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Single-crystal neutron diffraction studies on $CeCu_2Ge_2$ and $CeCu_{1.9}Ni_{0.1}Ge_2$

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We have performed single-crystal neutron diffraction studies on $CeCu_2Ge_2$ and $CeCu_{1.9}Ni_{0.1}Ge_2$ to get insight into the very unusual magnetic properties of these compounds. $CeCu_2Ge_2$ orders antiferromagnetically below T_N=4.15 K in an incommensurate sinusoidal amplitude modulated structure. $CeCu_{1.9}Ni_{0.1}Ge_2$ shows two successive magnetic phase transitions at T_{N1}=3.65 K and T_{N2}=2.65 K, respectively. The corresponding magnetic structures are very similar to each other as well as to the magnetic structure of pure $CeCu_2Ge_2$. Based on the temperature dependence of the intensities of the principal magnetic reflections, the two magnetic phases seem to superimpose independently of each other. [S0163-1829(97)02509-5]

INTRODUCTION

$CeCu_2Ge_2$ is a heavy-fermion system, which crystallizes in the tetragonal $ThCr_2Si_2$-type structure (space group I_4/mmm). In this compound, the energy scales of the Ruderman-Kittel-Kasuya-Yosida (RKKY) and the Kondo-type interactions reveal the same order of magnitude. Consequently, below T_N=4.15 K antiferromagnetic order with Kondo-compensated moments is established. At T=1.5 K the magnetic structure has been characterized as an incommensurate (IC) modulated structure of localized moments.[1] Guided by an enhanced Sommerfeld coefficient well below the Néel temperature, it has been speculated that long-range magnetic order may coexist with a coherent heavy-fermion (HF) state.[2] The substitution of copper by nickel compresses the unit cell and increases the hybridization between the $4f$ electrons and the band states. $CeNi_2Ge_2$ shows no magnetic order but a typical Fermi-liquid behavior with a characteristic temperature $T^*\approx30$ K.[3] For intermediate concentrations, experimental evidence for the existence of heavy-fermion band magnetism[4] (HFBM) as well as the appearance of non-Fermi-liquid (NFL) behavior[5] has been provided. In the regime of HFBM the spin degrees of freedom are assumed to be transferred from the $4f$ sites to the band states, while the $4f$ charges reside at the cerium sites. For a detailed discussion of the phase diagram, the reader is referred to Refs. 4 and 5 and references therein. With the availability of single-crystalline material, we have performed neutron diffraction measurements on $CeCu_2Ge_2$ and $CeCu_{1.9}Ni_{0.1}Ge_2$ to investigate the unusual magnetic properties and the complex phase diagram of these compounds in detail.

EXPERIMENTAL DETAILS

Single crystals have been synthesized by the Czochralsky technique. The crystals consisted of small plates along the principal axes with dimensions of approximately $7\times7\times0.5$ mm. The samples have been characterized by microprobe analysis and x-ray diffraction indicating single phase material. Experiments were carried out on the thermal triple-axis spectrometers IN3 at the high-flux reactor of the ILL, (Grenoble) and E7 located at the BERII reactor of the Hahn Meitner Institut, (Berlin). A pyrolytic graphite (0 0 2) monochromator has been used to select neutrons with incident energies of 8.29 and 14.44 meV, respectively. The collimation was set to /open/30′/30′/40′/ on the IN3 and /60′/40′/40′/60′/ on the E7. Graphite filters were used to suppress higher-order contamination. The samples were mounted in an orange-type cryostat covering the temperature range between 1.5 and 300 K. Additionally, a dilution refrigerator was used to investigate the magnetic structure of $CeCu_2Ge_2$ down to the lowest temperatures, from 40 mK$\leqslant T\leqslant$1.0 K. In all experiments, the crystals were oriented with the reciprocal-lattice vectors (1 1 0) and (0 0 1) in the horizontal scattering plane. The lattice constants were refined to a=4.186 Å and c=10.278 Å for $CeCu_2Ge_2$ and a=4.179 Å and c=10.299 Å for $CeCu_{1.9}Ni_{0.1}Ge_2$, respectively. The rocking curves of $CeCu_2Ge_2$ and $CeCu_{1.9}Ni_{0.1}Ge_2$ demonstrated the high perfection of the crystals leading to resolution limited linewidths of 0.28°. No twinning of the crystals was observed.

