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# Effects of nonmagnetic La impurities on the spin resonance of $Ce_{1-x}La_xCoIn_5$ single crystals as seen via inelastic neutron scattering

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The influence of La nonmagnetic impurities on the spin dynamics of $CeCoIn_5$ was studied by inelastic neutron scattering. In La-substituted systems, the spin resonance peak (observed at $\Omega_{\mathrm{res}} = 0.55$ meV in the pure system) is shifted to lower energies but the ratio $\Omega_{\mathrm{res}}/k_BT_c$ remains almost unchanged. The excitation broadens up to an energy of 0.3 meV which is equal to the value of the quasielastic signal in the normal state. The evolution of the excitation as a function of La substitution is compared with Ni- and Zn-substituted $YBa_2Cu_3O_7$.

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Superconductivity is a macroscopic quantum state resulting from the condensation of electrons in Cooper pairs. In the case of conventional superconductivity, the pairing mechanism is the weak electron-phonon interaction. However, in strongly correlated systems exhibiting a superconducting (SC) state, the pairing mechanism is thought to be of a different nature. Examples of such unconventional superconductors are high temperature superconducting cuprates (HTSC), heavy fermion compounds (HFs), and the iron-based superconductors. In these compounds, the origin of the pairing is strongly suspected to be the magnetic interaction and a seminal study of the magnetic excitation spectra by inelastic neutron scattering (INS) in the cuprate $YBa_2Cu_3O_{6+x}$ showed the appearance of a sharp excitation called a magnetic spin resonance[1] in the SC state. This was then generalized to other cuprates. Such a feedback of superconductivity on the magnetic excitation spectra was backed up by the theories of a pairing mechanism of magnetic origin. The recent discovery of similar excitations in HF superconductors $UPd_2Al_3$ (Ref. 2), $CeCoIn_5$ (Ref. 3), and $CeCu_2Si_2$ (Ref. 4) as well as the iron superconductors[5] suggests that the magnetic resonance could be a universal feature of unconventional superconductors.

Among HF superconductors, the compound $CeCoIn_5$ has the highest critical temperature, $T_c = 2.3$ K.[6] It crystallizes in the tetragonal space group $P4/mmm$ and is composed of alternating $CeIn_3$ and $CoIn_2$ layers. The quasi-2D nature is supported by de Haas van Alphen measurements, which established a Fermi surface composed of nearly cylindrical sheets.[7] As concerns the low energy magnetic excitations measured by INS, a quasielastic signal is measured above $T_c$ with a linewidth of 0.3 meV. Below $T_c$, the spectral shape switches from a quasielastic to a sharp inelastic peak which appears for an energy $\Omega_{\mathrm{res}} \approx 0.55$ meV ($\approx 2.7 k_BT_c$) at the antiferromagnetic position $\mathbf{Q} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$.[3]

The introduction of nonmagnetic impurities is a useful probe to investigate the microscopic nature of the SC state.[8] For a $d$-wave superconductor such as $CeCoIn_5$, the impurities are expected to have a Cooper pair breaking effect.[9] In $CeCoIn_5$, this seems to be achieved by La substitution.[10,11] Contrary to other types of substitution (Nd on Ce site,[12] Cd on In site[13]), La does not induce magnetic order but only reduces the critical temperature $T_c$ by $(-0.056T_c)/(1\%$ of La substitution).[10]

In this Brief Report, we report INS experiments performed on single crystal samples of $Ce_{1-x}La_xCoIn_5$ for $x = 0$, 0.02, 0.035, and 0.05. We find that the ratio between the resonance energy $\Omega_{\mathrm{res}}$ and $T_c$ remains almost constant when increasing the La concentration whereas the excitation lineshape broadens.

Single crystal samples were grown by the self-flux method[14] and characterized by specific heat measurements performed using a commercial quantum design physical properties measurement system (PPMS) down to 400 mK, which are shown in the inset of Fig. 1. From these measurements, we deduce the $T_c$ of each La-substituted system studied in this Brief Report. Without substitution, $T_c$ is 2.3 K as previously reported, for $x = 0.02$, 0.035, and 0.05, $T_c$ is 1.9, 1.7, and 1.5 K, respectively. Furthermore, the specific heat measurements are in agreement with the results obtained in Ref. 11: we observe a reduction at the transition of the specific heat jump while increasing La concentration, an increase of the Sommerfeld coefficient $\gamma$ for $T \to 0$ and a broadening of the transition for higher substitution. This broadening could be related to a distribution of $T_c$ in the crystal due to inhomogeneity.

