Deviations from Brillouin's Free-Spin Theory in Manganese Fluosilicate

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A method is proposed which allows one to calculate the magnetic moment of a paramagnetic ion in a crystalline electric field. The case of manganese fluosilicate is examined since one has complete information on the paramagnetic resonance spectrum of this salt. The result is that there are measurable deviations from the Brillouin free-spin theory due almost entirely to the trigonal part of the crystalline electric field (D term in Abragam-Pryce Hamiltonian) in the neighborhood of 1°K.

RECENT measurements on the magnetic moments of several paramagnetic ions[1] reveal measurable deviations from the well-known Brillouin free-spin theory.[2] These deviations are susceptible to theoretical analysis, if one has sufficient information on the paramagnetic resonance spectrum. To best exhibit the general method, a specific example will be studied. The case of manganese fluosilicate is investigated in which the concentration of $Mn^{++}(^6S_{5/2}$; nuclear spin $I=5/2)$ ions has been made sufficiently dilute (by substitution of diamagnetic Zn atoms, say, $Zn^{++}:Mn^{++}=10:1$) to ignore exchange and spin-spin coupling between neighboring Mn^{++} ions. Detailed information on the paramagnetic resonance spectrum for this salt can be found in the work of Abragam and Pryce,[3] and Bleaney and Ingram.[4] This fluosilicate has one Mn^{++} ion per unit cell, and it has trigonal symmetry; the axis of symmetry has the crystallographic designation (111) with respect to the axes (1, 2, 3) of the cubic field (see Fig. 1). One chooses the trigonal axis as the z axis in what follows. These authors furnish us with the following Hamiltonian:

$$\begin{aligned}\mathcal{H}=g\beta_0\mathbf{H}\cdot\mathbf{S}+D[S_z^2-\tfrac{1}{3}S(S+1)]\\ +\tfrac{1}{6}a(S_1^4+S_2^4+S_3^4)+A\mathbf{I}\cdot\mathbf{S}\\ -\gamma\beta_n\mathbf{H}\cdot\mathbf{I}+Q[I_z^2-\tfrac{1}{3}I(I+1)],\end{aligned}\quad(1)$$

where $D=-0.013$ cm^{-1}; $A=-0.0091$ cm^{-1}, $a=9\times10^{-4}$ cm^{-1} all at 20°K, $\beta_0\sim10^{-4}$ cm^{-1} gauss^{-1}, $g_{11}=g_1=2$, $\beta_n\sim10^{-7}$ cm^{-1} gauss^{-1}, and finally $Q\sim10^{-3}-10^{-4}$ cm^{-1}. One does not expect the constants D, A, a to change appreciably below 20°K.[4] No measurements have been made to determine these constants in the neighborhood of 1°K. In what follows, the above values at 20°K will be employed at lower temperatures near 1°K. The general definition of the magnetic moment per ion of a system with Hamiltonian $\mathcal{H}$ in thermal equilibrium is as follows ($\beta=1/KT$):

$$\mu=T\left(\frac{\partial\Psi}{\partial H}\right)_{N,T,V}=\frac{1}{\beta}\frac{\partial}{\partial H}\log Z$$
$$=\frac{1}{\beta}\frac{\partial}{\partial H}\log \mathrm{Sp}\exp(-\beta\mathcal{H}),\quad(2)$$

where H is the applied magnetic field whose orientation relative to the trigonal z axis is yet to be specified; Ψ is the Planck function of statistical thermodynamics,[5] which in turn equals $k\log Z$, where Z is the partition function;[6] finally, since the partition function is the spur of $\exp(-\beta\mathcal{H})$ in the energy diagonal representation, one can use the invariance of any spur to a unitary change of representation and employ any representation which is convenient for the problem at hand. Since the Hamiltonian $\mathcal{H}$ in (1) is for a system with complete quenching, and only low temperatures are of interest here, the only states available to the spin system are the lowest $(2S+1)(2I+1)$ degenerate spin states. Furthermore, one can evaluate all spurs in the so-called strong field representation in which sums over electronic and nuclear states can be done separately. For example,

$$\mathrm{Sp}_{NE}I_z^2S_z^2=\mathrm{Sp}_N I_z^2\,\mathrm{Sp}_E S_z^2$$
$$=\tfrac{1}{3}(2I+1)\cdot I(I+1)\cdot\tfrac{1}{3}(2S+1)S(S+1),$$

etc. The problem which confronts one is, therefore, the calculation of

$$\mathrm{Sp}\exp(-\beta\mathcal{H}),\quad(3)$$

where from (1) $\mathcal{H}$ contains several noncommuting operators. If one ignores everything in (1) except $g\beta_0\mathbf{H}\cdot\mathbf{S}$, one, of course, can then choose the magnetic field direction as the z axis and write $\mathcal{H}=g\beta_0H_zS_z$, which leads to Brillouin's result (see below). However, if one wants to calculate the deviations from the Brillouin result brought about by the remaining terms in (1), one is given the trigonal axis as the z axis with respect to which S_z is diagonal, and one must then choose the magnetic field to be along this axis or per-