EXPERIMENTAL RESULTS

The magnetic structure of $CeCu_2Ge_2$ has been investigated previously using neutron powder-diffraction techniques.[1] A modulated structure, incommensurate with the underlying nuclear lattice, has been detected below T_N=4.15 K with a propagation vector $\mathbf{q}$=(0.28, 0.28, 0.54). The size of the magnetic moment ($0.74\mu_B$ at T=1.5 K) was considerably smaller than the moment estimated from the crystal-field split ground state which was calculated to amount $1.54\mu_B$.[1] Using the highly increased precision and

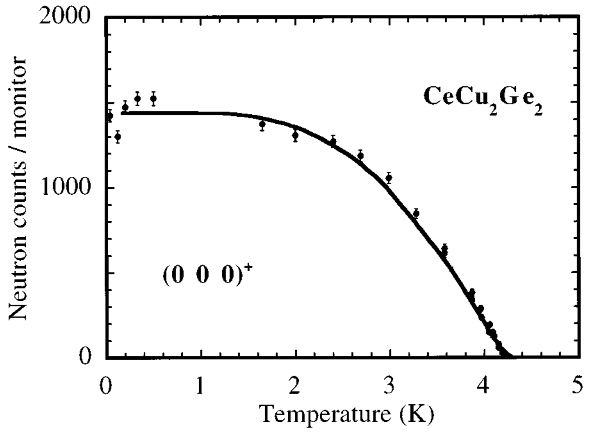

FIG. 1. Temperature dependence of the principal magnetic Bragg peak $(0\ 0\ 0)^{+}$ of $CeCu_2Ge_2$. The full line is the Brillouin function for $j=1/2$.

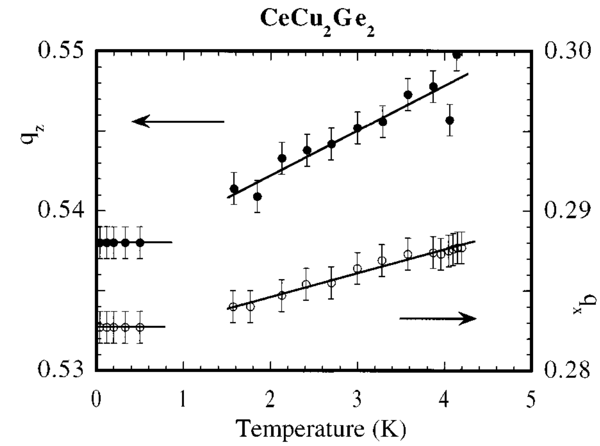

FIG. 2. Temperature dependence of the components q_x $(=q_y)$ and q_z of the propagation vector of $CeCu_2Ge_2$. Below $T\leqslant 1$ K, no further change of the propagation vector could be detected within the experimental accuracy.

