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Most experimental magnetic properties of solid bcc ^3He are described by a two parameter model : three and four spin exchange

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Résumé. — Un modèle à deux paramètres, comprenant exclusivement les échanges à quatre et trois spins reproduit remarquablement la courbe d'entropie pour $T \gtrsim 1$ mK ; il est en accord avec les résultats expérimentaux inhabituels concernant la susceptibilité et la chaleur spécifique et il donne les principales caractéristiques du diagramme de phase expérimentalement observé.

Abstract. — A two parameter model including only four and three spin exchange fits the entropy curve remarkably well down to 1 mK, agrees with the unusual experimental results on the susceptibility and specific heat and gives the main features of the observed phase diagram.

The experimental magnetic properties of bcc solid ^3He in the millikelvin range, near the melting curve are in contradiction with the usual antiferromagnetic Heisenberg model [1]. i) An abrupt drop of entropy suggesting a first order transition is observed at $T_{c1} = 1$ mK $\simeq -\theta/3$ ($\theta \simeq -3$ mK : Curie Weiss constant) [2]. In a magnetic field, the transition remains apparently first order with T_{c1} slightly decreasing with H up to $H_c \simeq 4$ kG. Above 4 kG, a second order transition is observed with T_{c2} increasing rapidly with H [2, 3]. The experimental phase diagram (see Fig. 4 of Ref. [1]) suggests a competition between two phases : one occurring at low field is antiferromagnetic with a low susceptibility, the second arising at high field has a high susceptibility and consequently some ferromagnetic tendency. The smallness of the critical field $\gamma\hbar H_c/2 k_B \theta \simeq 0.1$ indicates that these two phases are almost degenerate and suggests the proximity of a bicritical point. ii) At $T_{c1} < T \lesssim 10$ mK, the susceptibility $\chi(H \rightarrow 0)$, in the paramagnetic (P) phase is larger than the extrapolated Curie Weiss value [4]. The curve $\chi^{-1}(T)$ has been fitted with a high temperature series expansion limited to the first three terms [5] : $\chi^{-1}(T) = C^{-1}(T - \theta + B/T)$; ($C = N(\gamma\hbar/2)^2$), with $\theta = -2.6$ mK and $B = -2.7$ mK. This behaviour is the opposite of what is observed in usual antiferromagnets described by a Heisenberg model where

$$B = \sum_n z_n J_n^2/2$$

(J_n : interaction between the n th neighbours and z_n : number of n th neighbours) is positive. iii) The specific heat measurements [6, 7] give

$$C_v = 0.25 R(\tilde{e}_2 T^{-2} - \tilde{e}_3 T^{-3})$$

with $\tilde{e}_2 \simeq 7 \pm 0.5$ mK² at the melting molar volume $V = 24.25$ cm³ and $\tilde{e}_3$ less accurate but positive. A Heisenberg model with nearest (or nearest and next nearest) neighbour exchange gives $\tilde{e}_3 < 0$.

These unusual properties have led to different theoretical models. Some of them add to the nearest neighbour antiferromagnetic Heisenberg (HNNA) model a coupling to another system : a) phonons (i.e. magnetoelastic constraints [8]), b) ground state vacancies giving spin polarons [9, 10]. The models (b) lead to anomalies in the high temperature range (30 ~ to 200 mK) [10], for which there is at present no experimental confirmation [6, 7]. These models introduce ferromagnetic tendencies and reproduce some features of the system : in particular ii). Except for reference [9] which gives, in contradiction with experiment, a second order transition at low field and a first order transition at high field, there are few detailed theoretical studies of the phase diagram in the H, T plane for these models. Another type of model generalizes the Heisenberg Hamiltonian by adding multiple (three, four spin...) exchange interactions [11, 12, 13]; it gives no anomalies for $T \gg \theta$ and fits quantitatively the largest number of experimental data.

Starting here with the idea that some kinds of permutations : four spin exchange (with possibly three spin exchange) can be preponderant and thus

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neglecting pair exchange, we put forward a two parameter simpler multiple exchange model which fits all available data better than the previous models.