[1] W. Henry, Phys. Rev. **85**, 487 (1952); Phys. Rev. **87**, 229(A) (1952).
[2] R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge Press, London, 1949), p. 620.
[3] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).
[4] B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A205**, 336 (1951).
[5] E. Schrödinger, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1948), p. 13.
[6] J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 25.

pendicular to it. The reason for this restriction is that the spur formula to be introduced below is only convenient to use (i.e., without undue labor) when $\mathcal{H}$ contains *one* "large" operator and any number of "smaller" operators. In the case of nuclear specific heats in zero magnetic field,

$$C_{H=0}=k\beta^2\frac{\partial^2}{\partial\beta^2}\log \mathrm{Sp}\exp(-\beta\mathcal{H}); \quad (4)$$

where all terms in $\mathcal{H}$ are small, one can use Van Vleck's diagonal sum method in which the exponential operator is developed in a power series and the various spurs carried out. It may be noted that in this diagonal sum method one can subtract from the Hamiltonian (1) the spur of the cubic field term $\frac{1}{6}a(S_1^4+S_2^4+S_3^4)$ times the unit operator, without affecting any of the thermodynamical properties of the system. This has already been done for the D and Q terms in (1); one then has $\mathrm{Sp}\mathcal{H}=0$, and one can proceed in the usual manner with $\mathrm{Sp}\mathcal{H}^2$ etc., to obtain the nuclear specific heat[7] and the magnetic susceptibility at low fields ($H\ll 10^4$ gauss).

One can now proceed to use the following neat formula developed by Schwinger[8,9] to calculate the basic $\mathrm{Sp}\exp(-\beta\mathcal{H})$:

$$\mathrm{Sp}\exp(-\beta\mathcal{H}_0-\beta\mathcal{H}_1)=\mathrm{Sp}\exp(-\beta\mathcal{H}_0)+\sum_{n=0}^{\infty}\frac{(-)^{n+1}}{n+1}\{\beta\mathcal{H}_1\exp(-\beta\mathcal{H}_0)S_n\},$$

where

$$S_0=1,$$

$$n\geqslant 1:\quad S_n=\int_0^1 s_1^{n-1}ds_1\int_0^1 s_2^{n-2}ds_2\cdots \times\int_0^1 ds_n U(s_1)U(s_1s_2)\cdots U(s_1s_2\cdots s_n), \quad (5)$$

and

$$U(s')=\exp(-\beta s'\mathcal{H}_0)\beta\mathcal{H}_1\exp(-\beta s'\mathcal{H}_0).$$

For the problem at hand, one can first choose the magnatic field to be along the z axis of the crystalline electric field so that $\mathbf{H}\cdot\mathbf{S}\cdot=H_zS_z$, and then one defines:

$$\mathcal{H}_0=g\beta_0H_zS_z+D[S_z^2-\tfrac{1}{3}S(S+1)]$$
$$\mathcal{H}_1=\tfrac{1}{6}a(S_1^4+S_2^4+S_3^4)+A\mathbf{I}\cdot\mathbf{S}-\gamma\beta_N\mathbf{H}\cdot\mathbf{I}+Q[I_z^2-\tfrac{1}{3}I(I+1)]. \quad (6)$$

Up to $n=1$ Eq. (5) yields the following result:

$$\mathrm{Sp}\exp(-\beta\mathcal{H}_0-\beta\mathcal{H}_1)=\mathrm{Sp}\exp(-\beta\mathcal{H}_0)-\beta\,\mathrm{Sp}\{\exp(-\beta\mathcal{H}_0)\cdot\mathcal{H}_1\}+\frac{\beta^2}{2}\int_0^1 ds_1\,\mathrm{Sp}[\exp(-(1-s_1)\beta\mathcal{H}_0)\cdot\mathcal{H}_1\cdot\exp(-s_1\beta\mathcal{H}_0)\cdot\mathcal{H}_1]. \quad (7)$$

[7] See reference 4, p. 354.

[8] J. Schwinger, Phys. Rev. **82**, 664 (1951).

[9] E. N. Adams and M. L. Goldberger, J. