Electronic-nuclear magnetism of praseodymium and its compounds

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A consistent theory is constructed for the electronic-nuclear spin ordering in singlet magnets. In particular, the theory explains the results of recent experiments in $PrNi_5$. A study is made of how the phase transition is affected by a magnetic field imposed perpendicular to the basal plane. Depending on the strength of the exchange interaction, the magnetic field can increase or decrease the transition temperature. For example, an increase in the transition temperature upon application of the field should occur in the hexagonal modification of praseodymium.

Praseodymium and its intermetallic compounds ($PrCu_6$, $PrCu_2$, $PrNi_5$, etc.) are among the few substances in which nuclear magnetic ordering has been successfully observed under equilibrium conditions[1–5] (in this paper we always have in mind the hexagonal modification of praseodymium). The ground state of the $4f$ shell of the praseodymium ion in the crystalline field is a singlet, and the exchange interaction in the magnets under study is not strong enough to induce a magnetic moment by mixing the wave functions of the ground and excited states.[6–8] Therefore, below a few kelvins these substances are Van Vleck paramagnets with a temperature-independent magnetic susceptibility. At infralow temperatures, however (from 56 mK for Pr to 0.4 mK for $PrNi_5$), the nuclear spins induce a moment in the electronic subsystem through the hyperfine interaction, and, as a result, an electronic-nuclear spin ordering (ferromagnetic or antiferromagnetic) is established in the basal plane.

A molecular field theory for such an ordering was first developed by Murao.[9,10] However, as has recently become clear, this theory does not give a complete quantitative explanation of the properties of electronic-nuclear ferromagnets. Recent experiments[11] have revealed that the saturation moment and the Curie constant are not related in the way predicted by molecular-field theory. The authors of Ref. 11 regard this as proof that the system of nuclear spins undergoes strong quantum fluctuations, which are not taken into account by molecular field theory.

It is shown in the present paper that although the quantum fluctuations of the electron spins can be strong and can substantially renormalize the susceptibility of the electronic subsystem, the quantum fluctuations of the nuclear spins are always small and cannot explain the effect observed in Ref. 11.

The effect can be explained in the framework of molecular field theory if allowance is made for the quadrupole and pseudoquadrupole (proportional to the square of the hyperfine interaction energy) splitting of the nuclear spin levels.

It should be noted that in $PrNi_5$, the substance studied in Ref. 11, and in the other substances as well, the effective nuclear anisotropy constant can be of the same order as or even larger than the energy of the order-inducing indirect exchange of the nuclei through the matrix, and allowance for this anisotropy can therefore be important even for a qualitative understanding of the effect. For example, if the nuclear anisotropy is of the easy-plane type, this can suppress the nuclear ordering and sharply decrease the transition temperature.

In this paper we also investigate how the electronic-nuclear phase transition is affected by a magnetic field perpendicular to the basal plane. In particular, it turns out that in magnets in which the exchange interaction of the electron spins is close to the minimum value at which it can induce a moment, the transition temperature increases monotonically with increasing magnetic field. This effect should be observed, for example, in the hexagonal modification of praseodymium.

1. MOLECULAR FIELD THEORY

We shall use the usual expression for the magnetic Hamiltonian of the system:

$$\mathscr{H}=V_{cf}-\frac{1}{2}\sum_{ij}J_{ij}\mathbf{S}_i\mathbf{S}_j-A\sum_i\mathbf{S}_i\mathbf{I}_i-\mu_N\sum_i\mathbf{H}\mathbf{I}_i-\mu\sum_i\mathbf{H}\mathbf{S}_i+\mathscr{H}_Q. \tag{1}$$

Here V_{cf} is the Hamiltonian of the crystalline field acting on the total electronic moment S_i of the ions, and $\mathscr{H}_Q$ is the Hamiltonian of the quadrupole splitting of the nuclear levels. The rest of the notation is standard. We shall consider uniaxial magnets with an easy-plane anisotropy.

