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Local symmetry of the crystal-field Hamiltonian of CePtSn by polarized neutron scattering

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We present the results of a polarized neutron scattering study of crystal-field (CF) excitations in a CePtSn single crystal and their interpretation, describing the magnetic properties of the metallic Kondo antiferromagnet CePtSn in its paramagnetic phase. Using neutron polarization analysis, we demonstrate that all terms of the monoclinic site CF Hamiltonian have to be considered in order to account for all the available experimental data, including susceptibility and high-field magnetization measurements. The CF eigenstates, as probed by inelastic polarized neutron scattering, are not affected by cooperative phenomena neither in the vicinity of the Kondo temperature, T_K, nor below the Néel temperature, T_N.

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Experimental studies of crystal field (CF) effects in the magnetism of $4f$-electron systems often combine neutron spectroscopy on polycrystalline samples, used to obtain direct information on the energy level scheme of the CF Hamiltonian, with single crystal magnetization measurements to characterize the anisotropy of the CF eigenstates. Because of the averaging inherent to both methods this combination cannot provide complete information on the local CF Hamiltonian unless the magnetic atoms occupy only crystallographic positions that have the full point group symmetry of the host lattice. The purpose of this letter is to demonstrate that polarized neutron spectroscopy, if applied to a single crystal sample, permits us to obtain the complete information by directly measuring the three orthogonal components of the matrix elements corresponding to transitions between the eigenstates of the local CF Hamiltonian. Recent advances in the instrumentation render this task as feasible as the traditional investigations using unpolarized neutron beams.

As a case example, we have chosen CePtSn, which belongs to the family of ternary Ce compounds exhibiting intriguing electronic properties due to the competition between the RKKY interaction, the Kondo effect, and the CF interaction. CeNiSn and CePtSn are two of the prominent representatives of this class of intermetallic compounds. The former one is a valence-fluctuating semimetal with Kondo temperature $T_K = 50$ K.[1] Its low-temperature metallic behavior has been explained by an opening of a V-shaped anisotropic hybridization pseudo-gap at $T_\Delta \simeq 6$ K which is believed to originate in the interplay of the local CF excitations and a coherent Kondo state.[2] The Ce single-ion behavior in CeNiSn are rather difficult to study since the CF excitations, as probed by inelastic neutron scattering (INS), are strongly broadened due to the mixed valence state of cerium. On the other hand, in the isostructural Kondo antiferomagnet CePtSn, the Ce^{3+} state is well defined and can be studied more easily. In CePtSn, the determination of the Kondo temperature, $T_K \sim 10$ K, from the resistivity minimum is complicated by the onset of magnetic order in the same temperature range, at $T_N = 7.5$ K and a second magnetic phase transition at $T_M = 5.0$ K.[3] Both phases are well described by a spin-slip model stabilized by the interplay of the CF and an effective field rotating along the incommensurate wave vector direction, $\boldsymbol{\tau} = (0, 1/2 - \delta, 0)$.[4]

The Ce^{3+} ions in the orthorhombic unit cell of CePtSn occupy sites with the monoclinic C_s point symmetry. The CF splits the $^2F_{5/2}$ ground state into 3 Kramers doublets of Γ_5 symmetry. Indeed, early INS experiments on polycrystalline samples observed two magnetic dipole transitions at 23 and 35 meV.[5] This study was complemented by measurements of the bulk magnetic properties,[6,7] and two CF studies.[3,8] In both of them, a single-ion approach was used, with the aim to interpret the INS spectra, magnetic susceptibility and high-field magnetization data. In order to reduce the number of adjustable parameters, the CF Hamiltonian was approximated by assuming orthorhombic cerium site symmetry. The success of these calculations was only partial: the first reported set of CF parameters[3] yields the energy level splitting too large, while the second one[8] fails to reproduce the available bulk magnetic data adequately.

Possible origins of this failure include a simplification in the CF model itself, or the neglect of eventual collective effects. The aim of the present study is to revisit the problem by collecting polarized neutron scattering data on a single-crystalline sample, and to combine them with new magnetization and susceptibility data obtained on the same sample, in order to determine the entire monoclinic CF Hamiltonian.

In the dipole approximation, the scattering cross section of unpolarized neutron scattering from CF excitations is related to the matrix elements of the total momentum operator J (Refs. 9 and 10) by

$$\frac{d^2\sigma}{d\Omega d\omega} = N(\gamma r_0)^2 \frac{k_f}{k_i} F^2(\boldsymbol{Q}) \exp(-2W) \times \sum_{mm'} n_m |\langle m' | \boldsymbol{J}_\perp | m \rangle|^2 \delta(\omega_{m'} - \omega_m - \omega). \quad (1)$$

Here $F^2(\boldsymbol{Q})$ and $\exp(-2W)$ are the single-ion magnetic form factor and the Debye-Waller factor, respectively, and $\boldsymbol{J}_\perp$ is the projection of the angular momentum operator onto the plane perpendicular to the scattering vector, $\boldsymbol{Q}$. When working with a polarized beam, the scattering due to ***J***-components perpendicular to the incident beam polarization is accompanied by a neutron spin-flip.[11] This selection rule permits not only to separate the CF signal from lattice excitations (inherently non-spin-flip), but also to extract the individual ***J***-components from the intensity differences

$$I_x^{SF} - I_{y,z}^{SF} \propto \frac{k_f}{k_i} F^2(Q)\exp(-2W) \times \sum_{mm'} n_m |\langle m'|J_{y,z}|m\rangle|^2 \delta(\omega_{m'} - \omega_m - \omega). \quad (2)$$

Here $I^{\mathrm{SF}}_{x,y,z}$ represent the spin-flip (SF) scattering intensities measured with neutron spin parallel to the x,y,z coordinate axes, forming a right-handed system with $x \parallel \boldsymbol{Q}$, $y \perp \boldsymbol{Q}$ in the horizontal plane, and z vertical. By taking measurements along two perpendicular scattering vectors, $\boldsymbol{Q}_1 \perp \boldsymbol{Q}_2$, one can access all the three components of ***J*** individually. This is in contrast to neutron scattering from a polycrystal, where only the orientational average over J_x, J_y, and J_z can be obtained, and the polarization analysis only allows us to separate the magnetic excitations from the lattice modes.

Although this possibility has been known *in principle* for several decades it has never been exploited in practice for the study of CF excitations, because of severe neutron flux limitations in the polarization analysis mode. Only the recent upgrade of the polarized neutron three-axis spectrometer IN20 at the Institut Laue-Langevin (Grenoble, France),[12] resulting in a data collection rate increase by a factor 30–50, opened the way to this kind of experiment on a routine basis.

For the measurements presented here we used a single-crystal sample with volume of only 0.2 cm^3 grown by the Czochralski method at Tohoku University. The nominal stoichiometry and purity were checked by electron microprobe analysis. The orthorhombic crystal structure with space group *Pnma* and lattice parameters $a=7.4589(3)Å$, $b=4.6207(2)Å$, and $c=8.0102(4)Å$ was confirmed by single crystal x-ray diffraction.[13] dc magnetic susceptibility and magnetization measurements were carried out on a Quantum Design SQUID magnetometer in fields up to 5 T and on a PPMS (Ref. 14) in fields up to 14 T.

For the neutron scattering experiments the crystal was mounted into an Orange cryostat with its *b*-axis vertical [$b \parallel z$ in the notation of Eq. (1)]. In order to test the eventual influence of the ordering and Kondo effect on the CF spectra, we collected the $\boldsymbol{Q}_1=(3.25\ 0\ 0)$ and $\boldsymbol{Q}_2=(0\ 0\ 3.5)$ data at three different temperatures, T = 6, 10, and 50 K, corresponding to the upper ordered phase, to the proposed Kondo temperature, and to the paramagnetic phase well above the coherent effects range. For both $\boldsymbol{Q}_1$ and $\boldsymbol{Q}_2$, the energies and polarization of the CF lines remain independent of the temperature as shown for $\boldsymbol{Q}_1$ in Fig. 1. This result confirms that at low temperatures the CF ground state is not substantially altered with respect to the paramagnetic state, and that the magnetic ordering and Kondo effect influences are weak in the studied energy transfer range, as expected.

More extensive neutron scattering data sets were then collected at $T=15$ K at the above mentioned scattering vectors $\boldsymbol{Q}_1$ and $\boldsymbol{Q}_2$, chosen so as to allow for $\boldsymbol{Q}=$const. scans over the whole range of energy transfers between 0 and 40 meV with $k_f=4.1\ Å^{-1}$. At the same time the magnitudes of $\boldsymbol{Q}_1$ and $\boldsymbol{Q}_2$ are equal, so that no explicit corrections for the Q-variation of the form-factor and Debye-Waller factor are necessary. The spin-flip data were collected for neutron spin orientations along all the three principal axes, x, y, and z, defined above. Their differences (shown in Fig. 2) provide a complete information on magnitudes of the three components of the total angular momentum ***J***, e.g., $I_x^{\mathrm{SF}} - I_z^{\mathrm{SF}}$ corresponds to $|\langle J_b \rangle|^2$ [see Eq. (2)]. The overall beam polarization was checked by scattering from a non-dispersive phonon branch in silicon. At momentum and energy transfers close to those used in the present CF study, a polarization of 88% has been

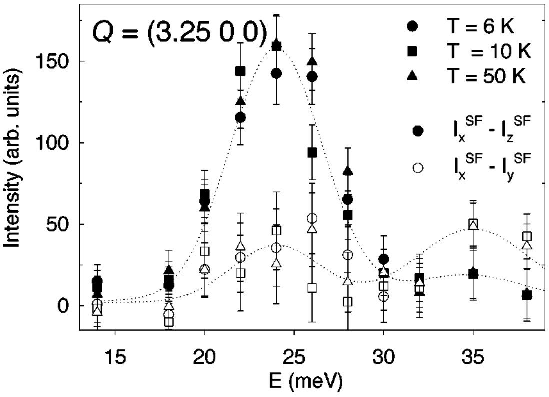

FIG. 1. The neutron spin-flip difference spectra of CF excitations in CePtSn at $Q_1=(3.25\ 0\ 0)$ measured at three different temperatures ($T=6,15$, and 50 K).

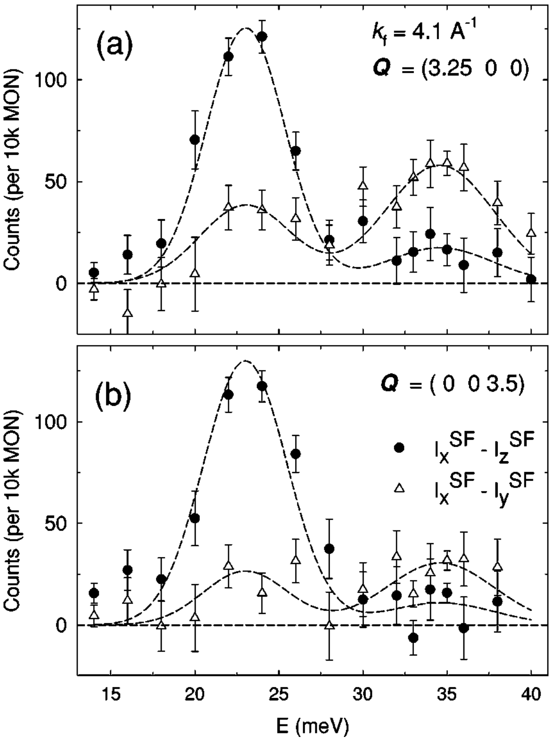

FIG. 2. The neutron spin-flip difference spectra of CF excitations in CePtSn at $T=15$ K measured at $\boldsymbol{Q}_1=(3.25\ 0\ 0)$ (a) and $\boldsymbol{Q}_2=(0\ 0\ 3.5)$ (b).

TABLE I. The CF parameter set of CePtSn obtained in the present work in comparison with the results of Diviš *et al.*[a]

	Experiment	Theoretical calculations	
		Monoclinic H_{CF}	Orthorhombic H_{CF}
	(this work)	(this work)	(Diviš *et al.*[a])
Δ_1(meV)	23.0(4)	24.0(8)	23.3
Δ_2(meV)	34.6(7)	34.6(−)	35.2
I_1/I_2	1.45(9)	1.34(25)	0.758
$\lvert\langle 0\lvert J_a\rvert 1\rangle\rvert^2$	262(71)	270(15)	324
$\lvert\langle 0\lvert J_b\rvert 1\rangle\rvert^2$	777(54)	715(12)	385
$\lvert\langle 0\lvert J_c\rvert 1\rangle\rvert^2$	166(40)	167(12)	168
$\lvert\langle 0\lvert J_a\rvert 2\rangle\rvert^2$	474(69)	518(20)	20
$\lvert\langle 0\lvert J_b\rvert 2\rangle\rvert^2$	113(56)	101(12)	405
$\lvert\langle 0\lvert J_c\rvert 2\rangle\rvert^2$	245(32)	259(16)	730
B_2^0(K)		8.83(42)	7.4
B_2^2(K)		2.50(67)	1.6
B_4^0(K)		−0.21(3)	0.45
B_4^2(K)		3.30(11)	−3.05
B_4^4(K)		2.43(13)	5.83
C_2^2(K)		0	
C_4^2(K)		±3.21(14)	
C_4^4(K)		±3.38(16)	

