Magnetic Excitons in Singlet—Ground-State Ferromagnets

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We report measurements of the dispersion of singlet-triplet magnetic excitons as a function of temperature in the singlet-ground-state ferromagnets fcc Pr and Pr_3Tl. Well-defined excitons are observed in both the ferromagnetic and paramagnetic regions, but with energies which are nearly temperature independent, in disagreement with existing theory.

It has been recognized for a number of years[1] that the magnetic properties of singlet–ground-state systems in which the exchange field and crystal field nearly balance differ in a fundamental way from those of conventional magnets. In particular, magnetic ordering occurs as a result of a polarization instability of the ground-state wave function rather than through the alignment of permanent moments. The magnetic excitations in this case are single-ion crystal-field transitions which propagate through the lattice via the exchange[2]; they should be well defined in both the paramagnetic and ordered regimes. Recently it has been proposed that the phase transition is actually driven by a softening of this magnetic exciton at the Q vector appropriate to the magnetically ordered phase, in analogy with soft-phonon modes observed in certain structural phase transitions.[3] In this Letter we report the first study of the dynamics in such singlet–ground-state systems.[4] The actual materials which we have studied are fcc praseodymium and Pr_3Tl.

We briefly summarize the current theory for the magnetic excitations. The Hamiltonian is generally assumed to be of the form

$$\mathcal{H}=\sum_i V_{ci} - 2\sum_{i>j} \mathcal{J}_{ij}\vec{J}_i\cdot\vec{J}_j, \qquad (1)$$

where V_{ci} is the single crystal-field term and for simplicity only the bilinear exchange is included. In cubic symmetry, the Pr^{3+} $4f^2\,{}^3H_4$ ground multiplet is split by the crystal field into a Γ_1 singlet, a Γ_4 triplet, a Γ_3 doublet, and a Γ_5 triplet with energies 0, Δ, $\frac{12}{7}\Delta$, and Δ', respectively[5]; here it is assumed that the Γ_1 singlet is lowest. For bilinear exchange the Γ_1 ground state is coupled only to the Γ_4 triplet so that at low temperatures when the ions are nearly all in the ground state only the Γ_1-Γ_4 excitons will propagate through the lattice. At 0°K *in the paramagnetic phase* the Γ_1-Γ_4 excitons are triply degenerate with energy[2]

$$\hbar\omega_{14}(\vec{Q}) = [\Delta^2 - 4\Delta\alpha^2\mathcal{J}(\vec{Q})]^{1/2}, \qquad (2)$$

where $\alpha = |\langle\Gamma_1|J^z|\Gamma_4\rangle|$ and

$$\mathcal{J}(\vec{Q}) = \sum_{\vec{r}_j} \exp[i\vec{Q}\cdot(\vec{r}_i - \vec{r}_j)]\,\mathcal{J}_{ij}.$$

The dispersion relation, Eq. (2), is identical to that for two singlets.

In the random phase approximation for the singlet-singlet case,[3] Eq. (2) is generalized to finite temperatures by multiplying $\mathcal{J}(\vec{Q})$ by a renormalization factor $R(T)$ which varies from ~ 0 for $k_BT > \Delta$ to ~ 1 at 0°K. Similar results are expected for the singlet-triplet system. Thus for $k_BT \sim \Delta$, the exciton should be relatively flat; however, as the temperature is lowered the mode should acquire dispersion and indeed for a ferromagnet its energy should ultimately go to 0 at $\vec{Q}=0$ at a phase transition temperature defined by $4\alpha^2\mathcal{J}(0) \times R(T_c)/\Delta = 1$. This softening may occur in either a real or a virtual sense depending upon whether the transition is second or first order. In the ordered regime the exciton energy should increase with decreasing temperature and in addition the triple degeneracy may be removed although this latter effect should be small.[6] Finally we note that for the momentum transfers appropriate to these experiments, the neutron scattering is purely magnetic dipole in character so that only the Γ_1-Γ_4 transitions may be seen at low temperatures.

Both fcc Pr[7] and Pr_3Tl[8] have been thoroughly documented as singlet-ground-state systems in which the exchange barely exceeds the critical value necessary for magnetic ordering. In both cases T_c (20°K, 11.6°K) is considerably reduced from Δ (~80°K) and the ordered moment is only about 20% of the free-ion value. Pr_3Tl has the Cu_3Au structure but for the purposes of this Letter it may be regarded as a dilute ordered fcc Pr metal.