The ground state of the electronic moment of the ion in the crystalline field is a nonmagnetic singlet. As we know, the exchange interaction of localized spins leads to an induced moment due to the mixing of the wave functions of the ground and excited sublevels and gives rise to long-range magnetic order if it is strong enough: $\eta=|J_0|\chi_0^\perp/\mu^2>1$. Here J_0 is the zeroth Fourier component of $J(r)$, and $\chi_0^\perp$ is the transverse Van Vleck susceptibility of an isolated ion without allowance for the exchange interaction. We shall assume that $\eta<1$, so that the ordering arises only at infralow temperatures on account of the hyperfine interaction.

The effective Hamiltonian of the nuclear subsystem, first introduced by Murao,[10] can be put in the form

$$\mathscr{H}_I=\beta_N\sum_i(I_i^z)^2-\sum_\alpha\sum_{ij}V_{ij}^{\alpha\alpha}I_i^\alpha I_j^\alpha-\sum_i\mu_{\text{eff}}^{\alpha\alpha}H^\alpha I_i^\alpha,$$

$$\alpha=x,\,y,\,z. \tag{2}$$

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The energy of the effective exchange interaction of the nuclei is proportional to the static inhomogeneous correlator of the electron spins:

$$V_{ij}^{\alpha\alpha}={}^1/_2A^2G^{\alpha\alpha}(\omega=0,\ r_{ij}), \tag{3}$$

$$G^{\alpha\alpha}(\omega, r)=\int_{-\infty}^{\infty} dt\langle TS_0^{\alpha}(0)S_r^{\alpha}(t)\rangle\exp[i\omega t],$$

while the effective magneton is

$$\mu_{\text{eff}}^{\alpha\alpha}=\mu_N(1+K^{\alpha\alpha}),\qquad K^{\alpha\alpha}=(\mu/\mu_N)AG_e^{\alpha\alpha}(\omega=0,\ q=0), \tag{4}$$

where $G_e(\omega,q)$ is the Fourier transform of $G_e(\omega,r)$, which is proportional to the total susceptibility of the electron spins, $G_e^{\alpha\alpha}(\omega,q)=\chi_e^{\alpha\alpha}(\omega,q)/\mu^2$. The correlators of the electron spins and, with them, the constants of the effective Hamiltonian depend, of course, on the external magnetic field.

The effective anisotropy constant of the nuclear spin is

$$\beta_N=\beta_A+\beta_Q, \tag{5}$$

where β_Q is the quadrupole splitting constant and β_A is the pseudoquadrupole splitting constant, given by

$$\begin{gathered}\beta_A={}^1/_2A^2[G_e^{\perp}(\omega=0,\ r=0)-G_e^{zz}(\omega=0,\ r=0)],\\ G_e^{\perp}(\omega,r)=G_e^{xx}(\omega,r)=G_e^{yy}(\omega,r).\end{gathered} \tag{6}$$

Writing (6) in the form of an integral over the momenta q, we see that the q dependence arising through the quantity J_q is unimportant up to order $1/z$ (z is the number of nearest neighbors), so that

$$\beta_A=(A^2/2\mu^2)(\chi_0^{\perp}-\chi_0^{zz}), \tag{7}$$

i.e., β_A and, hence, β_N do not depend on η.

To estimate the constants of the effective Hamiltonian, let us take the correlators of the electron spins in the molecular field approximation. Then

$$\begin{gathered}V_{ij}^{\alpha\alpha}=\frac{A^2}{2\mu^2}\chi_0^{\alpha\alpha}\frac{1}{N}\sum_q\frac{\eta^{\alpha}\gamma_q}{1-\eta^{\alpha}\gamma_q}\exp\{iq(r_i-r_j)\},\\ \chi_e^{\alpha\alpha}=\chi_0^{\alpha\alpha}/(1-\eta^{\alpha}),\quad \gamma_q=J_q/J_0,\quad \eta^{\alpha}=J_0\chi_0^{\alpha\alpha}/\mu^2.\end{gathered} \tag{8}$$

We shall henceforth assume that $\chi_0^{zz}<\chi_0^{\perp}$.