comfort of newly developed fitting routines we reanalyzed these diffraction data. Our new results are slightly different compared to those of Ref. 1. We first performed a group-theoretical analysis following the classical paper of Bertaut[6] to extract the possible magnetic structures allowed by symmetry. Then the magnetic intensities were fitted by employing the FULLPROF program.[7] The results indicated a static, sinusoidal amplitude-modulated spin wave with the magnetic moments confined to the [1 1 0] plane and inclined by approximately 10° with respect to the propagation vector. A magnetic moment of $1\pm 0.1\mu_B$ has been determined in agreement with magnetization measurements.[2] The single-crystal results on $CeCu_2Ge_2$ essentially confirmed the propagation vector of the powder-diffraction experiments. An incommensurate magnetic structure with a propagation vector of $\mathbf{q}=(0.284,\ 0.284,\ 0.543)\pm 0.001$ at $T=1.5$ K and a transition temperature of $T_N=4.2\pm 0.1$ K have been determined. The temperature dependence of the principal magnetic Bragg peak $(0\ 0\ 0)^{+}$ is shown in Fig. 1. In the critical region close to the Néel temperature T_N, the integrated magnetic intensities yield a critical exponent $\beta=0.44\pm 0.02$. This is close to the classical value of $\beta=0.5$. For comparison, a Brillouin function for $j=1/2$ is shown in Fig. 1 as well. Since neutron diffraction only yields the orthogonal component of the magnetic moment, an accurate magnetic structure determination by single-crystal diffraction requires the measurement of the magnetic intensities in absolute units. In the present case, this requirement is hampered by severe extinction problems due to the high quality and the correspondingly small mosaicities of the samples. Consequently, we could not determine the direction and the modulus of the magnetic moment. Figure 2 shows the temperature dependence of the propagation vector in detail. A small and continuous shift is evident for both independent components q_x and q_z of the propagation vector. This is a typical behavior of IC magnetic structures. Based on entropy arguments, for $T\rightarrow 0$ a squaring up of the incommensurate structure with shorter periodicities has to be expected (Ref. 8, and references therein). This is reflected by the appearance of higher harmonics. To observe such a change of the magnetic structure in $CeCu_2Ge_2$, we have extended our measurements down to $T\geqslant 40$ mK. The corresponding magnetic intensities of the $(0\ 0\ 0)^{+}$ Bragg reflection are indicated in Fig. 1. We scanned in the reciprocal space to look for higher harmonics. Unfortunately, no definite results could be obtained. A very weak signal corresponding to a reciprocal-lattice position of 5$\mathbf{q}$ was observed. In contrast, a corresponding third-order signal could not be detected, although it should be stronger in intensity. To exclude possible spurious effects, this experiment was repeated with reproducible results and the principal magnetic structure had been confirmed. The absence of higher-order harmonics might be related to the Kondo screening which allows the modulated structure to remain stable at low temperature. At $T=40$ mK, the propagation vector was refined to $\mathbf{q}=(0.283,\ 0.283,\ 0.538)$ and did not change within the experimental accuracy in the very low-temperature range $T\leqslant 1$ K. These low-temperature data have been included in Fig. 2. The problem is that no overlap exists in the data sets which were taken at different temperatures. It should be noted that the low-temperature values of the propagation vector are close to a commensurate modulation of $\mathbf{q}\approx(2/7,\ 2/7,\ 7/13)$. Hence, the data at hand could be interpreted as a lock-in phase transition from an IC high-temperature phase to a commensurate low-temperature state close to $T=1$ K. Further support for a low-temperature phase transition stems from macroscopic measurements, especially specific heat.[9] However, detailed neutron-scattering investigations for temperatures 0.5 $\mathrm{K}\leqslant T\leqslant 1.5$ K are necessary to clarify this point and with the present data also a smooth variation to a saturated low-temperature propagation vector cannot be excluded.

We now turn to $CeCu_{1.9}Ni_{0.1}Ge_2$. Already on the basis of macroscopic measurements, two magnetic phase transitions at $T_{N1}\approx 3.6$ K and $T_{N2}\approx 2.5$ K have been detected.[10] First, we checked the coexistence of two magnetic phases below $T\leqslant 2.5$ K. The result of our measurements at $T=1.75$ K is displayed in Fig. 3. Two magnetic Bragg peaks are clearly visible, corresponding to two propagation vectors of $\mathbf{q}_1=(0.282,\ 0.282,\ 0.530)$ and $\mathbf{q}_2=(0.282,\ 0.282,\ 0.502)$, respectively. The widths of the two magnetic reflections are clearly different amounting to 0.0029 and 0.0015 $Å^{-1}$ compared to the width of the nuclear reflection (0 0 2) with $\Delta q=0.0028$ $Å^{-1}$. The peak with modulation $\mathbf{q}_2$ is too narrow. At present, we have no definite explanation. A possible

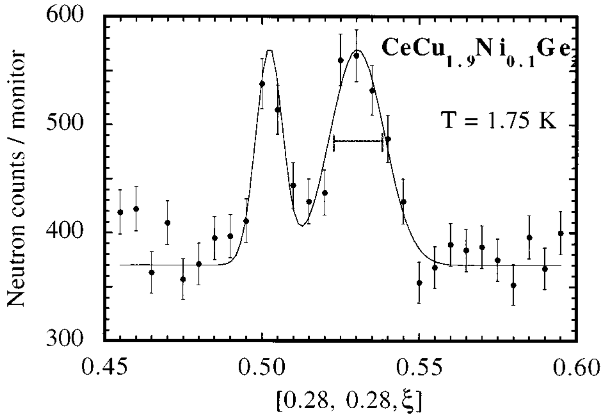

FIG. 3. Principal magnetic Bragg reflections $(0\ 0\ 0)_1^+$ and $(0\ 0\ 0)_2^+$ of $CeCu_{1.9}Ni_{0.1}Ge_2$ at $T=1.75$ K. The horizontal bar indicates the experimental resolution.