We cannot trust the exchange calculations based on the one particle gaussian wave function [11] which in ^3He does not satisfy the conditions defined by Herring for a reliable *Home based function* [14]. (The decrease of the real wave function in the exchange configuration has no reason to be gaussian [15].) So this approximation cannot even give the hierarchy of different kinds of exchange. We now put forward simple geometrical arguments based on the hard sphere model which [15] is valid for calculating the energy of solid ^3He [16]. For the problem of n exchanging hard spheres, two essential parameters are to be considered : a) the free space δ available in the box shaped by the surrounding atoms in the exchange configuration ; b) the total displacement

$$d = \left(\sum_i \delta r_i^2 \right)^{1/2}$$

of the particles in the 3 N dimensional space of configuration during the exchange process. The exchange increases with δ and decreases with d . There is an optimum between these two conditions which can favour one type of exchange. In bcc ^3He , the free space δ is much larger for three or four spin exchange than for pair exchange [15]. Although d increases with the number of exchanging atoms, four and three spin exchanges are probably larger than pair exchange. These conjectures have been corroborated by quantitative calculations [15]. Higher order (five, six spin...) exchanges have comparable free space δ with four spin exchange but they are disfavoured by the increasing d . (In hcp ^3He , we believe that three spin exchange is most likely the dominant contribution [17].)

We suppose here first that folded four spin exchange involving the most compact four atom tetrahedron (F) [12] dominates and we neglect all other exchanges. The Hamiltonian is :

$$\mathcal{H}_{\text{ex}} = - K_F \sum_{i < j < k < l}^{(F)} \mathcal{P}_{ijkl}$$

$\mathcal{P}_{ijkl}$ being the four particle cyclic permutation operator. Expressing $\mathcal{P}_{ijkl}$ in terms of spin operators, we obtain :

$$\begin{aligned} \mathcal{H}_{\text{ex}} = & - 6 K_F \sum_{i < j}^{nn} \mathbf{S}_i \cdot \mathbf{S}_j - 4 K_F \sum_{i < j}^{nnn} \mathbf{S}_i \cdot \mathbf{S}_j - \\ & - 4 K_F \sum_{i < j < k < l}^{(F)} \delta_{ijkl} \end{aligned}$$

with

$$\begin{aligned} \delta_{ijkl} = & (\mathbf{S}_i \cdot \mathbf{S}_j) (\mathbf{S}_k \cdot \mathbf{S}_l) + (\mathbf{S}_i \cdot \mathbf{S}_l) (\mathbf{S}_j \cdot \mathbf{S}_k) - \\ & - (\mathbf{S}_i \cdot \mathbf{S}_k) (\mathbf{S}_j \cdot \mathbf{S}_l) . \end{aligned}$$

Contrary to the other models, we can have exact results in the high temperature region $T \gg \theta$. A high temperature series expansion of the partition function $Z = \text{Tr} \exp(-\beta \mathcal{H})$, ($\mathcal{H}$ is the sum of the exchange and Zeeman Hamiltonians) gives [13] :

$$\begin{aligned} N^{-1} \ln Z = & \ln 2 + \tilde{e}_2 \beta^2 / 8 - \tilde{e}_3 \beta^3 / 24 + \\ & + 0.5(\gamma \hbar H / 2 k_B T)^2 (1 + \theta \beta + D \beta^2 + \dots) \end{aligned}$$

with

$$\begin{aligned} \tilde{e}_2 = & 175.5 K_F^2 ; \quad \tilde{e}_3 = - 2 277 K_F^3 ; \\ \theta = & 18 K_F ; \quad D = 324 K_F^2 \end{aligned}$$

we deduce the specific heat $C_v = 0.25 R(\tilde{e}_2 \beta^2 - \tilde{e}_3 \beta^3)$ and the inverse susceptibility

$$\chi^{-1}(T) = C^{-1}[T - \theta + B/T]$$

with $B = \theta^2 - D$. For this model $B \equiv 0$.

Taking a mean value of all available data, we estimate : $\tilde{e}_2 \simeq 7 \text{ mK}^2$ ($\pm 5\%$) [6, 7], and $\theta \simeq - 2.9 \text{ mK}$ ($\pm 15\%$) [5, 18], (see also experimental papers quoted in [1]). We choose $\tilde{e}_2 \simeq 7 \text{ mK}^2$ to determine $K_F = -0.2 \text{ mK}$. This gives $\theta = -3.6 \text{ mK}$ (slightly too high) and $\tilde{e}_3 \simeq 18.2 \text{ mK}^3$, positive but too large [7]. However it is interesting to see what is predicted for the phase diagram within the Molecular Field Approximation (MFA). Two phases are in competition : a two sublattice phase (the naf phase [12]) and a four sublattice phase (scaf phase [12] : two simple cubic antiferromagnetic lattices with orthogonal magnetizations). In zero field, their respective energies are