Comparing (7) and (8), we see that for $\eta\ll1$ we always have $V_q^{\alpha\alpha}\ll\beta_A$. Therefore, if there is no cancellation between the quadrupole and pseudoquadrupole terms in the expression for β_N (5), we have $\beta_N\gg V_q^{\alpha\alpha}$. However, even if such cancellation does occur, at small η the single-ion anisotropy term can be important at small η.

In the case of a strong exchange interaction $J(r)$, when η is close to the critical value, the pseudoquadrupole anisotropy is small compared to the effective interaction of the nuclear spins, $\beta_A/V_0^{\alpha\alpha}\sim1-\eta\ll1$. Because $\beta_Q\sim\beta_A$ in the substances under study, the single-site anisotropy in the effective Hamiltonian (2) is unimportant in this case.

Because the constant β_Q can be negative, the sign of β_N is determined, generally speaking, by the particular relationship of the parameters. Let us first assume that $\beta_N>0$, corresponding to the actual situation in praseodymium and many of its compounds. We note that for integral spins I the ground state in the anisotropy field is again a singlet, and the interaction will lead to the induction of an electronic moment only if it is sufficiently strong. The criterion for this is

$$2I(I+1)V_0^{\perp}/\beta_N>1.$$

Since $I=5/2$ in praseodymium, we shall henceforth be interested in half-integer I. In this case ordering arises regardless of how small the interaction is. Assuming that the external field **H** is directed along the z axis and introducing a molecular field $\mathbf{H}_e$ with projections

$$H_e^x=2V_0^{\perp}\langle I^x\rangle,\qquad H_e^z=\mu_{\text{eff}}^{zz}H+zV_0^{zz}\langle I^z\rangle, \tag{9}$$

for the coefficients C_m^k of the expansion of the wave functions ψ_k in the eigenfunctions $|m>$ of the operator $\hat{I}^z$

$$\psi_k=\sum_{m=-I}^{I}C_m^k|m\rangle,\qquad k=\overline{-I,I} \tag{10}$$

we obtain the system of equations

$$(E_k+H_e^zm-\beta_Nm^2)C_m^k=-\frac{1}{2}H_e^x(R_{m-1}C_{m-1}^k+R_mC_{m+1}^k), \tag{11}$$

$$R_m=[(I-m)(I+m+1)]^{1/2}.$$

Assuming $H_e^x/\beta_N\ll1$ and iterating with respect to this parameter, we obtain the energy levels of the system:

$$\begin{gathered}E_{\pm1/2}={}^1/_4\beta_N\mp{}^1/_2\{(H_e^z)^2+(H_e^x)^2(I+{}^1/_2)^2\}^{1/2},\\ E_k=\beta_Nk^2-H_e^zk+O[(H_e^x)^2],\qquad k\neq\pm{}^1/_2.\end{gathered} \tag{12}$$

The coefficients C_m^k that are nonzero to first order in H_e^x/β_N are

$$\begin{gathered}C_{1/2}^{\pm1/2}=\pm C_{-1/2}^{\pm1/2}=2^{-1/2}[1\pm H_e^z\{(H_e^z)^2+(H_e^x)^2(I+{}^1/_2)^2\}^{-1/2}]^{1/2},\\ C_{\pm3/2}^{\pm1/2}=-\frac{1}{2}\frac{H_e^xR_{1/2}}{E_{\pm1/2}-E_{\pm3/2}}C_{\pm1/2}^{\pm1/2};\\ C_k^k=1,\qquad C_{k\pm1}^k=-\frac{1}{2}\frac{H_e^x}{E_k-E_{k\pm1}}R_{k-1/2\pm1/2},\qquad k\neq\pm{}^1/_2.\end{gathered} \tag{13}$$

Evaluating the matrix elements of the components of the nuclear spin with the aid of (13) and making use of the fact that the parameter $H_e^x/H_e^z\to0$ as $T\to T_c$, we obtain the self-consistency equations

$$\begin{gathered}\langle I^z\rangle=\frac{1}{Z}\sum_{k=-I}^{I}k\exp\left\{\frac{1}{T_c}(H_e^zk-\beta_Nk^2)\right\},\\ 1=-\frac{2V_0^{\perp}}{\beta_N}\frac{1}{Z}\sum_{k=-I}^{I}\frac{I^2+I+k^2-(H_e^z/\beta_N)k^2}{[(H_e^z/\beta_N)-2k]^2-1}\\ \times\exp\left\{\frac{1}{T_c}(H_e^zk-\beta_Nk^2)\right\},\\ Z=\sum_{k=-I}^{I}\exp\left\{\frac{1}{T_c}(H_e^zk-\beta_Nk^2)\right\},\end{gathered} \tag{14}$$

which, taken jointly with (9), determine T_c.

