Magnetic-field and doping dependence of low-energy spin fluctuations in the antiferroquadrupolar compound Ce$_{1-x}$La$_x$B$_6$

G. Friemel,$^1$ H. Jang,$^{1,2}$ A. Schneidewind,$^3$ A. Ivanov,$^4$ A. V. Dukhnenko,$^5$
N. Y. Shitsevalova,$^5$ V. B. Filipov,$^5$ B. Keimer,$^1$ and D. S. Inosov$^6$

$^1$Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany
$^2$Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA
$^3$Jülich Center for Neutron Science (JCMS) at Heinz Maier-Leibeit Zentrum (MLZ), Forschungszentrum Jülich GmbH, Lichtenbergstr. 1, 85748 Garching, Germany
$^4$Institut Laue-Langevin, 6 rue Jules Horowitz, 38042 Grenoble Cedex 9, France
$^5$I.M. Frantsievich Institute for Problems of Materials Science of NAS, 3 Krzhizhanovsky str., Kiev 03680, Ukraine
$^6$Institut für Festkörperphysik, TU Dresden, D-01069 Dresden, Germany

CeB$_6$ is a model compound exhibiting antiferroquadrupolar (AFQ) order, its magnetic properties being typically interpreted within localized models. More recently, the observation of strong and sharp magnetic exciton modes forming in its antiferromagnetic (AFM) state at both ferromagnetic and AFQ wave vectors suggested a significant contribution of itinerant electrons to the spin dynamics. Here we investigate the evolution of the AFQ excitation upon the application of an external magnetic field and the substitution of Ce with non-magnetic La, both parameters known to suppress the AFM phase. We find that the exciton energy decreases proportionally to $T_B$ upon doping. In field, its intensity is suppressed, while its energy remains constant. Its disappearance above the critical field of the AFM phase is preceded by the formation of two modes, whose energies grow linearly with magnetic field upon entering the AFQ phase. These findings suggest a crossover from itinerant to localized spin dynamics between the two phases, the coupling to heavy-fermion quasiparticles being crucial for a comprehensive description of the magnon spectrum.

PACS numbers: 75.30.Mb, 75.30.Ds, 78.70.Nx

A current focus of research in heavy fermion (HF) compounds is the study of quantum critical points (QCP) — phase transitions achieved at zero temperature by tuning an external parameter such as magnetic field, doping, or pressure. One possible signature of a QCP is the change of the quasiparticle character from localized to itinerant, when the transition is connected with a breakdown of the Kondo effect and the removal of $f$-electrons from the Fermi surface (FS). Such an effect was observed, for example, by transport measurements in the prototypical QCP system YbRh$_2$(Si$_{1-x}$Ge$_x$)$_2$ at the critical field of the low-temperature antiferromagnetic (AFM) phase [1, 2]. Recently, the list of QCP materials was extended with the cubic Kondo lattice compound Ce$_x$Pd$_{20}$Si$_{16}$ [3, 4], whose magnetic phase diagram comprises an antiferroquadrupolar (AFQ) phase below $T_Q = 0.5$K and an AFM phase at even lower temperatures. For the latter phase, a field-induced QCP was observed at the critical field $B = 0.9$T and the concomitant FS reconstruction was related to the destruction of the Kondo effect [3].

CeB$_6$ was one of the first known AFQ compounds, where the multipolar order was observed both indirectly as an anomaly in specific heat at $T_Q = 3.2$K [5] and directly by resonant x-ray diffraction [6] or neutron diffraction [7, 8] as a weak magnetic Bragg peak centered at the QF$_{AFQ} = R(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ propagation vector. The magnetic phase diagram of CeB$_6$ [7] is similar to that of Ce$_x$Pd$_{20}$Si$_{16}$, yet with larger temperature and magnetic-field scales. Correspondingly, it features an AFM phase (phase III) below $T_N = 2.4$K, which exhibits a complex double-$q$ structure with $q_1 = \Sigma(\frac{1}{2} \frac{1}{2} 0)$, $q_2 = S(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ and $q_3 = S(\frac{1}{2} \frac{1}{2} 0)$, $q'_1 = S(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ [9]. The AFM phase can be suppressed in a magnetic field of $B_c = 1.05$T [7], however, in contrast to Ce$_x$Pd$_{20}$Si$_{16}$, resistivity and heat capacity exhibit Fermi-liquid-like behavior down to the lowest temperatures [10, 11], suggesting the absence of field-induced quantum-critical fluctuations. Instead, CeB$_6$ enters an intermediate magnetic phase (phase III′) for $B_c < B < B_Q [7, 12]$. For $B > B_Q = 1.7$T, the AFQ phase is established and stabilized up to very high fields, showing an increase of $T_Q$ with $B$ [5, 7]. Beside magnetic field, substitution with non-magnetic lanthanum in Ce$_{1-x}$La$_x$B$_6$ also leads to a suppression of the AFM phase with a critical doping level $x_c = 0.3$ [13]. However, the transition at zero temperature occurs into an enigmatic phase IV [14, 15] instead of the paramagnetic phase, also precluding the direct observation of quantum-critical fluctuations in transport properties [10]. The $B$–$T$ phase diagram as well as the temperature and magnetic-field dependencies of the uniform and staggered magnetization could be successfully modeled by a purely localized mean-field Hamiltonian consisting of Zeeman, dipolar, quadrupolar and octupolar exchange terms [16], which suggested that CeB$_6$ lies far from the critical point where the Kondo effect breaks down.

