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Observation of the singlet–singlet crystal-field excitons in $PrCu_2$ by inelastic neutron scattering

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Abstract. The crystal-field transitions in the paramagnetic state of $PrCu_2$ were studied by means of inelastic neutron scattering between 1.8 and 10 K in an energy transfer range 0.5–2.5 meV. We observed excitations from the singlet ground state to two singlet excited states. They were assigned as a J_x-polarized and a J_y-polarized transition. The J_x transition has acoustic and optical branches. While the J_y transition is very weakly dependent on the wavenumber, the J_x transitions are strongly dispersive, indicating an anisotropic RKKY interaction between the 4f electrons. A substantial softening of the exciton energy was observed in the optical branch of the J_x transition as a sharp minimum at the wavevector $Q_m = 0.24a^* + 0.68c^*$, which is the modulation vector of the magnetic order below $T_N = 54$ mK. The manner of softening above 1.8 K is discussed in terms of the mean-field theory.

1. Introduction

The study of magnetic excitation in materials with a singlet crystal-field ground state has a long history [1–3]. The simplest form of the Hamiltonian for a system where both the ground and the excited states are singlets is [4]

$$H = \sum_i V_{ci} - \sum_{i,j} K_{ij} J_i \cdot J_j \tag{1}$$

where V_{ci} is the single-site crystal field and K_{ij} is the exchange integral. This system has no phase transition unless the magnitude of the exchange interaction relative to the crystal-field energy represented by the parameter

$$A = 4K(Q_m)a^2/\Delta \tag{2}$$

exceeds unity, where $K(Q_m)$ is the maximum component of the canonical transformation of K_{ij}, and a and Δ are the matrix element $\langle E|J_z|G\rangle$ and the energy separation of the ground and excited states, respectively. Excitation at an atom propagates through K_{ij} and hence has a dispersion. The dispersion relation of the excitons at finite temperatures is given as [4]

$$\hbar\omega^{x,y,z}(q) = [\Delta^2 - 4\Delta a^2 K(q)R(T)]^{1/2} \qquad a = \langle E|J_{x,y,z}|G\rangle. \tag{3}$$

$R(T)$ represents renormalization of the energy by temperature and, within the mean-field theory, is expressed as

$$R(T) = (P_G - P_E)/Z \tag{4}$$

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where P_G and P_E are the Boltzmann factors of the ground and the excited states respectively, and Z is the partition function of the system. $R(T)$ varies from 0 at $T = \infty$ to 1 at $T = 0$ K when $A > 1$, $\omega(q_m)$ falls to zero at the transition temperature T_c for which $R(T_c) = \Delta/4a^2K(Q_m)$, showing an excitonic soft-mode phase transition.

The characteristic magnetic behaviour of the singlet ground-state system was first displayed in DHCP Pr which has a doublet excited state. Houmann *et al* [5] found that the energy of the exciton at the lowest minimum of the dispersion decreases rapidly as the temperature is lowered, but it becomes almost constant below about 7 K, in agreement with a random-phase approximation calculation.

The magnetism of the intermetallic compound $PrCu_2$ is in the same category as that of DHCP Pr, i.e., hyperfine coupled electron–nuclear magnetism [6]. While Pr is considered to be in the 'mixed regime' where the phase transition is conducted with comparable weights by electrons and nuclear spins, $PrCu_2$ is in the 'nuclear regime' where the phase transition is driven mainly by the nuclear spin system.

$PrCu_2$ has an orthorhombic $CeCu_2$-type structure (space group *Imma*) with the locations of the Pr atoms in the orthorhombic unit cell shown in figure 1. In the crystal field of local symmetry C_{2v}, the ground multiplet $^3H_4$ of the Pr^{3+} ion splits into nine singlets. Below $T_D = 7.3$ K, the second- and the third-lowest singlets increase their separation and the crystal undergoes a cooperative Jahn–Teller transition with a change in the crystallographic angle β. The energy level scheme of the lowest four levels and the manner in which they shift across T_D were reported by Kjems [7], as shown in figure 2.