[a] Reference 8.

found, equal for all the three spin orientations. As a consequence no explicit polarization correction is needed for the CF signal extracted from the spin-flip intensity differences. To avoid any confusion between the ***Q***-related and ***J***-related coordinate systems, in the following discussion we will always refer to the crystallographic axes a,b,c.

The spin-flip difference spectra have been fitted by a superposition of two Gaussian profiles. The peak widths were found to be resolution limited, and the observed energies of the two transitions, 23.0±0.4 and 34.6±0.7 meV, agree with the values of 23.3 and 35.2, respectively, found earlier by Adroja.[5] As all data were obtained at sufficiently low temperatures, the thermal population of the excited CF levels was negligible so that only the transitions from the ground state ($\omega_m=0$) had to be considered and the Bose factors could be neglected in the intensities. The integrated intensities, corrected for the factor k_f/k_i, summed over all the three components give a ratio for the unpolarized intensity of the two excitation peaks of 1.45±0.09, consistent with the value of 1.34±0.25 obtained by Adroja[5] from the unpolarized powder data.

The partial spin-flip intensities of Fig. 2 can be compared directly to the squared moduli of the matrix elements of the total angular momentum ***J*** [Eq. (1)]. The results are displayed in Table I together with the outcome of a model calculation using the CF wave functions of Diviš.[8] Clearly, there is a qualitative disagreement with the neutron data, in particular for the 35 meV transition. We have therefore repeated the model calculations over the whole CF parameter space as done before by Diviš,[8] but no satisfactory fit to the polarized neutron intensities could be found. Moreover, the parameter sets providing at least a crude approximation to the neutron data led to a qualitative disagreement in the inverse susceptibilities, in particular along the c-axis.

The absence of an orthorhombic CF parameter set which accounts for all the bulk magnetic properties and the inelastic scattering data, together with the fact that the lack of temperature dependence leaves little scope for eventual influence of collective effects, points towards the necessity to extend the model Hamiltonian. In fact, all the previous CF calculations[3,8] have been performed using the orthorhombic symmetry of the Ce site. This was consistent with the experimental data originating from the bulk magnetization data, which are sensitive to magnetic moments averaged over the orthorhombic crystallographic unit cell of CePtSn. On the other hand the neutrons are directly probing transitions between electron states of a single ion, whose crystal field splitting reflects the local symmetry of its site. Although the crystal symmetry of CePtSn is orthorhombic (TiNiSi-type), the Ce ions sit at points of lower, monoclinic, symmetry inside slightly distorted hexagonal prisms formed by alternating Pt and Sn ions. As a consequence one has to employ the full monoclinic Hamiltonian in the CF calculations:

$$H_{\mathrm{CF}}=B_2^0O_2^0+B_4^0O_4^0+B_2^2O_2^2+B_4^2O_4^2+B_4^4O_4^4+C_2^2\Omega_2^2+C_4^2\Omega_4^2+C_4^4\Omega_4^4, \tag{3}$$

where

$$O_n^m=1/2(O_n^{+m}+O_n^{-m}), \tag{4a}$$

$$\Omega_n^m=-i/2(O_n^{+m}-O_n^{-m}) \tag{4b}$$

are the Stevens operators[15,16] and the coefficients B_l^m and C_l^m are the CF parameters representing the strength of the interaction. For the orthorhombic symmetry, $C_l^m=0$, therefore we refer to them as to "monoclinic" CF terms and we call the subset B_l^m "orthorhombic" CF parameters. The only nontrivial symmetry operation preserved at the monoclinic site is the reflection in the (x,y) plane, which implies that the term containing the operator Ω_2^2, proportional to Σxy, should vanish. Therefore we have fixed the C_2^2 value to zero. For the calculation of the expectation values of the observables the CF Hamiltonian was rewritten in a reduced form (cf. Walter[17]), and the seven-dimensional parameter space has

TABLE II. The wave functions corresponding to the CF parameters of CePtSn obtained in the present work (cf. Table I).