However, this localized viewpoint has been challenged by recent inelastic neutron scattering (INS) experiments, demonstrating the appearance of a sharp resonant mode at $Q_{AFQ}$ centered at an energy $\hbar \omega_R = 0.5$meV in the AFM phase [8]. It can be explained as a pole in the itinerant spin susceptibility calculated in the random-phase-approximation (RPA) for the HF ground state [17], signifying a close relationship to the sharp resonant modes observed in the superconducting (SC) state of some other HF compounds, such as CeCoIn$_5$ [18] or CeCu$_2$Si$_2$ [19]. Furthermore, the exciton seems to be connected to a ferromagnetic collective mode, which is much more intense than the spin waves emerging from $q_1$ and $q'_1$ [20], putting CeB$_6$ close to a ferromagnetic instability. To differentiate between itinerant and localized descriptions of the spin dynamics, we study the evolution of the exciton mode at $R(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ upon the suppression of the AFM state by (i) dilution with non-magnetic La$^{3+}$ in Ce$_{1-x}$La$_x$B$_6$ and (ii) the application of an external magnetic field.

We prepared rod-shaped single crystals of Ce$_{1-x}$La$_x$B$_6$ ($x = 0$, 0.18, 0.23 and 0.28), grown by floating-zone
Here, the parameter $\Gamma$, which describes the damping of the mode, equals the half width at half maximum (HWHM) of the peak [Fig. 3 (a2)–(d2)]. The susceptibility $\chi'$ is proportional to the integrated intensity (area) [Fig. 3 (a3)–(d3)]. Furthermore, the amplitude vs. $B$ is shown in Fig. 3 (a1)–(d1), and the mode energy $\hbar\omega_0$ vs. $B$ is overlayed in Fig. 2. In the following, we will show that the field dependence of the spin excitations can be classified according to the field regimes as outlined in the inset of Fig. 3 (a3). In the AFM phase, the exciton energy stays nearly constant vs. $B$, see Fig. 2 (a) and Fig. 2 (b), while its amplitude in Fig. 3 (a1) and Fig. 3 (b1) shows a strong suppression. This contrasts with the resonant mode in the SC state of CeCoIn$_5$, whose energy splits in magnetic field with the main part of the spectral weight carried by the lower Zeeman branch [23].
The high-energy mode consecutive AFQ and AFM orderings. However, the energy of the degeneracy within the \( \Gamma \) netic field, which agrees with the complete lifting of the magnetic field. Its magnitude of \( \hbar \omega \propto \) diminishes with field with a varying slope between the compounds and a rather concave order-

For neither of the modes do we observe any splitting in mag-

The integrated spectral weight of the exciton, corre-

Moreover, upon entering phase III' at \( B_o \), we observe the appearance of a previously unknown second mode, which can be seen for the \( x = 0 \) and \( x = 0.18 \) compounds at a lower energy of \( \sim 0.2 \text{ meV} \) in Fig. 1 (a) and (b). This excitation, denoted here as AFQ_1, is very sharp and evolves smoothly into the phase II [see Fig. 3 (a1) and (a3)], its energy increasing parallel to that of the AFQ_1 mode, as seen in Fig. 2 (a) and (b). Clarification of the nature of this new mode is left for future studies, but one can already conclude that phase III' and phase II are very similar in terms of spin dynamics. The linear monotonic increase of both the AFQ_1 and AFQ_2 mode energies with magnetic field in phase II (Fig. 2) have a common slope \( g = (0.11 \pm 0.004) \text{ meV/T} = (1.90 \pm 0.07) \mu_B \), which is doping independent. This can be qualitatively explained by a transition between two Zeeman-split energy levels, consistent with the purely localized description of the spin dynamics in a mean-field model of ordered multipoles in magnetic field \([26]\). For comparison, electron spin resonance (ESR) measurements, which probe the modes at the Brillouin zone center, gave a value of \( g \approx 1.6 \) \([27]\). The localized model would also naturally explain the increasing line width \( \Gamma \) of the AFQ_1 mode with La doping, shown in Fig. 4 (d), since the La-substitution alters the environment of the Ce^{3+} ion, composed of six nearest neighbors.