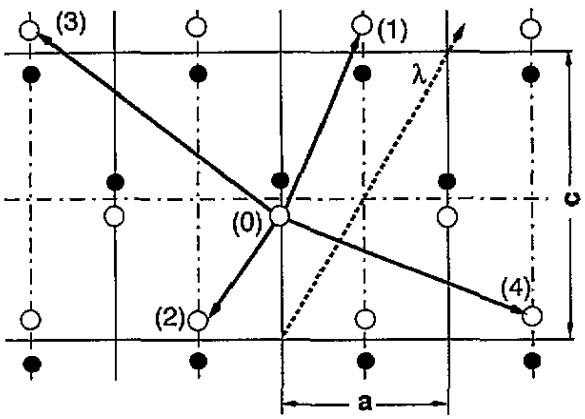

Figure 1. Configuration of Pr atoms in the a–c plane of $PrCu_2$. The open circles are in a plane and the full circles are $\frac{1}{2}b$ below it. The vector λ represents the direction and the wavelength of the magnetic modulation in the ordered phase below 54 mK.

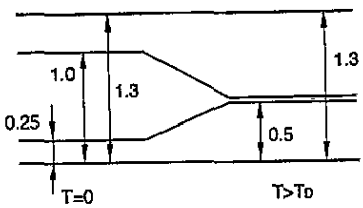

Figure 2. The energy level scheme of the low-lying crystal-field states of the $^3H_4$ multiplet of Pr^{3+} in $PrCu_2$ which appeared in [7]. The units of energy are millielectronvolts.

Kjems *et al* [8] measured the exciton dispersion of $PrCu_2$ along the [001]* axis in reciprocal space at 5 K and discovered that the dispersion has two branches with a gentle minimum at $q = (001)$ (in reciprocal-lattice units). On the basis of this observation, they predicted that the magnetic modulation vector of the ordered phase would be (001). However, in an elastic neutron scattering experiment Kawarazaki *et al* [9, 10] discovered magnetic Bragg reflections below 57 mK. The locations were

$$G \pm Q_m \qquad Q_m = 0.24a^* \pm 0.68c^* \tag{5}$$

where G is the reciprocal-lattice vector. The modulation vector Q_m is shown in figure 1. The direction of propagation coincides with the direction of the face diagonal $\langle 101 \rangle$ within experimental error. However, the wavelength is appreciably longer than the length of the face diagonal, and the magnetic modulation is apparently incommensurable with the crystal lattice. The transition is second order and the electronic and nuclear moments are sinusoidally modulated in magnitude and oriented approximately parallel to the crystal a axis.

Since $PrCu_2$ has singlet ground and excited states and is regarded as having A not very close to unity, one may expect the excitons to behave in a way most typical of the singlet–singlet system. However, as is shown in figure 2, there are several excited states which are located close to each other in energy, and this should have some effects on the soft mode. Taking this into account, we describe, in this present paper, the results of an inelastic neutron scattering experiment carried out between 1.8 and 10 K to study the paramagnetic behaviour of the excitons around the reciprocal-lattice positions (001) and Q_m.

2. Experimental details

The inelastic neutron scattering experiments were done at the Japan Atomic Energy Research Institute using the high-energy-resolution triple-axis spectrometer (HER) installed at the cold-neutron guide-tube of the JRR-3 reactor.

The single crystal of $PrCu_2$ used for the present experiment is the same crystal as used for the previous elastic experiment [10]. Its concentration of Pr is slightly below the exact stoichiometry. The mosaic width of the crystal is 0.6° (FWHM). The crystal is a cylinder of 8 mm diameter and 23 mm length. Measurements were made at 5 K. The angle divergence of the cold neutron beam incident to a pyrolitic graphite (PG) monochromator is 10′ and the collimation after the monochromator was 40′–80′–80′. Since the collimation of the incident beam is fixed, it was hard to use an ordinary symmetric configuration of the collimation system because it reduces the signal intensity too much. The energy resolution with this collimation system and a PG analyser was typically 0.24 meV in the E–Q space positions studied. The fixed wavenumber of the incident neutron was typically $k_i = 2\pi/\lambda = 1.55$ Å^{-1} and the scans were made with constant-q and neutron-energy-loss modes. A cooled beryllium filter was used to eliminate λ/n contamination.

