat{J}_{\mathbf{k}+\mathbf{q},\sigma'},$$

(2)

where $\omega_{\mathbf{q}}$ is the energy dispersion of the exciton. There are three bosonic modes ($\pi=a,b,c$) corresponding to the excitations between singlet $\Gamma_1$ and triplet $\Gamma_4^{(2)}$ states. $\sigma$ are the Pauli matrices ($c=x$, $b=z$, $a=y$) and $f_j(\mathbf{q})=\hat{q}_x \hat{q}_y$, $f_b(\mathbf{q})=\hat{q}_z$, and $f_c(\mathbf{q})=\hat{q}_x \hat{q}_z$, are the form factors of the quadrupolar interaction. The quadrupolar and magnetic excitations are written in terms of the bosonic operators $\hat{O}_{\mathbf{q},\nu}=i(\beta_{\mathbf{q},\nu}-\beta_{-\mathbf{q},\nu})$ and $\hat{J}_{\mathbf{q},\sigma}=\lambda_{\sigma\sigma'}^a \hat{O}_{\mathbf{q},\nu}+2D_M \gamma_\nu \omega_{\mathbf{q}}$, with $(\lambda_{a}^2)^2=\Delta_{CEF}+2D_M \gamma_\nu \omega_{\mathbf{q}}$, and $(\lambda_{b}^2)^2=\Delta_{CEF}+2D_M \gamma_\nu \omega_{\mathbf{q}}$, respectively. Here, $D_M$ and $D_0$ are the effective magnetic and quadrupolar coupling constants. $\gamma_\nu$ is the corresponding structure factor. Due to the weak dispersion of the excitons, $\lambda_{a}^2$ and $\lambda_{b}^2$ are almost momentum independent. Solving the Eliashberg equations, we use an effective interaction between quadrupolar excitons and conduction electrons averaged over the FS.

On the real frequency axis the finite temperature Eliashberg equations for the superconducting gap $\Delta(\omega,T)$ and the renormalization function $Z(\omega,T)$ are given by

$$\Delta(\omega,T) = \frac{1}{Z(\omega,T)} \int_0^\infty d\omega' \text{Re} \left\{ \frac{\Delta(\omega',T)}{\omega^2 - \Delta^2(\omega',T)} \right\} \times \left[ K_{\pi}(\omega,\omega',T) - \mu^2 \tanh \left( \frac{\beta \omega'}{2} \right) \right],$$

(3)

$$\omega(1-Z(\omega,T)) = \int_0^\infty d\omega' \text{Re} \left\{ \frac{\omega'}{\omega^2 - \Delta^2(\omega',T)} \right\} \times K_{\pi}(\omega,\omega',T),$$

(4)

where

$$K_{\pi}(\omega,\omega',T) = \int_0^\infty d\Omega H_{\pi}(\Omega) \times \frac{f(-\omega') + n(\Omega)}{\omega' + \omega + \Omega} \pm \frac{f(-\omega') + n(\Omega)}{\omega' - \omega + \Omega} + \frac{f(\omega') + n(\Omega)}{-\omega' + \omega + \Omega} - \frac{f(\omega') + n(\Omega)}{-\omega' - \omega + \Omega},$$

(5)

and $H_{\pi}(\Omega) = \alpha_{\pi}^2 \mathcal{C}(\Omega) + \alpha_{\pi}^2 \mathcal{F}(\Omega) = \alpha_{\pi}^2 \mathcal{F}(\Omega)$ is the generalized electron-boson coupling function averaged over the FS. Here, $\mu^2$ is the screened Coulomb repulsion, $f(\omega)$ and $n(\omega)$ are the Fermi and Bose distribution functions, respectively, and $\beta=1/k_BT$.

As mentioned above there are two types of bosonic excitations. In LaOs$_4$Sb$_{12}$ the superconductivity is driven by the electron-phonon interaction and we assume a single...
Both processes can be taken into account as separate contributing scattering processes of electrons by the excitons. Lorentzian phonon mode at \( \hbar \omega_F = 26 \text{ meV} \) with broadening \( \Gamma_p = \omega_F / 5 \). This corresponds to the Debye temperature of this compound, setting \( \mu = 0.1 \) and \( \lambda = 2 \int_0^\infty d \alpha \alpha^2 G(\alpha) / \Omega = 0.33 \) the Eliashberg equations yield \( T_c = 0.74 \text{ K} \) and \( 2 \Delta_0 / k_B T_c = 3.5 \). In Fig. 3(a) we show the calculated results for the real part of \( \Delta(\omega) \) and the renormalization function \( Z(\omega) \). In both cases one finds typical behavior of a BCS-like superconductor. In particular, \( \text{Re} \Delta(\omega) \) shows a peak structure at \( \omega_F \) and becomes negative at larger frequencies, reflecting the effective repulsion for \( \omega > \omega_F \). For \( \omega_F > \Delta_0 \), the renormalization function is close to 1 and the ratio \( 2 \Delta_0 / k_B T_c \) equals the BCS value.

A similar crystallographic structure and nearly equal ionic radii of the La and Pr ions allow to assume nearly the same phonon modes in LaOs4Sb12 and PrOs4Sb12. The main difference is the occurrence of the low-energy exciton in PrOs4Sb12 at about \( \Delta_{CEF} = 0.03 \omega_F \). As discussed above there are both (magnetic) pair-breaking and (quadrupolar) pair-forming scattering processes of electrons by the excitons. Both processes can be taken into account as separate contributions to the Eliashberg function \( \alpha^2 F(\omega) \). Using Eq. (2) and ignoring a weak dispersion of the exciton as observed by inelastic neutron scattering (INS) experiments, we obtain, after averaging over the FS, \( \lambda_M = 2 \int_0^\infty d \omega / \omega a_F^2 F(\omega) = I_{ac} M_{CEF}^2 / 2 N_0 / \Delta_{CEF} \) where \( M_{CEF}^2 = 35(1-d^2) \) is the quadrupolar scattering matrix element and \( N_0 = 7.625 \text{ eV}^{-1} \) is the bare (unrenormalized) electronic density of states. Furthermore, we set \( I_{ac} = 2 \text{ meV} \). Similarly, we find \( \lambda_{CEF} = 2 \int_0^\infty d \omega / \omega a_F^2 F(\omega) = (1-g_e)^2 I_{ex} M_{CEF}^2 / 2 N_0 / \Delta_{CEF} \) where \( M_{CEF}^2 = 20k_F^2 / 3 \) is the magnetic scattering matrix element and \( g_e = 0.8 \) is the Landé factor. Following our previous estimates, we set \( a_F^2 / a_M^2 = 7 \) and obtain \( I_{ac} = 16.4I_{ex} \) where \( I_{ex} \) is the on-site magnetic interaction constant between exciton and conduction electrons. All components entering the total Eliashberg function \( H_k(\Omega) \) are shown in Fig. 2. As expected the quadrupolar contribution is about 7 times larger than the magnetic one. Therefore an inclusion of the excitons yields an enhancement of the superconductivity in PrOs4Sb12 as compared to LaOs4Sb12. In particular, the total value of \( \lambda \) increases to 3.05, yielding strong-coupling superconductivity in PrOs4Sb12 with \( T_c = 1.85 \text{ K} \). Here, one has to remember that in PrOs4Sb12 there are three contributions to the total \( \lambda \) and their sum gives \( \lambda = 3.05 \). This yields a strong renormalization of the quasiparticle mass in PrOs4Sb12 compared to its LaOs4Sb12 counterpart. At the same time \( T_c \) and \( \Delta(\omega) \) are determined by Eq. (5) where the difference between quadrupolar and magnetic scattering enters. Therefore the enhancement of \( T_c \) is moderate despite the large change in \( \lambda \).

Figure 3(b) shows the calculated frequency dependence of the real part of the superconducting gap function and the renormalization function for PrOs4Sb12. One notices a sharp feature at an energy of about \( \Delta_{CEF} + \Delta_0 \) and a strong renormalization of the quasiparticle mass due to the presence of the low-energy exciton. It is interesting to note that both magnetic and quadrupolar scatterings contribute to the renormalization of the quasiparticle mass while only their difference contributes to Cooper-pair formation. We suggest that the low-energy peak in \( \Delta(\omega) \) should be visible in the tunneling density of states which could be checked experimentally. Another remarkable feature is that we find \( 2 \Delta_0 / k_B T_c = 5.4 \) typical for a strong-coupling superconductor. Therefore, within this approach we find PrOs4Sb12 to be a conventional s-wave strong-coupling superconductor, with enhanced \( T_c \) due to low-energy excitons with mainly quadrupolar scattering. It has been proposed previously that quadrupolar scattering may alone yield unconventional superconductivity in PrOs4Sb12 due to the exciton dispersion. Indeed such a possibility cannot be excluded from our calculation. At the same time we find it difficult to reconcile with the experimental evolution of \( T_c \) in La1-xPr_xOs4Sb12 as a function of \( x \). In particular, assuming the linear dependence of the exciton’s contribution to \( H_k(\omega) \) as a function of \( Pr \) concentration we find good agreement between calculated and measured \( T_c(x) \) [see Fig. 4(a)]. At the same time, unconventional superconductivity in PrOs4Sb12 would be unstable with respect to nonmagnetic La impurities and \( T_c \) should vanish at a small concentration of La. In Fig. 4(b) we show the evolution of the effective mass as a function of \( Pr \) concentration. We find that the effective mass increases by a factor of 2.5 from LaOs4Sb12 to PrOs4Sb12 which agrees with dHvA data. An inclusion of the higher-
lying CEF energy levels provides stronger renormalization of the effective mass. This is interesting to note that experimentally $\Delta C/T_c$ shows a nonlinear dependence on the La concentration, in particular close to PrOs$_4$Sb$_{12}$, which cannot be explained by our theory. Whether this is a sign of the first-order phase transition between different symmetries of the superconducting order parameter or is a result of the Pr-Pr interaction neglected in our theory remains to be understood both theoretically and experimentally. Finally, let us note that our theory allows us also to explain qualitatively the behavior of $T_c$ in Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ for $x<0.6$. In particular, it has been found that the CEF level splitting between the lowest levels increases as a function of $x$ while $T_c$ decreases. According to our Fig. 1(a) the Cooper-pair constructive quadrupolar scattering decreases with increasing $x$ while the magnetic pair-breaking contribution tends to saturate. Therefore, the $T_c$ should decrease as it is also observed in the experiment.

In conclusion by solving the nonlinear Eliashberg equations we find that in La$_{1-x}$Pr$_x$Os$_4$Sb$_{12}$ the dominant quadrupolar scattering due to the specific $T_c$ crystal group symmetry of the lattice is responsible for the observed increase of $T_c$ as a function of Pr concentration. Our analysis suggests that a combination of conventional electron-phonon interaction together with pairing mediated by quadrupolar excitons yields strong-coupling superconductivity in the PrOs$_4$Sb$_{12}$ system.

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23. T. Westerkamp and G. Zwicknagl (private communication).
25. One should note, however, that the substitution of Os by Ru results not only in the change of CEF effects but also in the change of spin-orbit coupling strength within the conduction band and also different electronic correlations.