The INS experiments were performed on the cold neutron triple-axis spectrometers IN14 and IN12 at Institut Laue Langevin, Grenoble and 4F2 at Laboratoire Léon Brillouin, Saclay. In the three experiments, the incident beam was provided by a vertically focusing pyrolytic graphite (PG) monochromator (double monochromator in the case of 4F2). A liquid-nitrogen-cooled Be filter was placed before the sample in order to avoid any higher order contaminations. Measurements were performed with a fixed final wave vector $k_f = 1.3$ Å$^{-1}$ for IN14 and IN12, and $k_f = 1.35$ Å$^{-1}$ for 4F2. The collimations were 60′-open-open. The energy resolution determined from the full width at half-maximum (FWHM) of the incoherent signal was 0.12 meV on IN14, 0.10 on IN12, and 0.15 meV on 4F2. The different samples consisted of assemblies of about 30 single crystals of $Ce_{1-x}La_xCoIn_5$ coaligned and glued with Fomblin oil on two thin aluminum plates. The mosaic spread of the three assemblies, as measured

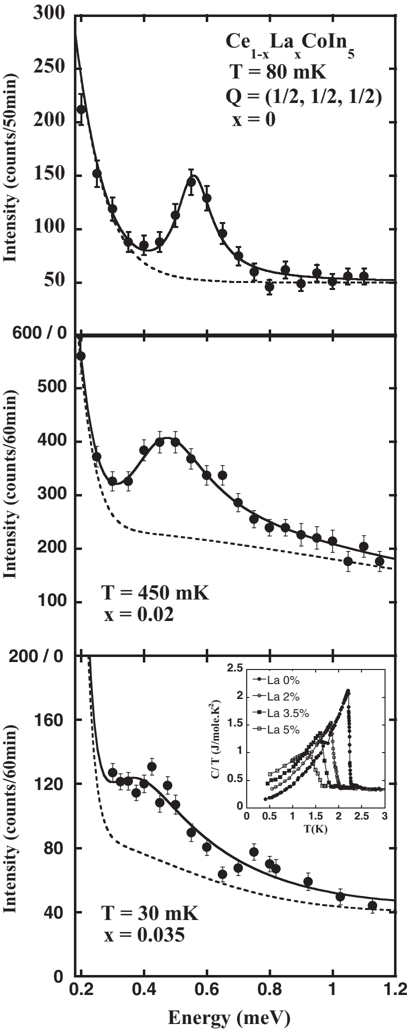

FIG. 1. Excitation spectra measured at $\mathbf{Q}=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ for $Ce_{1-x}La_xCoIn_5$ with $x=0$, 0.02, and 0.035. The solid lines are "inelastic Lorentzian" fits and the dashed line indicates the background as described in the text. The inset shows the specific heat ($C_p$) measurements of La substitution of 0%, 2%, 3.5%, and 5%.

on a rocking curve through the (1,1,1) Bragg reflection, extends from 1° to 1.5°. The sample was put in a $^3$He insert for the experiments on IN14 and IN12, and in a dilution insert on 4F2 with [1,1,0] and [0,0,1] defining the scattering plane.

The measured neutron intensity without the background is proportional to the scattering function $S(\mathbf{Q},E)$ itself related to the imaginary part of susceptibility $\chi''(\mathbf{Q},E)$.

$$S(\mathbf{Q},E) = n(E,T)\ \chi''(\mathbf{Q},E),$$

$\chi''$ was analyzed using an "inelastic Lorentzian" spectral function:

$$\chi''(\mathbf{Q},E) = \frac{1}{2}\left[\frac{\chi_Q\Gamma_Q E}{(E-\Omega_{\rm res})^2+\Gamma_Q^2} + \frac{\chi_Q\Gamma_Q E}{(E+\Omega_{\rm res})^2+\Gamma_Q^2}\right],$$

$n(E,T)=1/(1-e^{-E/k_BT})$ is the detailed balance factor, $\Gamma_Q$ is the relaxation rate, $\Omega_{\rm res}$ is the resonance energy, and $\chi_Q$ is susceptibility at the wave vector $\mathbf{Q}$. All the energy spectra were taken at $\mathbf{Q}=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ except the background measurements.

The magnetic excitation spectrum measured at $\mathbf{Q}=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ as a function of La substitution is shown in Fig. 1. The data for $x=0$ are taken from Ref. 15. The dashed line corresponds to the background signal obtained by performing an energy scan shifted in $\mathbf{Q}$ position. For the experiment on IN12 and IN14, the background was measured at $\mathbf{Q}=(0.8,0.8,\frac{1}{2})$ and for 4F2 at $\mathbf{Q}=(0.412,0.412,0.8)$. Without substitution, the resonance peak is reported in Ref. 15 at 0.55 meV with a relaxation rate of 0.07 meV. In the 2% La-substituted system, the resonance peak shifts to $\Omega_{\rm res}=0.45$ meV and undergoes a substantial broadening reaching a relaxation rate $\Gamma$ of 0.3 meV. A La substitution of 3.5% shifts the resonance peak to $\Omega_{\rm res}=0.35$ meV but $\Gamma$ remains constant at $0.3\pm0.05$ meV. For this latter concentration, it is worthwhile to note that the resonance peak is no more a well-defined inelastic excitation since $\Omega_{\rm res}\approx\Gamma$. The spectra with a 5% La substitution (not shown here) presents no resonance peak. Either the peak is too broad to be resolved or the excitation occurs at too low energy to be separated from the incoherent signal. The parameters extracted from the data fit are summarized in Fig. 2. In this figure, the linear fit for the evolution of the resonance energy $\Omega_{\rm res}$ as a function of La substitution corresponds to a rate of $(-0.058\Omega_{\rm res})/(1\%$ of La substitution).

Constant energy scans were performed along the $a$ and $c$ axes around $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ in order to measure the correlation lengths of the resonance under La substitution. Figure 3 shows spectra measured at 0.5 meV with a substitution of 2%. The scans are analyzed with a Gaussian lineshape. The background is

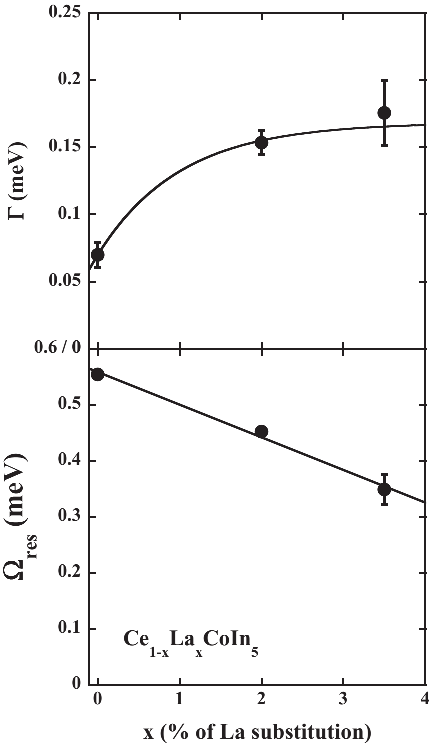

FIG. 2. Evolution of the relaxation rate $\Gamma$ and the resonance energy $\Omega_{\rm res}$ as a function of La-substitution in $CeCoIn_5$. The lines are a linear fit to the resonance energy and a guide to the eyes for the relaxation rate.

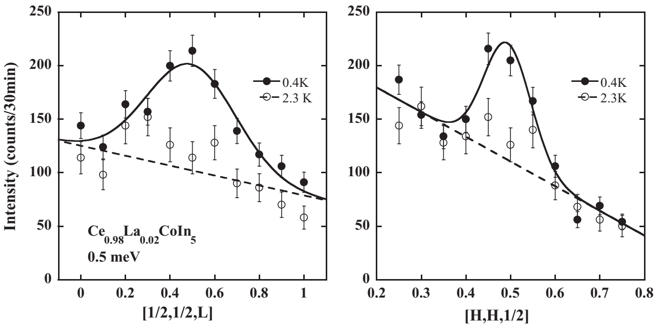

FIG. 3. Excitation spectra measured at $E = 0.5$ meV in the direction $[\frac{1}{2},\frac{1}{2},L]$ and $[H,H,\frac{1}{2}]$ for $\mathrm{Ce_{0.98}La_{0.02}CoIn_5}$. The solid line is a Gaussian fit and the dashed line indicates the background as described in the text.

determined by the measurements at high temperature where the magnetic spectrum is no longer peaked in **Q**. The signal still peaks at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ as for the pure compound. The correlation lengths obtained from the inverse of the Gaussian half-width at half maximum are $\xi_c = 5.1 \pm 0.1$ Å and $\xi_a = 11.8 \pm 0.6$ Å. In comparison with the pure compound,[3] the correlation lengths remain similar in both directions (for the pure compound $\xi_c = 6.5 \pm 0.9$ Å and $\xi_a = 9.6 \pm 1$ Å).