Let us first consider the phase transition in the absence of external field. In this case $\langle I^z \rangle = 0$, and T_c is determined by the second of equations (14). For $I > 1/2$, solution (14) depends on the relationship between $V_0^\perp$ and β_N. If $V_0^\perp (I + 1/2)^2 \ll \beta_N$, we may limit consideration to the two lowest levels, and in the opposite limiting case we can expand the exponentials. As a result we obtain

$$T_c = \begin{cases} {}^1/_2 (I+{}^1/_2)^2 V_0^\perp, & V_0^\perp (I+{}^1/_2)^2 \ll \beta_N \\ {}^2/_3 I(I+1) V_0^\perp, & V_0^\perp \gg \beta_N \end{cases}. \tag{15}$$

For $I > 1/2$, the expression for T_c does not depend on $V_0^\perp/\beta_N$, and for the model with $V_{cf} = \Sigma_i D(S_i^z)^2$ it agrees with the expression obtained previously by Murao.[9]

The saturation moment per magnetic ion at $H = 0$ is

$$M_s = \mu_{\text{eff}}^\perp \langle I^\perp \rangle$$

and it depends even more importantly on the parameter $V_0^\perp/\beta_N$ than T_c does. As the parameter $V_0^\perp/\beta_N$ increases, it increases smoothly from the value $1/2(I + 1/2)\mu_{\text{eff}}^\perp$ at $V_0^\perp/\beta_N \ll 1$ to the value $I\mu_{\text{eff}}^\perp$ at $V_0^\perp/\beta_N \gg 1$.

Since experiment shows that in praseodymium compounds β_A and β_Q are of the same order of magnitude, it is quite possible that β_N can be negative (easy-axis anisotropy). Here, if the energy of the exchange interaction is not close to the critical value $\eta^\perp \sim 1$ and if $\beta_N \gtrsim V_0^\perp$, then the state of the magnetic system depends on the particular structure of the electronic sublevels. If this structure is such that $\chi^{zz} = 0$ [e.g., in the model $V_{cf} = \Sigma_i D(S_i^z)^2$], then a moment is induced in the basal plane only if $V_0^\perp/\beta_N$ is larger than a certain critical value of the order of unity. Otherwise, the is no ordering all the way down to $T = 0$. If, on the other hand, $\chi^{zz} \neq 0$, then a spontaneous moment will arise along the z axis even for $V_0^\perp/\beta_N \ll 1$ (for $T_c \sim V_0^{zz}$).

2. PHASE TRANSITION IN A MAGNETIC FIELD

Let us find the change in the Curie temperature in a weak magnetic field $\mu_{\text{eff}}^{zz} H \ll T_c (H = 0)$. Solution of equations (9) and (14) gives

$$\frac{T_c(H) - T_c(0)}{T_c(0)} = \frac{V_0^\perp(H) - V_0^\perp(0)}{V_0^\perp(0)} - Q_I \left(\frac{\mu_{\text{eff}}^{zz} H}{V_0^\perp(0)} \right)^2, \tag{16}$$

where

$$Q_I = \begin{cases} {}^1/_3 [(I+{}^1/_2)^2 - V_0^{zz}/V_0^\perp]^{-2}, & V_0^\perp (I+{}^1/_2)^2 \ll \beta_N \\ {}^3/_{40} [I^{-2} + (I+1)^{-2}] (1 - V_0^{zz}/V_0^\perp)^{-2}, & V_0^\perp \gg \beta_N \end{cases}$$

For $I > 5/2$, we have $Q_I \sim 0.02$ when $\beta_N \ll V_0^\perp$.