reason may be the fact that the second magnetic modulation is not exactly correct and the scan as shown in Fig. 3 is slightly off center with respect to the modulation vector $\mathbf{q}_2$. The magnetic structures are very similar to that of pure $CeCu_2Ge_2$. The temperature dependence of the magnetic intensities of the principal magnetic reflection $(0\ 0\ 0)_1^+$ and $(0\ 0\ 0)_2^+$ are shown in Fig. 4. The full line corresponds to normalized $j=1/2$ Brillouin functions. Amazingly, the onset and evolution of the second magnetic phase does not seem to influence the first magnetic phase at all. To confirm this very unusual magnetic behavior, a similar experiment has been performed with a different $CeCu_{1.9}Ni_{0.1}Ge_2$ single crystal. This time, the complete principal magnetic reflections were recorded by scanning the reciprocal space in fine steps. The result is shown in Fig. 5. The intensity corresponding to the second magnetic phase is vanishing with increasing temperature without any influence onto the magnetic Bragg peak originating from the first magnetic phase. We point out that beyond the standard characterization by microprobe and x-ray diffraction, the samples had been scanned by x-ray diffraction to exclude any variation of the lattice constants within the sample size that would indicate mesoscopic inhomogeneities. We note not only that two different single crystals yielded to the same unusual magnetic behavior, but even

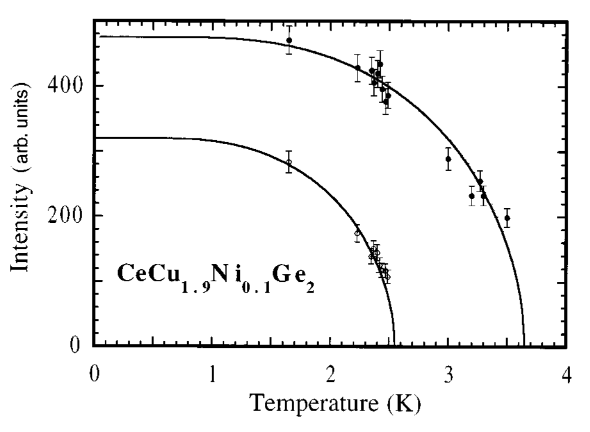

FIG. 4. Temperature dependences of the intensities of the principal magnetic Bragg reflections of $CeCu_{1.9}Ni_{0.1}Ge_2$, indicating the two successive phase transitions. The solid lines are normalized $j=1/2$ Brillouin functions.