The evolution of the resonance peak of the substituted system was studied as a function of temperature. Indeed in the pure compound, the resonance peak has been observed only in the SC state[3] showing the strong relationship between the resonance excitation and superconductivity. In Fig. 4, we report the evolution of the $\Omega_{\mathrm{res}}/\Omega_{\mathrm{res}}(T=0)$ as a function of $T/T_c$ for the pure compound 0% (extracted from the Ref. 3) and a La substitution of 2%. The evolution in temperature of $\Omega_{\mathrm{res}}$ for a 2% La-substituted system matches the evolution of the pure compound. The presence of impurities seems to have no influence on the coupling between superconductivity and the resonance excitation since there is no persistence of the resonance above $T_c$.

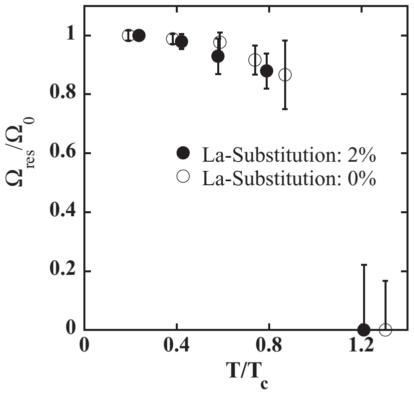

FIG. 4. Evolution of the resonance energy $\Omega_{\mathrm{res}}$ of $\mathrm{Ce_{0.98}La_{0.02}CoIn_5}$ and $\mathrm{CeCoIn_5}$ from Ref. 3 at $\mathbf{Q} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$ as function of the ratio $T/T_c$ (for the pure compound $T_c = 2.3$ K and for a 2%-substituted compound $T_c = 1.9$ K).

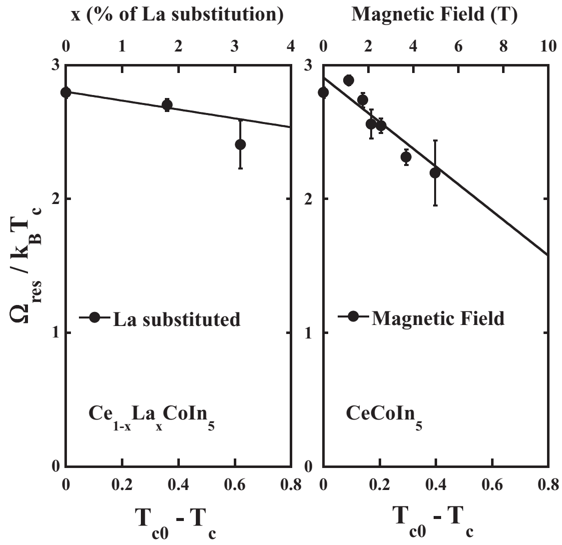

FIG. 5. Evolution of the resonance energy $\Omega_{\mathrm{res}}$ divided by the critical temperature as a function of $T_{c0} - T_c$ controlled by La substitution (left panel) or magnetic field (right panel; data from Ref. 15). $T_{c0}$ corresponds to the value of $T_c$ for the pure compound without magnetic field, i.e., $T_{c0} = 2.3$ K.

The nature of the resonance in $\mathrm{CeCoIn_5}$ is still controversial with two models proposed: either as an exciton (a $S = 1$ bound state in the particle-hole channel)[16] or as a magnon (a magnetic mode visible in the SC state due to the suppression of the Landau damping).[17] Without a definitive theoretical model, it is therefore difficult to analyze our results beyond a phenomenological approach. In the present experimental study of the resonance peak in $\mathrm{Ce_{1-x}La_xCoIn_5}$, we find that $\Omega_{\mathrm{res}}/k_BT_c \approx 2.7$ (see Fig. 5, left panel). Such a linear relation between $\Omega_{\mathrm{res}}$ and $T_c$ is reported for HTSC (Ref. 18) and iron-based superconductors.[19] In these cases, the doping acts as a tuning parameter. In contrast, La substitution in $\mathrm{CeCoIn_5}$ corresponds to the insertion of nonmagnetic impurity with pair breaking effects. For *d*-wave superconductor, the impurities suppress the gap following $\Delta \propto k_BT_c$ (Ref. 9) and as often pointed out,[3] the energy scale $\Omega_{\mathrm{res}}$ is related to the superconducting gap $\Delta$, $\Omega_{\mathrm{res}} \propto \Delta$. Therefore, the proportionality between $\Omega_{\mathrm{res}}$ and $k_BT_c$ is expected in first approximation and observed in our work. There are few theoretical calculations which have been developed concerning the effect of nonmagnetic impurities on the resonance for a d-wave superconductor. To our knowledge there is only one study which describes precisely this effect, showing a decrease of the resonance energy and an increase of the resonance width[22] upon the introduction of impurities. The mechanism of the broadening corresponds to impurity scattering leading to a damping of spin excitations. Our results are in agreement with this theory even if this theory was developed using a band structure adequate for the cuprates and an exciton model.