3. Experimental results

The inelastic neutron scattering by the singlet ground-state excitons is due to the dipole–dipole interaction of the neutron spin with the 'induced moment' $\langle E|J|G\rangle$. Hence, the scattering cross section involves a factor to represent the anisotropy of this interaction. For a singlet–singlet system with dispersion the cross section in the zero temperature limit is [1],

$$\frac{d^2\sigma}{d\Omega\, dE'} = \left(\frac{1.91e^2}{2mc^2}\right)^2 \frac{k_f}{k_i} F^2(k)(\sin^2\chi)\alpha^2 \frac{\Delta}{\hbar\omega(q)}\,\delta[\hbar\omega(q) - E'] \tag{6}$$

where χ is the angle between the scattering vector κ and $\langle E|J|G\rangle$, and $f(\kappa)$ is the form factor of the induced moment. By using the factor $\sin^2\chi$, one can often identify the origin of the observed crystal-field transition.

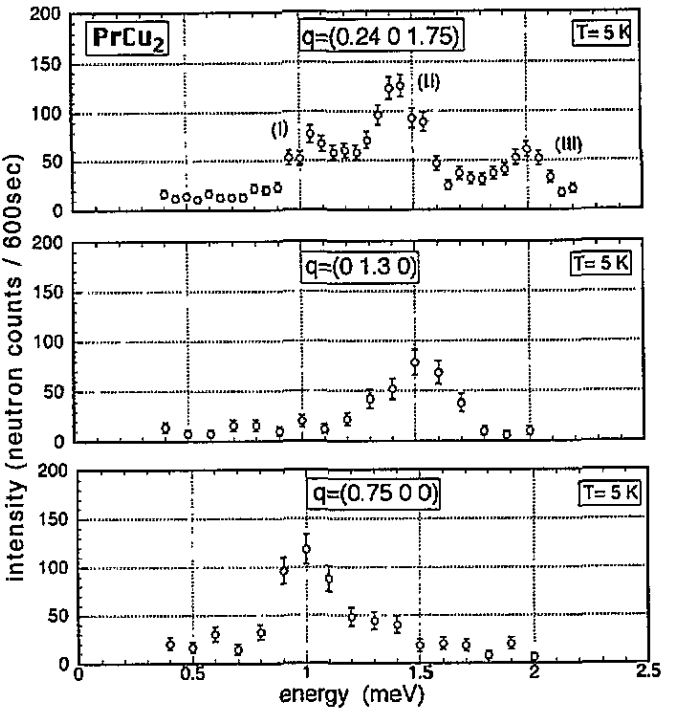

Figure 3. The spectra of inelastic neutron scattering from paramagnetic $PrCu_2$ at 5 K for different momentum transfers.

In figure 3, the energy spectra of excitons with different momentum transfers are shown. In the figure, one can see that the spectrum for $q = (0.24\,0\,1.75)$ is composed of three peaks (denoted as peaks (I), (II) and (III) as shown in the figure). The location of peak (I) at $E \simeq 1$ meV depends very weakly on q and hence it represents a well localized excitation. This peak also appears on the a^* axis, but it has no intensity on the b^* axis, as seen in the spectra for $q = (0\,1.3\,0)$ and $q = (0.75\,0\,0)$. According to equation (6), one can immediately conclude that this peak is due to a transition with J_y polarization. The locations of peaks (II) and (III) are strongly dependent on q. One of these peaks is also observed on the b^* axis in the energy range between 0.4 and 2.0 meV. On the a^* axis, there are two peaks, one of which corresponds to the J_y transition, and another peak has slight q dependence and is less intense than the other peaks. We, therefore, consider that peaks (II) and (III) do not reside on the a^* axis and that they represent transitions with J_x polarization. Since the lattice of the Pr atoms in $PrCu_2$ is of a non-Bravais type and is composed of two interpenetrating sublattices, any collective excitations in the Pr atoms should have, in principle, two branches due to interactions between two sublattices. We assign the peaks (II) and (III) to J_x transitions. Each spectrum measured for different q-values was analysed to obtain the peak position by the least-squares method to fit three Gaussians.

For comparison with the previous results obtained by Kjems *et al* [8], the exciton dispersion along the c^* axis was measured and is shown in figure 4. One can see that the J_y transition (open circles) is quite dispersionless but that the other two transitions have a strong q-dependence. The overall features of the dispersions of the J_x transitions are significantly different from those measured by Kjems *et al*; while in their measurement the dispersion has a moderate minimum $q = (001)$, the present result shows sharp minima in

one of the J_x transitions at $q = (0\,0\,0.9)$ and its equivalent $q = (0\,0\,1.1)$. We suppose that this difference might be caused by the different resolutions of the two experiments. The excitation energy at the minimum positions is 1.01 ± 0.05 meV.