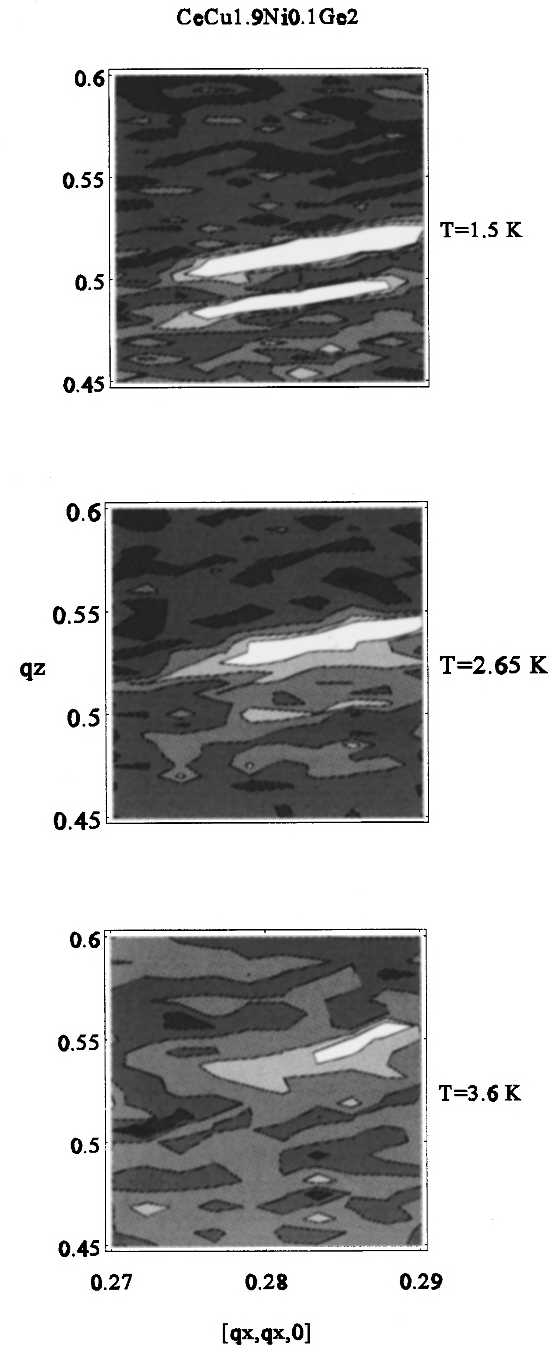

FIG. 5. Contour plot of the magnetic intensity of the principal magnetic reflections $(0\ 0\ 0)+\mathbf{q}_1$ and $(0\ 0\ 0)+\mathbf{q}_2$ of $CeCu_{1.9}Ni_{0.1}Ge_2$. The maxima of the intensity correspond to propagation vectors $\mathbf{q}_1=(0.282,\ 0.282,\ 0.530)$ and $\mathbf{q}_2=(0.282,\ 0.282,\ 0.502)$ at $T=1.6$ K. The detailed shape of the Bragg peaks is determined by the convolution with the instrumental resolution. Dark areas correspond to weak and white areas to strong magnetic intensities (arbitrary units).

polycrystalline material which has been grown using completely different sample preparation conditions revealed two magnetic phase transitions for 5% Ni as well. Furthermore, as mentioned above no twinning of the crystals could be detected. Therefore, we conclude that the results of our present single-crystal neutron diffraction study are really reflecting intrinsic properties of $CeCu_{1.9}Ni_{0.1}Ge_2$. Since these measurements had been performed employing two crystals of different shape, due to the different extinction effects, the magnetic intensities of Figs. 4 and 5 cannot be compared directly with each other and at present we cannot give correct values of the magnetic moments corresponding to the two different magnetic phases.