The present measurements were performed on a triple-axis spectrometer at the DR 3 reactor at Risö. Two different fcc Pr samples, both in the form of ~20 g of 3-mm pellets, were studied. The Pr_3Tl sample was a 40-g polycrystalline ingot. Because of the polycrystalline nature of the samples all experiments were performed around the (0, 0, 0) reciprocal-lattice point so that a spherically averaged dispersion relation was obtained. However, because of the high symmetry of the fcc lattice, considerable information may still be gained using this technique. Indeed in other fcc ferromagnets[9] such as Ni, Co, EuO, and EuS the spin waves are spherically symmetric far out into the Brillouin zone so that a sharp, well-defined dispersion relation may be obtained in a powder.

Before beginning the inelastic measurements it was first necessary to determine the magnetic structure using two-axis neutron-scattering techniques. These measurements will be described in detail elsewhere[6]; for our purposes here it is only necessary to quote the final results. Pr_3Tl appears to be a simple ferromagnet with a moment of $\sim 0.8\mu_B$ and $T_c = 11.6 \pm 0.3$°K; furthermore the magnetization curve is identical to that observed in many other magnetic phase transitions, so that the transition must be at least nearly second order. For fcc Pr the results are rather more complicated. Bulk magnetization measurements indicate a ferromagnetic transition at ~8°K but with some remanence persisting up to 20°K. However, neutron measurements of the (111) peak intensity show clearly that a continuous phase transition occurs at 20 ± 2°K with a saturation moment of $0.8\mu_B$ in agreement with the bulk value. Neutron depolarization measurements by Koehler[10] in a field of 100 G also indicate the presence of ferromagnetism to above 20°K. We conclude therefore that our sample orders at

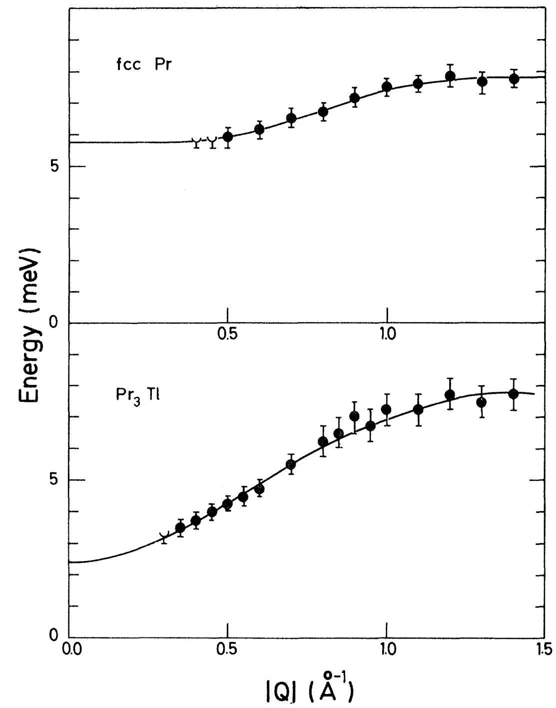

FIG. 1. Γ_1-Γ_4 spherically averaged exciton dispersion relations in fcc Pr and Pr_3Tl; the dispersion relations are independent of temperature up to ~60°K, above which temperature the excitons are no longer observable. The solid lines are calculated using Eq. (2) with the parameters given in Table I.

20°K, possibly to a simple ferromagnetic state, and the transition is at least nearly second order.

The results of the inelastic measurements are illustrated in Figs. 1 and 2. In both systems, at each $\vec{Q}$ and at all temperatures up to 60°K a single well-defined inelastic peak is observed, in accordance with our expectations from the theory. The relative intensities of the peaks at various $\vec{Q}$'s are consistent with the theoretical structure factor $2\alpha^2\Delta/\hbar\omega(\vec{Q})$. The resultant spherically averaged dispersion curves are shown in Fig. 1. Both have their minimum energies at or near $Q = 0$ as expected for ferromagnetic ordering. The measurements cease around 0.4, 0.3 Å^{-1} because of kinematic restrictions; that is, for smaller $\vec{Q}$'s the exciton energies are such that it is not possible to close the momentum triangle without undue contamination from the direct beam.