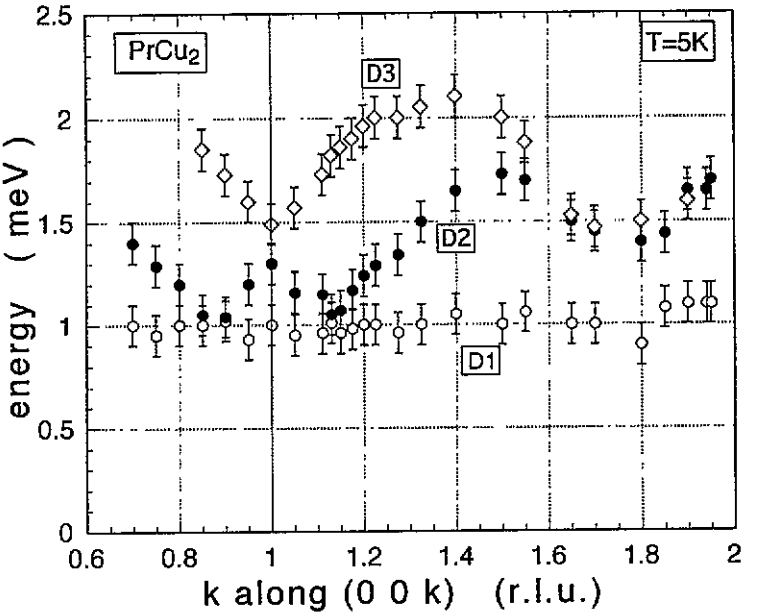

Figure 4. The dispersion curves of the three excitons (see the text) in paramagnetic $PrCu_2$ along the (00k) reciprocal-space line (r.l.u., reciprocal-lattice units).

The exciton dispersions around the magnetic Bragg point $Q_B = (0.24\,0\,1.32)$, which is equivalent to Q_m, are shown in figures 5(a) and 5(b), where the scans are through Q_B parallel to a^* and c^* axes, respectively. In these figures, one can see that the dispersion of the optical mode of the J_x transitions (D2) has a clear minimum at $q = Q_B$. The excitation energy at Q_B is 0.93 meV and smaller than that at $q = (0\,0\,0.9)$, but the difference is small.

The dispersions D3 and D4 in figure 5(a) are somewhat peculiar; to be consistent with, for instance, the dispersions shown in figure 4, they should be linked together to form a single dispersion. Both dispersions, however, loose scattering intensity rapidly at around $h = 0.15$. More experiments with better energy resolution are necessary to explain the behaviours of these dispersions.

In figure 6 the temperature dependence of the exciton energy of the J_y and the optical J_x transitions measured at the wavevector $q = Q_B$ is shown. In the figure, one can see that, with decreasing temperature, the energy of the J_y transition increases rapidly below 7 K and that of the J_x transition decreases rather slowly. The behaviour of the J_y transition is quite consistent with the level scheme proposed by Kjems [7] if we suppose that it is the transition between the ground state and the second excited state in figure 2. It is of interest to study further the behaviours of this excitation and of its counterpart of the cooperative Jahn–Teller transition. This aspect will be investigated in future.

One may suppose that the energy shift of the J_x transition involves the effect of the Jahn–Teller transition. However, this should not be the case because we observed very