$$E_{\text{naf}} = 1.5(2 p^2 - p^4) K_F$$

and

$$E_{\text{scaf}} = 1.5(2 p^2 + p^4) K_F ;$$

with $p = 2 \langle S_z \rangle$. The values of the quadratic terms are the same, hence their second order critical temperatures are degenerate and we have a bicritical point. However, the p^4 terms being of opposite sign, the scaf phase is stable at low temperature and zero field and this p^4 term gives at $T \simeq 1.4 \text{ mK}$ (before the second order transition) a first order transition to the paramagnetic (P) phase with a large drop of entropy. (This result has been quoted in Ref. [1].) The deformation of the scaf phase in a magnetic field $\mathbf{H}$ is shown on figure 1. The magnetizations $\mathbf{A}$, $\mathbf{B}$, $\mathbf{A}'$, $\mathbf{B}'$ of the four sublattice and $\mathbf{H}$ remain in the same plane. (This gives at $\mathbf{H} \rightarrow 0$ the higher susceptibility) [13]. $\mathbf{A}$ remains perpendicular to $\mathbf{B}$ and $\mathbf{A}'$ to $\mathbf{B}'$; with increasing $\mathbf{H}$, the two right angles ($\mathbf{A}$, $\mathbf{B}$) and ($\mathbf{A}'$, $\mathbf{B}'$) rotate in opposite directions, $\mathbf{B}'$ and $\mathbf{A}$ crossing at some field, until they become superposed ($\mathbf{A} = \mathbf{A}'$; $\mathbf{B} = \mathbf{B}'$); there we obtain a second order transition

to the two sublattices naf phase. The phase diagram is shown on figure 1. $H \gtrsim 44$ kG being fixed, the naf phase gives a second order transition to the paramagnetic phase at $T_{c2}(H)$. T_{c2} increases with H , up to $H \simeq 89$ kG where the slope of the transition line changes sign. This feature provides a way to decide experimentally between our model and that of reference [9], where $T_{c2}(H)$ increases monotonically. This ferromagnetic behaviour at $H < 89$ kG is due to the four spin term. The same ferromagnetic tendency is observed in the behaviour of the susceptibility in the P phase, near the transition : the parameter B being null (contrary to the Heisenberg model where $B > 0$) the susceptibility is increased (but not enough : the experiment gives $B < 0$). So this simple model gives *qualitatively* the main features of the experimental phase diagram.

Now we complicate this model slightly by introducing three spin cyclic permutation, J_t , of the most compact triangle. An even permutation is ferromagnetic [19]: $J_t > 0$; thus we increase the ferromagnetic tendencies and are able to obtain a better quantitative agreement with the experiments (in particular with $B < 0$). We therefore take the Hamiltonian :

$$\mathcal{H}_{\text{ex}} = -J_t \sum_{i < j < k} \mathcal{P}_{ijk} - K_F \sum_{i < j < k < l} \mathcal{P}_{ijkl};$$

where $\mathcal{P}_{ijk}$ is the three particle cyclic permutation operator. In terms of spin operators :

$$\begin{aligned} \mathcal{H}_{\text{ex}} = & -6(K_F + J_t) \sum_{i < j}^{nn} \mathbf{S}_i \cdot \mathbf{S}_j - 4(K_F + J_t) \times \\ & \times \sum_{i < j}^{nnn} \mathbf{S}_i \cdot \mathbf{S}_j - 4K_F \sum_{i < j < k < l}^{(F)} \mathcal{P}_{ijkl}. \end{aligned}$$

The coefficients of the high temperature series expansion are [13] :

$$\theta = 18(K_F + J_t); \quad B = 8\theta J_t/3;$$

$$\tilde{e}_2 = 39\theta^2/72 - 7\theta J_t/2 + 63J_t^2/2;$$

$$\begin{aligned} \tilde{e}_3 = & -253\theta^3/648 + 5J_t\theta^2/12 + \\ & + 63J_t^2\theta/2 + 27J_t^3. \end{aligned}$$

Taking $\tilde{e}_2 = 7 \text{ mK}^2$ and $\theta = -2.9 \text{ mK}$, we obtain $K_F = -0.322 \text{ mK}$ and $J_t = 0.161 \text{ mK}$. This gives $\tilde{e}_3 \simeq 7.8 \text{ mK}^3$ and $B = -1.24 \text{ mK}^2$. With these values, we obtain a remarkable fit to the entropy curve [2] $S(T) = \ln 2 - \tilde{e}_2 \beta^2/8 + \tilde{e}_3 \beta^3/12$ (Fig. 2b) down to the transition. With $B = -1.24 \text{ mK}^2$, at low temperature the susceptibility is larger than the extrapolated Curie Weiss value. Reference [5] gives $B = -2.7 \text{ mK}^2$, but the experimental determination of B is not accurate and near 1 mK, higher power term in $1/T$ can change the apparent value of B , and this difference is therefore not significant. The phase diagram within the MFA is shown on figure 2a. It has the same essential features as that of figure 1.