The first term in (16) describes the increase of the transition temperature due to the effective decrease of the single-ion anisotropy of the electron spins when the field is applied. The decrease of the single-ion anisotropy is proportional to $(\chi_0^\perp H/\mu)^2$ and arises as a result of the narrowing of the distance between the singlet ground state and the lowest Zeeman sublevel of the excited state of the praseodymium ion. On the other hand, the orientation of the nuclear and electron spins by the field leads to a decrease of the component of the spins in the basal plane and, hence, to a decrease in T_c [the second term in (16)]. To analyze the values of the two terms in (16), we use molecular field approximation (8) for the constants of the effective Hamiltonian. We then have

$$\frac{T_c(H) - T_c(0)}{T_c(0)} = \left(\frac{\chi_0^\perp H}{\mu} \right)^2 \left[\frac{\partial \ln \chi_0^\perp(H)}{\partial (\chi_0^\perp H/\mu)^2} \left(1 + \frac{1}{1 - \eta^\perp} \right) - 4 Q_I \gamma \left(\frac{1 - \eta^\perp}{\eta^\perp} \right)^2 \right], \tag{17}$$

$$\gamma = \left[\frac{\mu_N}{\mu} \frac{1 + K^{zz}}{(A\chi_0^\perp/\mu^2)^2} \right]^2.$$

The coefficient ∂ In $\chi_0^\perp(H)/\partial(\chi_0^\perp H/\mu)^2$ is positive and of order unity; its numerical value is determined by the structure of the electronic sublevels. The value of the coefficient γ depends strongly on the particular parameters of the material. This is because γ, as we see from (17), is proportional to a high power of A and $\chi_0^\perp$. Furthermore, the factor $(1 + k^{zz})^2$ can change the value of γ by about two orders of magnitude, depending on the structure of the electronic sublevels, which determines the ratio $\chi_0^{zz}/\chi_0^\perp$. If $\chi_0^{zz}/\chi_0^\perp \ll 1$ [e.g., $\chi_0^{zz} = 0$ in the model with $V_{cf} = \Sigma_i D(S_i^z)^2$], then $\gamma \approx 1$–100. If, on the other hand, $\chi_0^{zz}/\chi_0^\perp \sim 1$, then γ will be two orders of magnitude larger for the same values of $A\chi_0^\perp$. It is therefore impossible to reach any general conclusions as to the relative size of the first and second terms in (12). We see only that as η approachs unity, the first term in (17) increases and the second term decreases, so that these would be the most favorable conditions for observing an increase in T_c with field.

The hexagonal modification of praseodymium exhibits an antiferromagnetic spin ordering. With the obvious changes in notation our results apply in this case as well. The experimental data [7,12,13,16,17] for praseodymium give $1 - \eta \approx 0.1$, $K^{zz} \approx 0$, and $K^\perp \approx 100$, from which we get $\gamma \approx 100$, so that the first term in braces in (17) is two orders of magnitude larger than the second (hence, in praseodymium the transition temperature should increase with field).

In PrCu$_2$ we have $K^{zz} \approx 10$ (Ref. 4). Therefore, the second term in braces in (17) for this substance is two orders of magnitude larger than for praseodymium, and the two terms are approximately of the same order. The experimental data obtained for polycrystalline samples of PrCu$_2$ show a decrease of T_c with increasing H, i.e., the second term in (17) is nevertheless larger than the first. It is possible that by applying pressure and decreasing the parameter $1 - \eta$ one could observe an increase of T_c with H.

The behavior of T_c in stronger fields $\mu_{\text{eff}}^{zz} H \gtrsim T_c$ depends on the value of η. If η is larger than a certain γ-dependent critical value η_1, then T_c increases monotonically with field all the way up to the field at which

$$\eta(H_0) = J_0 \chi_0^\perp(H_0)/\mu^2$$

becomes equal to unity; $T_c(H_0)$ is the order of A. At larger

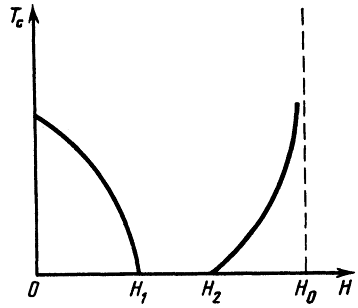

FIG. 1. $T_c(H)$ for $\eta < \eta_2$.

fields the spins of the electrons and nuclei are directed parallel to the field.