$\lvert\Psi_0\rangle=$	$(0.62+0.42i)\lvert +1/2\rangle$	$+(0.15+0.43i)\lvert -3/2\rangle$	$-0.48\lvert +5/2\rangle$
$\lvert\Psi_1\rangle=$	$(-0.56+0.13i)\lvert +1/2\rangle$	$+(0.75+0.06i)\lvert -3/2\rangle$	$-0.32\lvert +5/2\rangle$
$\lvert\Psi_2\rangle=$	$(-0.30+0.15i)\lvert +1/2\rangle$	$-(0.28-0.39i)\lvert -3/2\rangle$	$+0.82\lvert +5/2\rangle$

been searched using a Monte Carlo technique. The trial events were first tested to match the polarized INS intensities. In this way some 700 points have been selected among about 10^{10} events in the reduced CF parameter space. In the second step, the calculated magnetization and susceptibility curves have been compared to the experimental ones. Six points in between 12 and 300 K on the $\chi(T)$ curves and three points from the $M(B)$ data at 15 K were used in the procedure as a reference. All sets leading to an unrealistic $\chi(T)$ or wrong easy axis were excluded, leaving only two regions of possible solutions, both with the same "orthorhombic" terms but with "monoclinic" CF parameters of opposite sign. The two solutions correspond to the two possible Ce atom positions in the lattice and they are equivalent due to the symmetry conditions. The change of sign of the "monoclinic" terms does not affect the calculated polarized neutron intensities and bulk magnetic data. These regions have been inspected in more detail using a least-squares parameter-search method. The resulting set of CF parameters, is displayed in Table I together with the calculated values of the square modulus of the angular momentum $\boldsymbol{J}$ matrix elements (rescaled), which agree with the experimental data within their error bars. The uncertainty in the determination of the best set of CF parameters depends to some extent on the relative weight given to the results of polarized INS spectra with respect to the susceptibility and magnetization data in the least-squares refinement. In any case, however, the values of the monoclinic parameters C_4^2 and C_4^4 are highly significant. The corresponding wave functions are given in Table II.

The calculated magnetic susceptibility curves reproduce correctly all the main features of the experimental data, namely their drop at low temperatures, the crossing point of the a- and c-axis curves and the high-temperature anisotropy (see Fig. 3).

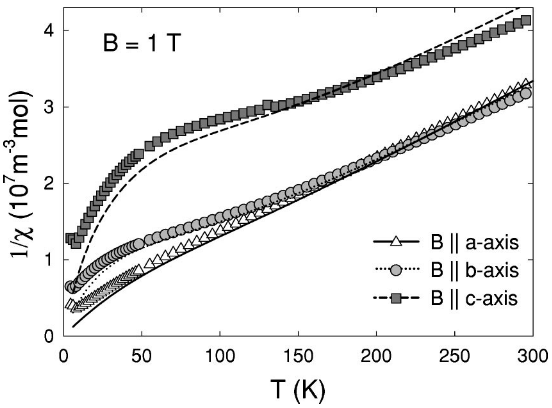

FIG. 3. The inverse magnetic susceptibilities in CePtSn along the three principal directions measured at $B=1$ T (symbols); the curves result from calculations using our final CF parameter set (cf. Table I).

We conclude that by taking into account the local monoclinic site symmetry of the cerium atoms, the behavior of the $4f$ electrons, responsible for the magnetic properties of CePtSn in paramagnetic phase (above 8 K), is to a good accuracy described by the local (single-ion) crystal field. The temperature independence of the energy and polarization of the CF excitations implies that the magnetic ordering, although resulting in a complicated spin arrangement, and the eventual Kondo effect are only weak perturbations to the local crystal field. These new conclusions are to a large extent based on the results obtained by the polarization analysis of the neutrons scattered by the CF excitations in a single crystal sample, which has provided additional independent input data revealing the importance of the local site symmetry. Although the fundamental principles of this technique are known since several decades, it was only the recent dramatic progress in neutron instrumentation, which has opened the way to its routine application, of which the present experiment is the first example.

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