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Four-Spin Exchange Model and ^{3}He Magnetism

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A two-parameter model based on three-spin exchange and planar four-spin exchange gives at low field a first-order transition to the ordered phase suggested by Osheroff, Cross, and Fisher and at high field gives a second-order phase agreeing with the experiments of Godfrin *et al.* and Adams *et al.* It also fits well the high-temperature expansion coefficients and the susceptibility of the low-field phase.

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Four experiments[1-4] have recently been reported which clarify the nature and location of the magnetic phases of solid ^{3}He. Figure 1 summarizes their contributions. The work of Adams *et al.*[3] has confirmed that the high-field branch of the phase diagram is a second-order phase transition and has given information about possible phase structures below the transition temperatures. Godfrin *et al.*[4] have followed a feature which seems to correspond to this phase line to the region of 7 T and 3 mK. The work of Prewitt and Goodkind[2] has confirmed the first-order nature of the transition below 0.41 T and discovered another phase transition line below the second-order transition at about 0.42 T.

Finally and most remarkably the experiment of Osheroff, Cross, and Fisher[1] on single crystals of ^{3}He below the phase transition and at low field indicates that the magnetic structure of that phase is probably of the 100 up-up-down-down (uudd) form, and in any case the sublattice structure is not cubic and is characterized by a vector along the 100 direction.

Of the theories put forward to explain the magnetic properties of solid ^{3}He magnetism[5] only the idea that four-particle ring exchanges are large enough to induce first-order transitions[6-8] still seems viable. We show that this theory can explain all the measured high-temperature coefficients and give an approximate phase diagram.

The kinds of exchanges which we might have considered include (i) nearest-neighbor exchange $J(nn)$, (ii) three-particle ring exchange J_t, (iii) four-particle planar ring exchange K_P, (iv) four-particle folded ring exchange K_F. K_F and K_P lead to four-spin terms in the Hamiltonian.[9] Other exchanges such as two-particle second-neighbor exchange or five-particle ring exchange are expected to be smaller.[8,10] Early calculations[11] indicated that the four-spin exchange terms were very small but those calculations were based on variational wave functions which could not be correct on the tunneling path. Estimates of the wave function inside the tunnel indi-

cate that four-spin exchange is at least comparable to two-spin exchange.[8,10]

Prior to reports of Osheroff's experiment, we had assumed[6,7] that K_P was the larger of the four-spin parameters because we failed to imagine a phase structure which lowered the energy of the K_P exchange Hamiltonian. After Osheroff's preliminary report of large zero-field resonance frequencies[12] it was evident that phases with simple cubic sublattice structure were eliminated. By concentrating on noncubic structures we found two that are induced by K_P exchange.[13]

In this report we explore the two-parameter (J_t, K_P) spin Hamiltonian:

$$H = -\sum_{N=1}^{3} \frac{J_N}{2} \sum_{i<j}^{N} \vec{\sigma}_1 \cdot \vec{\sigma}_j - \frac{K_P}{4} \sum_{i<j<k<l}^{P} \{(\vec{\sigma}_i \cdot \vec{\sigma}_j)(\vec{\sigma}_k \cdot \vec{\sigma}_l) + (\vec{\sigma}_j \cdot \vec{\sigma}_k)(\vec{\sigma}_i \cdot \vec{\sigma}_l) - (\vec{\sigma}_i \cdot \vec{\sigma}_k)(\vec{\sigma}_j \cdot \vec{\sigma}_l)\} - \mu \sum_i \vec{H} \cdot \vec{\sigma}_i, \quad (1)$$

where the σ's are Pauli spin matrices, where $J_1 = -6J_t + 3K_P$, $J_2 = -4J_t + K_P$, $J_3 = \frac{1}{2}K_P$, and where the summation labeled N is over the Nth neighbor pairs while that labeled by P is over planar nearest-neighbor quadrilaterals.

Figure 2 shows the limits in parameter space which result from error estimates on the high-temperature expansion coefficients $e_2, \tilde{e}_3, \theta, B$ defined by

$$C_v/R = \tfrac{1}{4}(e_2 T^{-2} - \tilde{e}_3 T^{-3}), \quad (2)$$

$$\chi^{-1} N\mu^2/Vk = T - \theta + B/T. \quad (3)$$

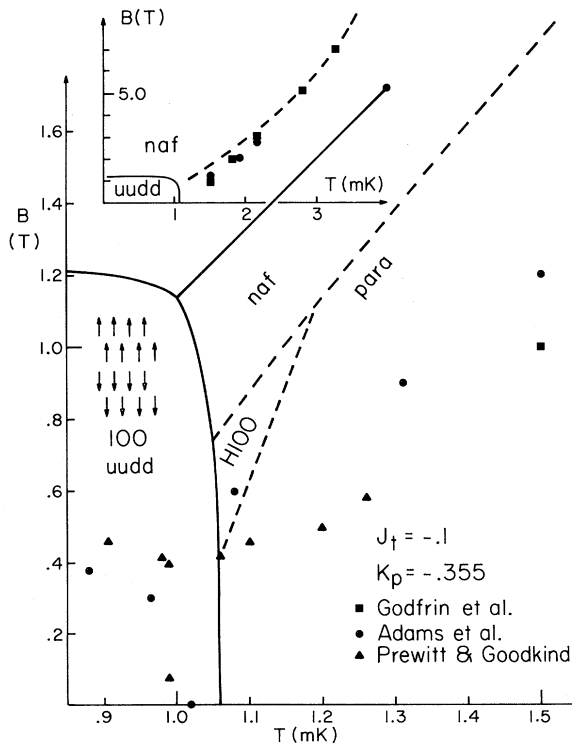

FIG. 1. The experimental data of Refs. 2, 3, and 4 as regards to the location of phase transitions. Also shown is the theoretical phase diagram for the parameters J_t = -0.1 mK, K_p = -0.355 mK. Labeling of phases is according to the theoretical result.

These coefficients are given in terms of J_1, J_2, J_3, K_P by Roger and Delrieu.[14] Since e_2 is relatively well measured, a narrow long region of acceptance in parameter space results, the ends of which are defined by the simultaneous effect of the errors on θ and $\tilde{e}_3$. B is more or less constant in the whole region. For the parameter values of Fig. 1, $B = -0.52$ mK^2 which is smaller in magnitude than the value quoted by Prewitt and Goodkind[15] but probably within the error of measurement.[16]

The two phases we find at low field in this parameter region are the simple square antiferromagnetic (ssqaf) phase and the 100 uudd phase described by Osheroff, Cross, and Fisher.[1] They are illustrated in Fig. 2 by projection onto basal planes. The boundary between them approximately bisects the acceptance region. We have used Monte Carlo (Metropolis on a sixteen-element periodic lattice) to search for other phases in this parameter region. No other phases of lower energy have been found. The 100-uudd phase leads to the single zero-field resonance observed in Ref. 1. The ssqaf phase leads to two resonances at zero field as well as three resonances at nonzero fields (for each domain orientation) in disagreement with the observations of Ref. 1. At high field, we find the normal (spin-flop) antiferromagnetic phase (naf) for all reasonable parameter values.

As an illustration of the kind of phase diagram obtained by mean field theory in this parameter region we show in Fig. 1 the phase diagram corresponding to the point marked with the cross in Fig. 2 ($J_t = -0.1$; $K_P = -0.355$). The calculation yields a first-order phase line at low field and a second-order phase line at high field. Both transitions fit the experimental results for field values very different from 0.4 T.

For parameter values nearer the center of the "window" in Fig. 2, we find that mean field theory gives a second-order transition above the

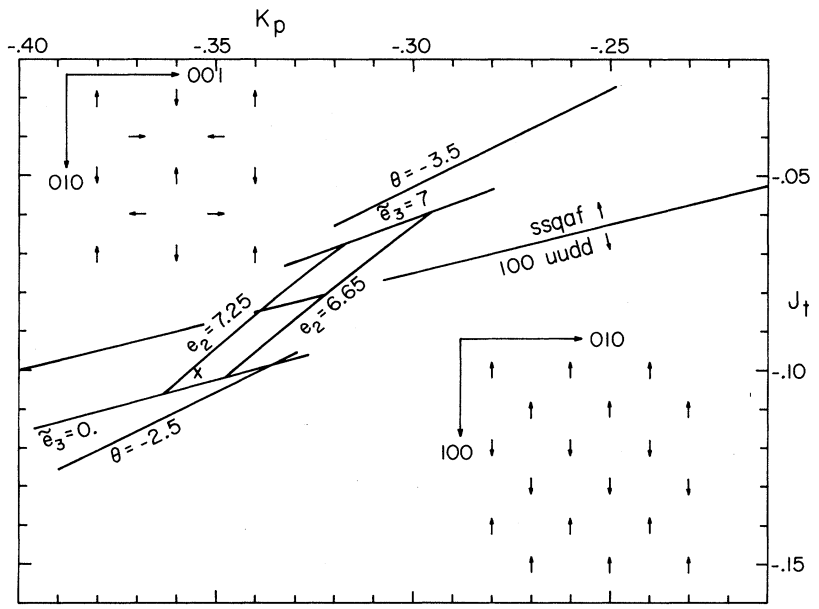

FIG. 2. The parameter space K_p, J_t and the boundary lines implied by the high temperature coefficients as labeled. The line bisecting the whole graph labeled ssqaf/100 uudd marks the boundary between the two phases illustrated. The phases are shown by projection onto the 001 plane (100 uudd) and onto the 100 plane (ssqaf). All atoms of the bcc lattice projecting onto the same point have the same orientation.