DISCUSSION AND CONCLUSIONS

In $CeCu_2Ge_2$ the two relevant energy scales of HFS ($k_B T_{\mathrm{RKKY}}$ and $k_B T^*$) are equal in size. This can be inferred already by the anomalous behavior of its quasielastic scattering.[4] The magnetic moment of $1.7\mu_B$, as determined by integrating the quasielastic scattering intensities exceeds the value of the magnetic moment of the powder neutron-diffraction data, thus displaying the dominant role of magnetic fluctuations and the dynamic character of its magnetism. The close connection between the spin structure and the Fermi surface has been demonstrated early by Yosida and Watanabe[11] for heavy rare-earth metals. Experimentally this has been verified in compounds with the $ThCr_2Si_2$-type structure by Leciejewicz and Szytula.[12] They found that the modulation vector sensitivity depends on the a/c ratio and on the number of conduction electrons of the compounds under consideration. Slater[13] and Overhauser[14] have shown that interacting electrons also can yield modulated spin structures using essentially the same interaction mechanism as proposed by Yosida and Watanabe.[11] Our observations are in good agreement with the results of specific-heat measurements.[3,15] The magnetic phase transition of $CeCu_2Ge_2$ is reflected by a jump of the specific heat at $T=4.15$ K. The considerable deviations from a λ-shaped anomaly can be ascribed to the onset of an IC amplitude-modulated structure. Within such structures, the magnetic moments close to the node of the modulation are almost paramagnetic and therefore do not contribute to the specific heat. This reduction of the height of the λ anomaly at T_N increases the heat capacity at low T, leading to a humplike feature to compensate for the loss of entropy at T_N.[8,16] However, at T_N the magnetic entropy only reaches 70% of R ln2. This reduction may partly be ascribed to the Kondo-compensation effect and partly to magnetic fluctuations. The specific-heat data indicate that a significant amount of magnetic entropy (13% of R ln2) is associated with fluctuations above T_N. The situation has similarities with the heavy-fermion superconductor URu_2Si_2.[17] There, magnetic fluctuations start to develop already at 100 K, i.e., above 5 T_N. The different results of different experimental techniques concerning the magnetic phase transition (for example, extremely small ordered magnetic moments but a considerable change in magnetic entropy) are based on the fact that the magnetic response is mainly inelastic in nature. Recent investigations seem to clarify that two different types of magnetism are responsible for the unusual properties of URu_2Si_2. The magnetic phase transition at $T_N=17.5$ K is characterized by the ordering of small magnetic moments with a **Q** vector of (0 0 1/2), while the fluctuating part takes place on a sphere (and therefore only depending on the modulus of **Q**) enclosed by the Brillouin zone. Such a separation in reciprocal space, on the one hand, of the long-range order of well localized, but partly Kondo-compensated magnetic moments, and on the other hand, of the fluctuating quasielastic part of the magnetic scattering seems to be present as well in $CeCu_2Ge_2$. The magnetic behavior of $CeCu_{1.9}Ni_{0.1}Ge_2$ is particularly remarkable for the appearance of a second magnetic phase which does not seem to influence the original magnetic structure at all. The propagation vector of the second structure $\mathbf{q}_2=(0.282,\ 0.282,\ 0.502)$ is very close to $\mathbf{q}_1=(0.282,\ 0.282,\ 0.530)$. From the phase diagram of Ref. 4 it is known that the 5% Ni compound is located in a region between two different types of magnetism. It has been speculated that HFBM appears for the compound with a Ni concentration $x=0.5$. Hence, the two magnetic phases in $CeCu_{1.9}Ni_{0.1}Ge_2$ may be interpreted as a coexistence of localized magnetic moments ($T_N\approx3.6$ K) with a bandlike magnetism of heavy fermions ($T_N\approx2.5$ K). However, two facts make this speculation less plausible. First, the compound is close to the regime characterized by well-localized magnetic moments and only a moderate Kondo compensation. Second, the fact that the ordering wave vectors are so close indicate that only slight changes in the Fermi surface are responsible for this effect. Hence, it could be that the effects of the local environment, like the number of Ni nearest neighbors, drive the two different magnetic structures. It is intriguing to compare the behavior of $Ce(Cu_{1-x}Ni_x)_2Ge_2$ with the phase diagram of $CeCu_2(Si_{1-x}Ge_x)_2$.[18] If only volume-dependent effects should govern the physical properties of these compounds, then $Ce(Cu_{1-x}Ni_x)_2Ge_2$ and $CeCu_2(Si_{1-x}Ge_x)_2$ should behave very similarly. Indeed, applying pressure leads to a superconducting phase in $CeCu_2Ge_2$.[19] This pressure is required to compress the unit-cell volume of $CeCu_2Ge_2$ to the volume of its Si homologue at ambient pressure. On the other hand, at ambient pressure pure $CeCu_2Si_2$ becomes superconducting below $T=0.6$ K,[20] and shows a magnetic phase in moderate magnetic fields[21–23] of a yet unknown nature. Unlike the behavior of uranium-based HF superconductors, superconductivity and magnetism do not coexist in $CeCu_2Si_2$. Pure $CeNi_2Ge_2$ is a nonmagnetic heavy Fermi-liquid.[4] The IC magnetic structure of pure $CeCu_2Ge_2$ seems essentially preserved in both alloy series.[4,18] Measurements of the specific heat, magnetic susceptibility, and resistivity showed three different low-temperature transitions in $CeCu_2(Si_{1-x}Ge_x)_2$,[18] two of them definitively of magnetic origin. Powder neutron diffraction revealed almost identical magnetic structures for $x=1$, $x=0.8$, and $x=0.6$, whereas no magnetic intensities could be observed for $x=0.4$. The neutron-scattering studies have been performed well below the second phase transition. Hence, like in the case of $CeCu_{1.9}Ni_{0.1}Ge_2$, the appearance of a second magnetic phase transition does not seem to affect the modulated structure established at T_{N1}.

In conclusion, a fascinating and unusual sequence of magnetic phase transitions seems to occur in Ce-based HF systems close to the critical hybridization strength which separates magnetic and nonmagnetic ground states. Much more experimental work is needed to elucidate these complex magnetic phase diagrams.

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