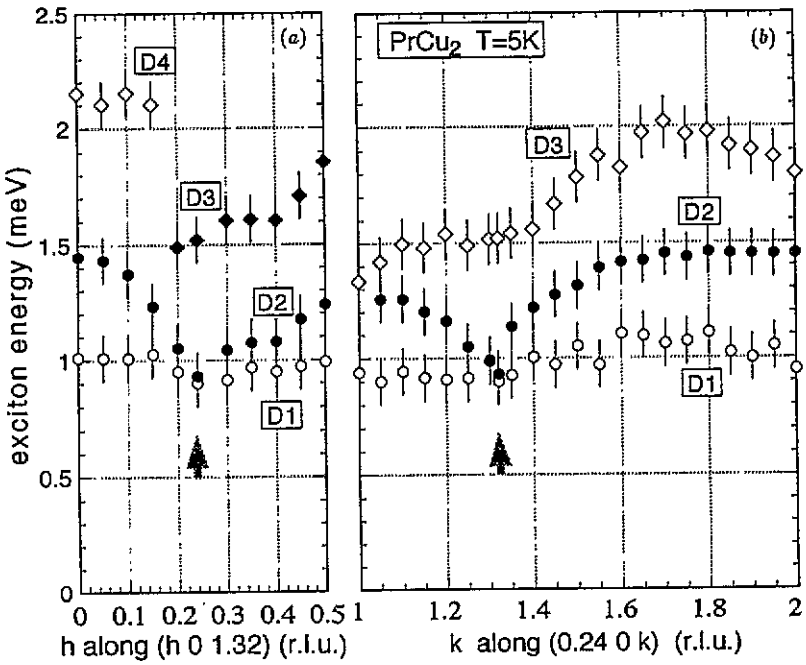

Figure 5. The dispersion curves of the excitons in the paramagnetic phase of $PrCu_2$ around the magnetic Bragg point Q_B = (0.24 0 1.32) at low temperatures (r.l.u., reciprocal-lattice units): (*a*) scan parallel to the a^* axis; (*b*) scan parallel to the c^* axis. The arrows indicate the position of Q_B.

little shift in the J_x transition, when the temperature changed across T_D at the reciprocal-space positions where the dispersion is very weak. Kjems *et al* [8] also confirmed that this transition is completely unaffected by the phase transition at T_D.

4. Discussion

Group theory predicts that the ground multiplet $^3H_4$ of Pr^{3+} in C_{2v} symmetry is split into nine singlets: $3A_1+2A_2+2B_1+2B_2$. In these singlet states, the J_x operator has a matrix element only between A_1 and B_2 and between A_2 and B_1, and so does the J_y operator between A_1 and B_1 and between A_2 and B_2. Since there is no common pair of wavefunctions for the J_x and J_y transitions, one can conclude that the observed J_x and J_y transitions correspond to different excited states from each other.

While the observed J_x transitions are quite dispersive, the J_y transition seems to be very localized. Equation (3) shows that the dispersion depends on the magnitude both of the square a^2 of the matrix element and of the exchange interaction $K(q)$. One may, therefore, suppose that the weak dispersion of the J_y transition is attributed to a possibly small value of a. One should, however, note that the scattering cross section (equation (6)) also depends on a. Since the observed scattering due to the J_y transition is as intensive as that due to the J_x transition, it is reasonably assumed that both of the trtansitions have similar magnitudes for their matrix elements. We therefore consider that the difference between the dispersions of the J_y and J_x transitions is due mostly to a possible anisotropy in the interaction $K(q)$. Since the major magnetic interaction in rare-earth compounds is the RKKY interaction, our

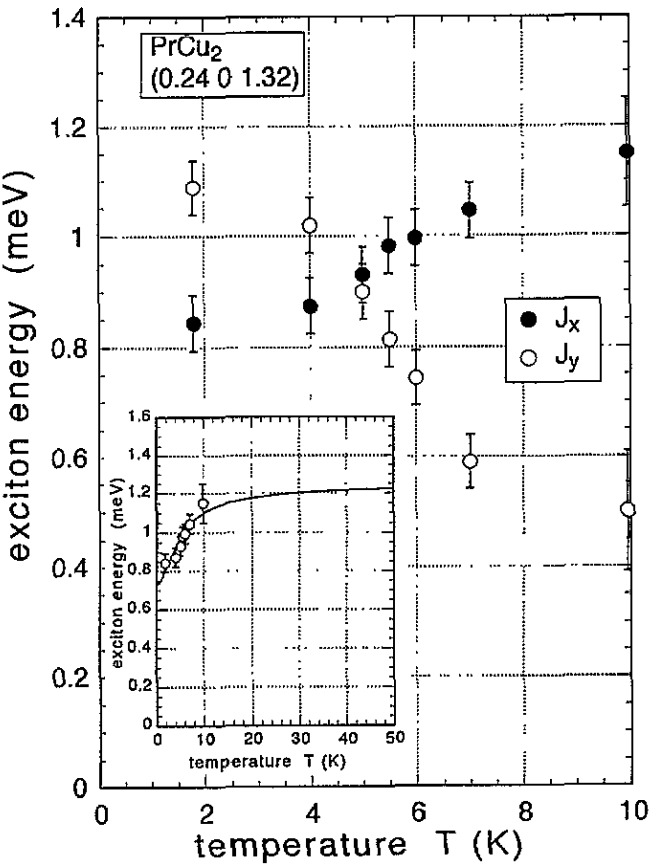

Figure 6. Temperature dependence of the energy of the J_x and J_y excitons at $q = Q_B = (0.24\,0\,1.32)$ in $PrCu_2$. The solid curve in the inset shows the best-fit curve of equation (3) to the data of the J_x transition. The rapid shift in the J_y transition is due to the cooperative Jahn–Teller transition.

observation indicates that the magnetic susceptibility of the conduction electrons of $PrCu_2$ is strongly anisotropic and, hence, that $K(q)$ depends on the direction of magnetic polarization.