first-order transition. All parameter sets we have tried which fit the high-temperature parameters give reasonable fits to the second-order phase line, the transition temperature in the region of 6 T varying about 10%. The depression of the first-order transition temperature with field is smaller than observed[17] or than inferred from measured changes in susceptibility[15] and entropy.[17] Our value of susceptibility in the low-T phase is close to that of Prewitt and Goodkind,[15] and the entropy change we calculated is approximately as observed. Thus the depression is not large enough because the mean field theory gives too low a value for the susceptibility of the paramagnetic phase just above the phase transition.

Prewitt and Goodkind's observation of an extension of the first-order transition line past the junction with the second-order line (although they suggest it is second order there) presumably correlates with our continuous first-order transition which bends sharply at the juncture.

The unobserved first-order phase line extending into the naf phase from the knee of the 100-uudd boundary represents a transition where the degree of cant of the naf phase changes discontinuously. The line ends at a critical point. The phase diagram also has a small region of $H100$ helical phase (see Ref. 7 for a description). We presume that these are artifacts of the mean field approximation. We expect an exact calculation to place the naf-para transition at a lower temperature with a somewhat weaker effect on the position of the 100 uudd–para transition. The freedom obtained by such an effect would be in the direction to allow the removal of these unwanted transitions.

Three-parameter fits (K_P, K_F, J_t) have also been obtained which give improvement in the quantitative fit to the data (i.e., the value of B is nearer the value of Prewitt and Goodkind and the junction of the first- and second-order phase lines is lower). The unwanted features of the phase diagram cannot be eliminated this way, however, and so we decline to fine tune at the expense of an extra parameter.

We agree with the calculation of Osheroff, Cross, and Fisher[1] of the zero-field antiferromagnetic resonance frequency because our value of the susceptibility there is $\chi^{-1}(N\mu^2/Vk) = -1.91\theta$, in good agreement with measurement.[13]

In the high-field-ordered phase (naf) no significant line splitting is expected in NMR because the sublattices are cubic so that dipolar anisotropy cancels. This agrees with the observations of Adams *et al.*[3] They observed a broadening and shift of the resonance line almost independent of

the field between 0.43 and 2.9 T as we expect for the naf phase. The maximum shift, 1.6 G, in the shoulder of the observed line must equal the maximum possible demagnetizing field $M/M_0 \times (3.3$ G). This gives $M/M_0 \simeq 0.5$ and is in relatively good agreement with the results of Ref. 2 and our model.

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Magnetoelastic Interactions in Ionic π-Electron Systems: Magnetogyration

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The alkali hyperoxides AO_2 exhibit elastic and magnetic interactions due to the nature of the diatomic molecule ion O_2^-. These anion sublattices represent simple magnetic spin-$\frac{1}{2}$ systems. In contrast to $3d$- or $4f$-electron systems, where magnetoelastic interactions induce magnetostriction, the $(2p)\pi$-electron system KO_2 exhibits magnetogyration. A crystallographic phase transition involving a considerable change in the molecular orientation can be induced by an applied magnetic field. A theoretical model based on the exchange modulation produced by this reorientation describes the salient features.

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The alkali hyperoxides $A^+O_2^-$ (A = Na, K, Rb, Cs) are model substances to investigate π-electron magnetism.[1,2] The small symmetric and inorganic molecule anion, effectively a "pseudohalide," gives rise to interesting magnetic order. The peculiarities of the hyperoxide ion O_2^- are important for the understanding of the many fascinating properties of the AO_2: (i) The magnetic moment is localized on a $(2p)\pi_g$ orbital. (ii) The ground state $X^2\Pi_g$ of the free molecule ion is orbitally and spin degenerate. (iii) The spin-orbit (sl) coupling of O_2^- is of the order of 200 cm^{-1} (Känzig and Labhard[3]), whereas this quantity for the widely studied oxygen molecule in the solid state[4] is two orders of magnitude smaller. (iv) The O_2^- radical can reorient in alkali halides even at very low temperatures,[3] thereby modulating orbital overlaps and magnetic exchange interactions.

The alkali hyperoxides undergo many phase