The dispersion curves may be fitted by Eq. (2) as an interpolation formula to obtain the effective crystal-field splitting, and the relative value of the nearest-neighbor and more-distant-neighbor exchange fields.[6] The results of such fits are

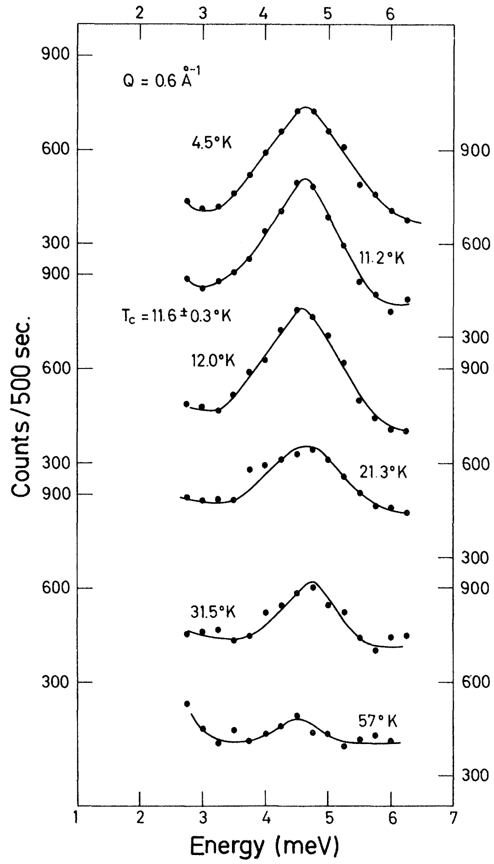

FIG. 2. Typical exciton scans in Pr_3Tl as a function of temperature. Similar behavior is observed at all other wave vectors in both Pr_3Tl and fcc Pr. The instrumental width for these scans was 1.25 meV.

given in Table I; the solid lines in Fig. 1 are the corresponding spherically averaged fitted dispersion relations. Because of the long-range nature of the exchange in rare-earth metals, the extrapolation into $Q = 0$ must be considered as rather unreliable; however, we would not expect too serious departures from the suggested curves. It should be noted, however, that there are some difficulties associated with the use of Eq. (2) in the ordered regime. Our high-temperature results, which we now discuss, indicate that the present theory is seriously deficient; these difficulties must be resolved before unambiguous interaction parameters can be extracted from the data.

Typical spectra as a function of temperature are shown in Fig. 2 for Pr_3Tl; similar behavior is observed in fcc Pr. The results are most surprising. The exciton energies are nearly independent of temperature while the intensity decreases gradually with increasing temperature

TABLE I. Crystal-field and interaction parameters.

	Δ (meV)	$24\alpha^2\mathcal{J}_1$ (meV)	$2\alpha^2(6\mathcal{J}_2+24\mathcal{J}_3+\cdots)$ (meV)
fcc Pr	7.2	2.4	−1.1
Pr_3Tl	6.8	3.8	−0.8

as the ground state is depopulated. By 78°K in both fcc Pr and Pr_3Tl the exciton is no longer observable and instead a broad continuum of scattering extending out to 10 meV is observed. We note, in particular, that there is no abrupt change either in energy or intensity in going from the ordered to the paramagnetic regime. Similar behavior is observed at all of the other wave vectors shown in Fig. 1. In the soft-mode theory, dramatic effects should have been readily observable at the $\vec{Q}$'s accessible to us, particularly in fcc Pr; indeed, we had anticipated being able to reach much smaller $\vec{Q}$'s as the exciton energy decreased near T_c. As a final test an energy analysis of the scattering at the (1, 1, 1) position below, at, and above T_c was made; this measures the density of states weighted at long wavelengths. Again the spectra at each temperature are indistinguishable except for an overall scaling factor in the intensities. We must conclude therefore that the present finite-temperature theories of magnetic excitons in singlet–ground-state systems are incorrect both in their prediction of a soft mode driving the phase transition and more generally in their overall predictions of a marked temperature dependence of the exciton energies in the paramagnetic region.

These results seem to call into question not only the details of the calculations of Ref. 3 but more generally our whole picture of magnetism in singlet–ground-state systems using Eq. (1) as a starting point. Alternative models involving the Γ_3 and Γ_5 levels via higher-order exchange also seem inadequate since all such theories require a distinct change in the ground-state wave function in the ordered phase which in turn should manifest itself in the dynamics. Impurity effects are ruled out by the smooth and rapid variation of T_c and $M(0)$ with Th doping in fcc Pr[7] and La doping in Pr_3Tl.[8] One possibility which we cannot completely rule out is that $\mathcal{J}(\vec{Q})$ has a near-singular behavior near $Q = 0$ which produces the phase transition via a soft mode at $Q = 0$, but which does not manifest itself at finite $\vec{Q}$'s in our powder spectra. However, this seems quite unlikely to us and in any case it leaves the temperature independence of the excitation energies for $Q > 0.4$, 0.3 Å^{-1} unexplained. Finally, nuclear specific-heat measurements[7] confirm that the ordered moment originates in the $4f$ subshell so that explanations on the basis of conduction-electron polarization must be ruled out. Clearly some fresh theoretical insight is required; we hope that these results will serve to stimulate such theory.