Thus, it remains to be clarified how the exciton and the AFQ_1 mode are related. One possible scenario \([17]\) describes the exciton as a collective mode below the onset of the particle-hole continuum at \( 2\Delta_{\text{AFM}} \). An alternative approach would understand the exciton as a multipolar excitation, which is overdamped by the coupling to the conduction electrons in the AFQ state \( T > T_N \), but emerges as a sharp peak in the AFM state where the damping is removed by the opening of a partial charge gap \([8, 20]\). On the one hand, it would be an oversimplification to identify the exciton with the AFQ_1 mode, according to the second scenario, since the field dependence of the energy and the amplitude is completely different for both excitations (Figs. 2 and 3). On the other hand, the zero-field extrapolation of the AFQ_1 mode energy \( E_0 \) almost coincides with the exciton energy \( \hbar \omega_{\text{Q}} \) [see Fig. 2 (d)], both following the suppression of the magnetic energy scale, \( k_B T_N \), as shown in Fig. 4 (a).

Another piece of information is given by the doping and field dependencies of the exciton line width, \( \Gamma \). Figure 4 (b) shows that it increases with the ratio of the exciton energy to the AFM ordering temperature, \( \hbar \omega_{\text{Q}}/k_B T_N \), which can be considered as a rough measure of the relative distance between the exciton and the onset of the particle-hole continuum. The points for all samples in which the exciton has been observed appear to fall on the same line, indicating that proximity to the continuum dominates the mode damping. A similar picture is given in Fig. 4 (c), where the...
line width is plotted directly vs. $T_N$, whose dependence on the magnetic field has been taken into account. The universality of these dependencies among all measured samples suggests that the suppression of the AFM order and the associated closing of the partial charge gap leads to a broadening of the exciton rather than the chemical disorder for both. Instead, the line width is smaller for the exciton and decreasing towards smaller fields, as best explained with the similar disorder effect because of chemical fluctuations. The same applies presumably to the ferromagnetic mode, which together with the exciton and spin-wave excitations are forming the dominant thermodynamic critical fluctuations in CeB$_6$ above $T_N$ [20]. As the $E_0$ energy scale of the AFQ$_1$ mode also vanishes [Fig. 4 (a)], one can regard the AFM QCP here as coincident with the zero-field-extrapolated QCP of the AFQ phase. This QCP may also explain an enhancement of the effective mass upon approaching $x_c$ as observed in transport [10].

In conclusion, we reported the magnetic-field and doping dependence of the spin-excitation spectrum at the exciton wave vector. We demonstrated that the exciton mode of itinerant origin transforms into a localized Zeeman-type mode above the critical field $B_c$, which cannot be fully understood within the available multipolar models of the spin dynamics [26]. Contrary to the cases of CePt$_2$Si$_2$ and YbRh$_2$Si$_2$, these fluctuations do not become critical at $B_c$, however, they are critically softened upon doping, indicating a QCP near $x_c = 0.3$, which is hidden inside the enigmatic phase IV. These results outline rich prospects in the research of competing correlated ground states in the structurally simple three-dimensional system CeB$_6$.

We thank A. Akbari, G. Jackeli, Yuan Li, and J.-M. Mignot for stimulating discussions. D. S. I. acknowledges financial support by the German Research Foundation (DFG) under grant No. IN 209/3-1. H. J. was supported by the Max Planck POSTECH Center for Complex Phase Materials with KR2011-0031558.

Thanks to Planck POSTECH Center for Complex Phase Materials with KR2011-0031558.
[5] T. Fujita, M. Suzuki, T. Komatsubara, S. Kunii, T. Kasuya and T. Ohtsuka, Solid State Commun. 35, 569–572 (1980).

[6] H. Nakao et al., J. Phys. Soc. Jpn. 70, 1857–1860 (2001); Y. Tanaka et al., Europhys. Lett. 68, 671–677 (2004); T. Matsumura et al., Phys. Rev. Lett. 103, 017203 (2009); Phys. Rev. B 85, 174417 (2012).

[7] J. M. Effantin, J. Rossat-Mignod, P. Burlet, H. Bartholin, S. Kunii and T. Kasuya, J. Magn. Magn. Mater. 47–48, 145–148 (1985); J. M. Effantin and P. Burlet and J. Rossat-Mignod and S. Kunii and T. Kasuya, Valence Instabilities, edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982), p. 559.

[8] G. Friemel et al., Nature Commun. 3, 830 (2012).

[9] P. Burlet, J. Rossat-Mignod, J. M. Effantin, T. Kasuya, S. Kunii and T. Komatsubara J. Appl. Phys. 53, 2149–2151 (1982); O. Zaharko, P. Fischer, A. Schenck, S. Kunii, P-J. Brown, F. Tasset and T. Hansen, Phys. Rev. B 68, 214401 (2003).