If $\eta < \eta_1(\gamma)$ but larger than a certain $\eta_2(\gamma)$, then T_c at first falls off with increasing field, then it reaches a minimum, and on further increase in field it grows on account of the growth of $\eta(H)$.

Finally, if $\eta < \eta_2(\gamma)$, then a field region arises in which there is no ordered phase: $H_1(\eta,\gamma) < H < H_2(\eta,\gamma)$ (Fig. 1). A numerical calculation shows that in the actual situation $\eta_1(\gamma)$ and $\eta_2(\gamma)$ are very similar in value, so that the first and third types of dependence are the most likely to be observed in experiment.

3. QUANTUM CORRECTIONS

The role of quantum corrections in the electronic-nuclear magnetism of praseodymium compounds was first discussed in Ref. 11, where it was asserted on the basis of the experimental data of that study that the zero-point oscillations of the nuclear spins rather strongly alter (by about 30%) the ratio of the Curie constant C to the saturation magnetization M_s in comparison with the value of C/M_s in the molecular field approximation.

In view of the importance of the question of quantum corrections for the interpretation of the experimental data, let us calculate these corrections without using the approximation of an effective Hamiltonian. To determine the Curie constant we consider temperatures higher than both T_c and the maximum splitting $\beta_N I^2$ of the hyperfine sublevels but much lower than the characteristic splitting Δ of the electronic sublevels by the crystalline field.

We calculate the transverse magnetic susceptibility $\chi(\omega,q)$ (we drop the symbol $\perp$ in this section) as the analytical continuation of the function $\chi(\omega_n,q)$ given by the Kubo formula

$$\chi(\omega_n,q)=\int_0^{1/T} d\tau\, d^3r \langle T(\mu_N I_i^x(\tau)+\mu S_i^x(\tau), \mu_N I_j^x(0)+\mu S_j^x(0))\rangle \times \exp[i\omega_n\tau - iqr_{ij}], \quad \omega_n=2\pi nT \tag{18}$$

onto the real axis.

In the paramagnetic phase we can take V_{cf} as the zeroth Hamiltonian. In the graphs for $\chi(\omega_n,q)$ we set apart the single-cell blocks joined by the interaction $J(r)$ (Ref. 18). An example of a single-cell block arising in second order in A from the correlator of the electron spins in (18) is shown in Fig. 2. Here the points correspond to A, and the solid and dashed lines are the correlators of the electron and nuclear spins, $G_e^0(\omega_n,q)$ and $G_N^0(\omega_n,q)$, in which the averaging is done with the zeroth Hamiltonian V_{cf}. For $T \gg T_c, \beta_N I^2$

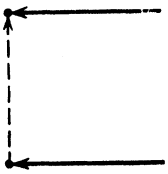

FIG. 2. The simplest graph of second-order in A for $\chi(\omega_n,q)$.

$$G_N{}^0=\frac{I(I+1)}{3T}\delta_{n,0}. \tag{19}$$

The correlator $G_e^0(\omega_n,q)$ is of order $1/\Delta$ for $\omega_n \lesssim \Delta$ and falls off with frequency as $G_e^0 \sim 1/\omega_n^2$ for $\omega_n \gg \Delta$. For example, if $V_{cf}=D\sum_i(S_i^z)^2$, then

$$G_e{}^0=2D/(\omega_n{}^2+D^2). \tag{20}$$

To calculate $\chi(\omega,q)$ in the molecular field approximation, which corresponds to the zeroth order of a perturbation theory in $(a/r_0)^3$ (r_0 is the exchange interaction radius, which for now is assumed larger than the lattice constant a), we must replace the correlators G_e^0 in the graphs by the boldface correlators by summing the corresponding chain of solid arrows joined by the interaction $J(r)$:

$$G_e=G_e{}^0/(1-J_qG_e{}^0). \tag{21}$$

In the case $V_{cf}=D\sum_i(S_i^z)^2$ we have

$$G_e=2D/(\omega_n{}^2+\omega_q{}^2), \quad \omega_q{}^2=D^2(1-\eta\gamma_q). \tag{22}$$