Fig. 1. — One parameter model : phase diagram within the molecular field approximation ; full lines and dotted lines indicate respectively first and second order transitions (in both figures).

Fig. 2. — Two parameter model : (a) Phase diagrams : the results of the molecular field approximation (MFA) and of our approximation at second order (app. 2nd) are compared with the experimental data [2, 3] (exp); (b) Insert compares the experimental entropy curve in zero field [2] (dotted line and circles) with the high temperature series expansions (full line).

In zero field, the second order temperatures of transition of the scaf and naf phases are degenerate (bicritical point). The scaf phase is stable at low field and gives at $T \simeq 1.45 \text{ mK}$ a first order transition to the paramagnetic phase. The susceptibility of the scaf phase is practically constant : $\chi^{-1} = -C^{-1} 4\theta/3$. Reference [5] measures $\chi^{-1} \simeq -2\theta C^{-1}$. In the usual cases (HNN model) the fluctuations increase the susceptibility by 20 to 30 %. Here, with the presence of a bicritical point, it can even be more. Thus we can expect to obtain a good agreement using reliable calculations beyond the MFA. (The preceding multiple exchange models [12, 13] gave a much higher value for χ , in disagreement with [5].) At $H \gtrsim 35 \text{ kG}$, the naf phase is stable. Its ferromagnetic tendencies

are increased by J_t . The agreement with the experimental phase diagram [3] is only qualitative. But the MFA is certainly not reliable owing to the bicritical point. We are now investigating approximations beyond the MFA. We propose an extension of the high temperature series expansion converging below T_c . The unperturbed hamiltonian $\mathcal{H}_0$ is similar to that of the MFA : i.e. free spins in arbitrary fields $\mathbf{h}_i$ (free and different from the MFA). The free energy is expanded in power of $\beta(\mathcal{H} - \mathcal{H}_0)$. At finite order n the $\mathbf{h}_i$ are determined by $\partial F^{(n)}(\beta, H, \mathbf{h}_i)/\mathbf{h}_i = 0$, giving the fastest convergence. When a solution $\mathbf{h}_i \neq 0$ appears, we get approximations $T_c^{(n)}$ to T_c identical to the successive ratio of the coefficients of the high temperature series expansion of the staggered susceptibility [20, 21]. Below $T_c^{(n)}$, $\mathbf{h}_i$ is finite and, at order two, the $T_c(H)$ curve in an external field for the HNNA model has an accuracy comparable to that of the Constant Coupling Approximation [21]. For our four spin model, we obtain at order two the diagram shown on figure 2 (app. 2nd). The first order transition is lowered to $T_{c1} \simeq 1$ mK; the second order transition line is nearer the experimental result. But on account of the presence of a bicritical point we must go at higher orders to get reliable results. Further investigations along these lines are in progress.

With the idea that four and three spin exchanges are preponderant, this simple model agrees with most experimental data available to date. We have neglected planar four spin exchange K_p but there is no evidence that it is smaller than folded four spin exchange K_F . High temperature results can also be approximately fitted within a model including only

$$K_p \simeq -0.33 \text{ mK} \quad \text{and} \quad J_t \simeq 0.16 \text{ mK}.$$

The phase diagram in high field is practically unchang-

ed (the naf phase is stable). At low field ($H < 10$ kG) a new phase (cf. Fig. 3) appears. It has two planar simple square interpenetrating antiferromagnetic sublattices with orthogonal spin orientations (« sqaf phase ») and is invariant by translation along one axe (100). It gives a first order transition at $T \simeq 1$ mK. This phase has a large dipolar anisotropy (in contrast to the scaf phase in which the magnetic dipolar interactions vanish at first order). We need now new experimental investigations such as neutron diffraction studies or magnetic resonance to decide between these two models.

Fig. 3. — Square antiferromagnetic phase (sqaf) appearing at $T \simeq 1$ mK through a first order transition (at low field); with planar four spin exchange $K_p = -0.33$ mK and triple exchange $J_t = 0.16$ mK.

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