[10] S. Nakamura, M. Endo, H. Yamamoto, T. Iishiki, N. Kimura, H. Aoki, T. Nojima, S. Otani and S. Kunii, Phys. Rev. Lett. 97, 237204 (2006).

[11] C. Bredl, J. Magn. Magn. Mater. 63–64, 355–357 (1987).

[12] K. Kunimori, M. Kotani, H. Funaki, H. Tanida, M. Sera, T. Matsumura and F. Iga, J. Phys. Soc. Jpn. 80, SAI06 (2011).

[13] T. Tayama, T. Sakakibara, K. Tenya, H. Amitsuka and S. Kunii, J. Phys. Soc. Jpn. 66, 2268–2271 (1997).

[14] S. Kobayashi, M. Sera, M. Hiroi, N. Kobayashi and S. Kunii, J. Phys. Soc. Jpn. 69, 926–936 (2000).

[15] S. Kobayashi, Y. Yoshino, S. Tsuji, H. Tou, M. Sera and F. Iga J. Phys. Soc. Jpn. 72, 2947–2954 (2003).

[16] M. Sera, H. Ichikawa, T. Yokoo, J. Akimitsu, M. Nishi, K. Kakurai and S. Kunii, Phys. Rev. Lett. 86, 1578 (2001); M. Sera and S. Kobayashi, J. Phys. Soc. Jpn. 68, 1664–1678 (1999); R. Shina, O. Sakai, H. Shiba and P. Thalmeier, ibid. 67, 941–949 (1998).

[17] A. Akbari and P. Thalmeier, Phys. Rev. Lett. 108, 146403 (2012).

[18] C. Stock, C. Broholm, J. Hudis, H. J. Kang and C. Petrovic, Phys. Rev. Lett. 100, 087001 (2008).

[19] O. Stockert et al., Nature Phys. 7, 119–124 (2011).

[20] H. Jang, G. Friemel, J. Ollivier, A. V. Dukhnenko, N. Y. Shitsevalova, V. B. Filipov, B. Keimer and D. S. Inosov, Nature Mater. 13, 682–687 (2014).

[21] T. Furuno, N. Sato, S. Kunii, T. Kasuya and W. Sasaki, J. Phys. Soc. Jpn. 54, 1899–1905 (1985).

[22] O. Suzuki, T. Goto, S. Nakamura, T. Matsumura and S. Kunii, J. Phys. Soc. Jpn. 67, 4243–4250 (1998).

[23] C. Stock, C. Broholm, Y. Zhao, F. Demmel, H. J. Kang, K. C. Rule and C. Petrovic, Phys. Rev. Lett. 109, 167207 (2012); J. Panarin, S. Raymond, G. Lapertot and J. Flouquet, J. Phys. Soc. Jpn. 78, 113706 (2009).

[24] E. Paulus and G. Voss, J. Magn. Magn. Mater. 47–48, 539–541 (1985).

[25] A. Bouvet, Ph.D. Thesis, Grenoble (1993).

[26] P. Thalmeier, R. Shinia, H. Shiba and O. Sakai, J. Phys. Soc. Jpn. 67, 2363–2371 (1998).

[27] S. V. Demishev, A. V. Semeno, A. V. Bogach, N. A. Samarina, T. V. Ishchenko, V. B. Filipov, N. Y. Shitsevalova and N. E. Sluchanko, Phys. Rev. B 80, 245106 (2009).

[28] O. Suzuki, S. Nakamura, M. Akatsu, Y. Nemoto, T. Goto and S. Kunii, J. Phys. Soc. Jpn. 74, 735–741 (2005).

[29] J. Flouquet et al., J. Low Temp. Phys. 161, 83–97 (2010).

[30] H. Aoki, S. Uji, A. K. Albessard and Y. Onuki, Phys. Rev. Lett. 71, 2110–2113 (1993).

[31] S. Kobayashi, M. Sera, M. Hiroi, N. Kobayashi and S. Kunii, J. Phys. Soc. Jpn. 68, 3407–3412 (1999).

[32] D. Mannix, Y. Tanaka, D. Carbone, N. Bernhoeft and S. Kunii, Phys. Rev. Lett. 95, 117206 (2005); A. Schenck, F. N. Gygax and G. Soli, Phys. Rev. B 75, 024428 (2007); H. Takagiwa, K. Ohishi, J. Akimitsu, W. Higemoto, R. Kadono, M. Sera and S. Kunii, J. Phys. Soc. Jpn. 71, 31–34 (2002).

[33] S. Nakamura, T. Goto, O. Suzuki, S. Kunii and S. Sakatsume, Phys. Rev. B 61, 15203–15212 (2000).