To date, there are no INS experiments on the effects of nonmagnetic impurities on the resonance in HF compounds. However, we could compare our results with two INS experiments which have been performed on the system YBCO with the substitution of Cu by Zn nonmagnetic impurities and Ni magnetic impurities.[20,21] If we make a quantitative comparison with these two cases, some features draw attention: the Zn substitution and the Ni substitution both induce a $T_c$ reduction but the Zn one has a higher rate of suppression of $T_c$: $(\approx -0.13T_c)/(1\%$ of Zn substitution) compared with $(\approx -0.04T_c)/(1\%$ of Ni substitution).[21] The influence of both impurities is totally different concerning the evolution of the spin resonance in energy and in temperature. The 1% Zn substitution does not shift $\Omega_{\text{res}}$ and so increases the ratio $\Omega_{\text{res}}/k_B T_c$ compared with the pure $YBa_2Cu_3O_7$ compound. Though the 3% Ni substitution leads to a decrease of $\Omega_{\text{res}}$ while conserving the ratio $\Omega_{\text{res}}/k_B T_c$. Concerning the width of the resonance peak in energy for $YBa_2Cu_3O_7$ with both Zn and Ni substitution, no noticeable increase of the relaxation rate is observed at low values of substitution[21] contrary to our case. But the large value of the relaxation rate in $YBa_2Cu_3O_7$ could hide a small increase of the width. Moreover, the magnetic signal in the 1% Zn-substituted compound does not disappear at $T_c$ but half of the integrated intensity remains above $T_c$. Concerning the Ni-case, the magnetic signal vanishes upon increasing the temperature up to $T_c$ as in the La-substituted $CeCoIn_5$ compound. In conclusion, the case of La impurities in $CeCoIn_5$ is closer to the case of Ni magnetic impurities than of Zn nonmagnetic impurities in $YBa_2Cu_3O_7$. A recent INS experiment[23] has been performed to study the effect of Zn substitution in the underdoped $YBa_2Cu_3O_{6.6}$. It points out the appearance of an incommensurate order and a spectral weight transfer from the resonance to low energy. In this experiment, the resonance peak still remains at the same position in energy even if its intensity strongly decreases as has been observed in the Zn-substituted optimally doped $YBa_2Cu_3O_7$.[20,21]

Finally, we compare the La substitution with another way to tune the superconductivity, the application of a magnetic field. While in the La substitution, $\Omega_{\text{res}}$ is related to the superconducting gap $\Delta$, under magnetic field, the situation is quite different as illustrated in the right panel of Fig. 5: $\Omega_{\text{res}}/k_B T_c$ is substantially decreasing as a function of $T_c$. For $CeCoIn_5$, the Pauli and orbital effects are present in magnetic field. In the model of the spin exciton, the former effect leads to a decrease of the resonance energy related to a decrease of the SC gap with increasing field[24] while the latter effect leads to Zeeman splitting of the excitation.[25] The reduction of $\Omega_{\text{res}}/k_B T_c$ with magnetic field seems to rule out an evolution only related to the SC gap. A recent theoretical work devoted to the case of $CeCoIn_5$ (Ref. 26) emphasized the importance of Zeeman effect to analyze the evolution of the resonance with the magnetic field.

The accurate study of the resonance as a function of La substitution in $CeCoIn_5$ shows a quasiconstant ratio $\Omega_{\text{res}}/k_B T_c \approx 2.7$ with a broadening of the excitation. Theses observations are in agreement with a theoretical model developed for $YBa_2Cu_3O_7$ but our results are in stark contrast with the INS experiments performed on $YBa_2Cu_3O_7$ with Zn nonmagnetic impurities. These overall issues deserve further theoretical studies.

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