The fact that the minimum at Q_B is in the J_x transition is consistent with the fact that the observed polarization of the electronic moment in the magnetically ordered state [10] is parallel to the a axis.

The renormalization factor $R(T)$ in equation (3) should vanish at very high temperatures. Figure 6 indicates that the softening of the J_x exciton at Q_B is already close to saturation at 1.8 K. Because we have several low-lying singlet levels and the nearby Jahn–Teller transition, the soft mode is hard to analyse rigorously. However, by taking the lowest three excited states (optical J_x and the two Jahn–Teller-related states) into account, we could reproduce the approximate temperature dependence of the energy of the soft-mode exciton. We carried out a least-squares fit of the exciton energy data to equation (3) using the mean-field expression, equation (4), for $R(T)$. Since we have no data on the energy level of the lower Jahn–Teller-related state as a function of the temperature, we assumed, as a first approximation, that it changes linearly from 0.25 meV at 0 K to 0.5 meV at 7.3 K. The

best-fit values obtained for Δ and A are 1.30 meV and 0.64, respectively, and the best-fit curve thus obtained is shown in the inset of figure 6. The value of Δ is consistent with figure 2 as is the value of A with the estimation from the neutron experiment [10] and the theory of Murao [11]. However, since we have neglected the possible effects from all the excited states other than the three mentioned above and also since the information about the lowest excited state is so poor, the present result of the analysis should be considered provisional, and more data are necessary to construct a detailed model of the system.

Some characteristics of the measured dispersion relations can be understood by considering qualitatively the canonical transformation of a limited number of exchange parameters. Since the direction of Q_m coincides with the direction of the face diagonal $\langle 101 \rangle$ and since Q_m is very close to the commensurable reciprocal-space point $\frac{1}{4}(103)$ (denoted Q_c), we first consider the interactions which prefer magnetic order with the modulation vector Q_c. One can reasonably suppose that the exchange interactions between atom (0) and atoms (1), (2), (3) and (4) (denoted respectively as bonds (i), (ii), (iii) and (iv)) in figure 1 are effective in realizing this order because they are located either in the direction of $\langle 101 \rangle$ or perpendicular to this direction. One should note that these atomic pairs of interaction bonds are consistent with the observed splitting of the J_x transition because the two atoms in each pair reside on different sublattices of the non-Bravais lattice from each other. The magnitude of the splitting is given as a function of q as [12],

$$C(q)^{\pm} = \pm \left| \sum_m K_m \exp(-iq \cdot m) \right| \tag{7}$$

where m is the position vector connecting two atoms on the different sublattices, and the $+$ and $-$ signs denote the optical mode and the acoustic mode, respectively. We calculated the contribution to $C(q)$ from the interactions of the atomic pairs (i) to (iv) (denoted K_1, K_2, K_3 and K_4, respectively). If one assumes that $K_1 < 0$ and $K_2 < 0$ (antiferromagnetic interactions) and $K_3 = K_4 = 0$, the minimum-energy plane of $C(q)$ is the $(101)^*$ reciprocal-lattice plane. With these interactions only, the minimum points of the exciton energy must be $q = (100)$ and (001). In order to stabilize the point $q = Q_m$, more interactions are needed. The introduction of interactions between the atom (0) and the atoms at positions farther in the $\langle 101 \rangle$ direction may produce frustration in the interactions and may change the distance of the minimum-energy plane to the incommensurable $|Q_m|$. In this case, the minimum-energy plane of $C(q)$ must be perpendicular to Q_m. The intersection of this plane with the c^* axis is calculated to be the position $q = (00 0.92)$ which, within the experimental error, is the same as the position where the local minimum of the $[00k]$ dispersion was observed.

With further calculations it can be shown that introducing a ferromagnetic K_3 and K_4 in addition to K_1 and K_2 gives a minimum to $C(q)$ at Q_c. The small difference between this point and Q_m might also be explained in terms of the possible frustrations of interactions as mentioned above.

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