As a result, the homogeneous susceptibility $\chi(\omega,0)$ comes out to be

$$\chi(\omega,0)=(C/T)\delta(\omega)+\chi_e(\omega,0), \quad C=\mu_N{}^2(1+K^{\perp})^2I(I+1)/3. \tag{23}$$

Here $K^{\perp}$ is determined by relation (4), with the electronic susceptibility calculated in the molecular field approximation substituted in, and $\chi_e(\omega,0)$ is the electronic susceptibility calculated in the molecular field approximation.

The corrections to $\chi(\omega,0)$ arising in the next orders in $(a/r_0)^3$ can be of two types. First, there are graphs which do not contain a summation over the frequency which appears in the correlator of the nuclear spins. Clearly, these graphs make it necessary to substitute the total electronic susceptibility, renormalized by quantum fluctuations, into relation (4) for $K^{\perp}$. If η is sufficiently close to unity, the quantum corrections to χ_e are large and, generally speaking, can substantially alter the value of the susceptibility.[15] However, the relation [Eq. (4)] between the effective magneton and the electronic susceptibility is not altered.

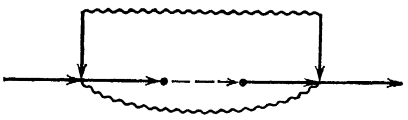

FIG. 3. Example of a graph for $\chi(\omega_n, q)$ that contains a summation over the frequency of the nuclear spin correlator.

There are also graphs in which there is a summation over the frequency of the correlator of the nuclear spins and which do not reduce to a renormalization of $\chi_e(\omega_n, 0)$. An example of such a graph is given in Fig. 3, where the wavy lines correspond to the effective interaction[18]

$$J_{\text{eff}} = J_q[1 - J_q G_e^0(\omega_n, q)]^{-1}. \qquad (24)$$

However, owing to the delta-function dependence of G_N^0 on one of the frequencies (over which we sum), the contribution of such graphs to $\chi_e(\omega, 0)$ is independent of temperature and does not contain $\delta(\omega)$, i.e., it does not affect μ_{eff}, but gives a correction to $\chi_e(\omega, 0)$ that is of no interest to us here.

Thus, to second order in the parameter $(A\chi_0^\perp) \sim 0.01$ the quantum fluctuations do not alter relation (4) between K and χ if the total electronic susceptibility is substituted in. This means that even in the case of strong quantum fluctuations of the electron spins, the fluctuations of the nuclear spins in the paramagnetic phase are always small.

This conclusion depends essentially only on the different frequency dependence of G_N^0 and G_e^0 and has nothing to do with the value of the parameter $(a/r_0)^3$. Therefore, it is valid even if $(a/r_0)^3 \sim 1$.

Let us now turn to the saturation magnetization. We can evaluate it by differentiating with respect to the field the expression for the energy of the zero-point oscillations in an external field H_x directed along the magnetization[19]:

$$\Delta E = \Big[\sum_i \sum_q \varepsilon_i(q) - \sum_i E_i\Big] \Big/ 2\,. \qquad (25)$$

Here $\varepsilon_i(q)$ is the frequency of the ith branch of excitations, and E_i is the energy of the ith sublevel in the molecular field approximation. Hamiltonian (1) gives three types of excitations. These are electronic spin modes, which exist in both the paramagnetic and ferromagnetic phases and have a frequency that remains unchanged to within $(A\chi_0^\perp)^2$ upon the onset of ordering [these frequencies were calculated in Ref. 9 for a model with $V_{cf} = D\,\Sigma_i (S_i^z)^2, S = 1$]. It can be shown that these excitations make it necessary to replace χ_e and K in expression (4) by their true renormalized values.

Excitations due to transitions between hyperfine levels split by the effective nuclear anisotropy β_N are also present in both the paramagnetic and ferromagnetic phases. As is easily verified, they are dispersionless and do not contribute to (25) or to M_s.