[1]G. T. Trammell, Phys. Rev. 131, 932 (1963); B. Bleaney, Proc. Roy. Soc., Ser. A 236, 19 (1963). For a recent review see B. R. Cooper and O. Vogt, J. Phys. (Paris), Colloq. 32, C1-958 (1971).

[2]G. T. Trammell, J. Appl. Phys. 31, 362S (1960); B. Grover, Phys. Rev. 140, A1944 (1965).

[3]Y.-L. Wang and B. R. Cooper, Phys. Rev. 172, 539 (1968), and 185, 696 (1969). These calculations were actually performed for the singlet-singlet case, but the authors (B. R. Cooper, private communication) expect the results to apply at least qualitatively for singlet-triplet systems considered here.

[4]For previous experiments on magnetic excitons in metals see B. D. Rainford and J. C. G. Houmann, Phys. Rev. Lett. 26, 1254 (1971); T. M. Holden, W. J. L. Buyers, E. C. Svensson, and O. Vogt, Bull. Amer. Phys. Soc. 16, 325 (1971).

[5]K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).

[6]B. R. Cooper, private communication; R. J. Birgeneau, J. Als-Nielsen, E. Bucher, and B. R. Cooper, to be published.

[7]E. Bucher, C. W. Chu, J. P. Maita, K. Andres, A. S. Cooper, E. Buehler, and K. Nassau, Phys. Rev. Lett. 22, 1260 (1969).

[8]E. Bucher, K. Andres, J. P. Maita, L. D. Longinotti, and A. S. Cooper, to be published; H. Haschke, H. Nowotny, and F. Benesovsky, Monatsh. Chem. 97, 716 (1966).

[9]See for example, G. Shirane, V. J. Minkiewicz, and R. Nathans, J. Appl. Phys. 39, 383 (1968); L. Passell, O. Dietrich, and J. Als-Nielsen, to be published.

[10]W. C. Koehler, private communication.

Exact Wave-Type Solution to f-g Theory of Gravity*

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The well-known plane-fronted waves with parallel rays, exact solutions of the vacuum Einstein gravitational field equations, are generalized to exact solutions of the equations of f-g gravity theory proposed by Isham, Salam, and Strathdee in regions free from matter.

Recently, Isham, Salam, and Strathdee[1] proposed to modify Einstein's equations of general relativity into a two-tensor theory of gravitation. In this modified theory one has, besides the usual $g^{\mu\nu}$ field, a second "metric" tensor $f^{\mu\nu}$ which is thought to describe the massive f-meson spin-2 field. It is assumed that the g field couples directly only to leptons (weak gravity), and the f field only to hadronic matter (strong gravity). A mixing term between f and g ensures that the g field interacts with hadronic matter indirectly via the f field ("f dominance of hadronic gravity"). However, so far no nontrivial, i.e., $g^{\mu\nu} \neq f^{\mu\nu}$, exact solution of the field equations has been found. We give here a class of exact solutions for the f-g field equations known from general relativity as plane-fronted waves with parallel rays (pp waves).

pp waves have been extensively studied in Einstein's theory. The search for pp waves in f-g theory was therefore strongly motivated by the following properties of pp waves (see Ehlers and Kundt[2] and Bonnor,[3] and references given there): (i) pp waves are pure radiation fields, for which the curvature and Einstein tensor are of a simple algebraic structure. (ii) Einstein's equations are linear for pp waves when written in a suitable coordinate system. (iii) As a consequence of (ii), pp waves propagating in the same direction can be superposed linearly. (iv) Nonvacuum pp waves can be superposed by superposing their sources. (v) Exact and linearized solutions of Einstein's equations coincide for pp waves.

The idea was to carry this over to f-g theory and look for pp-wave vacuum solutions. By vacuum we mean a space-time region without (leptonic and hadronic) matter and electromagnetic radiation, in which case the equations of f-g theory are of the form

$$\begin{aligned} &\frac{G_{\mu\nu}(f)}{\kappa_f^2(-f)^{1/2}} + \frac{\partial \mathfrak{L}_{fg}}{\partial f^{\mu\nu}} = 0, \\ &\frac{G_{\mu\nu}(g)}{\kappa_g^2(-g)^{1/2}} + \frac{\partial \mathfrak{L}_{fg}}{\partial g^{\mu\nu}} = 0, \end{aligned} \tag{1}$$