Only the gapless (in the absence of magnetic field) spin-wave branch which is due to the magnetization oscillations, contributes to M_s, breaking down relation (4) between M_s and χ_e. In the case of a strong magnetic anisotropy of the nuclear spins, $\beta_N \gg V_0^\perp (I + 1/2)^2$, these corrections are given by

$$\frac{\Delta M_s}{M_s} = -\sum_q \Big[\Big(\frac{U_q}{V_0^\perp - V_q^\perp}\Big)^{1/2} + \Big(\frac{U_q}{V_0^\perp - V_q^\perp}\Big)^{-1/2} - 2\Big], \qquad (26)$$

where

$$U_q = V_0^\perp - V_q^{zz}/(I + {}^1/_2)^2. \qquad (27)$$

If, on the other hand, the single-site anisotropy of the nuclei is unimportant, $\beta_N \ll V_0^\perp$, then the expression for $\Delta M_s/M_s$ differs from (26) in that it has a coefficient $1/2I$ and also in that formula (27) for U_q is replaced by

$$U_q = V_0^\perp - V_q^{zz}.$$

It is easy to see that our quantum correction is a maximum when $V_q^{zz} = 0$ and the anisotropy β_N is strong, and in this case is given by

$$|(\Delta M_s/M_s)_{max}| = \sum_q [(1-\gamma_q)^{1/2} + (1-\gamma_q)^{-1/2} - 2]. \qquad (28)$$

An estimate for different types of crystal lattices shows that the maximum value of $\Delta M_s/M_s$ is not more than a few percent.

4. DISCUSSION OF THE EXPERIMENTAL DATA

The electronic-nuclear ferromagnetic ordering in $PrNi_5$ was studied in Refs. 3 and 11. The main result of these studies is that the value of $K^\perp = K^{xx} = K^{yy}$, found from the relation

$$M_s = \mu_N(1 + K^\perp) I \qquad (29)$$

after measuring the saturation moment, differs by 30% from the value obtained, using the relation

$$C/M_s = \mu_N(1 + K^\perp)(I + 1)/3\,, \qquad (30)$$

from the measured value of the Curie constant C. In the first case $K_1^\perp = 11.2$, while in the second case $K_2^\perp = 15.1$. Since classical correlation effects do not alter the ratio C/M_s from its value calculated in molecular field theory, the authors of Ref. 11 concluded that $PrNi_5$ has strong quantum fluctuations of the nuclear spin, leading to substantial corrections to molecular field theory. By analogy with the result of Ref. 14, it was assumed that the most important quantum corrections were the corrections to the Curie constant C.

As is shown in the preceding section, this assumption is incorrect. To the order of interest here, i.e., to lowest order in $A\chi_0^\perp \lesssim 0.01$, there are no quantum corrections to C, while the corrections to M_s are of the order of a percent and are also unimportant.

On the other hand, the results obtained in Ref. 11 are explained by our theory in a very natural way. With allowance for their effective anisotropy, the saturation moment of the nuclear spins is not given by formula (29) but, as we have mentioned, is always less than $\mu_{\text{eff}} I$ and varies from $1/2\mu_{\text{eff}}(I + 1/2)$ to $\mu_{\text{eff}} I$ with increasing parameter $V_0^\perp/\beta_N$. Therefore, the use of formula (29) leads to an understated value of $K^\perp$, while the use of formula (30) leads to an overstated value. Using for M_s the expression $M_s=\mu_N(1+K^\perp)\langle I^\perp\rangle$, we find that the results obtained in Ref. 11 can be explained if

$$\langle I^\perp\rangle/I=[(1+K_1^\perp)/(1+K_2^\perp)]^{1/2}=0.86. \tag{31}$$

In $PrNi_5$ the quadrupole and pseudoquadrupole terms in the effective anisotropy of the nuclear spins largely cancel each other, so that β_N is five to seven times smaller than β_A. Because $\eta\approx0.1$ in $PrNi_5$, $V_0^\perp$ and β_N are of the same order of magnitude, so that the value $\langle I^\perp\rangle/I=0.86$ is entirely reasonable.

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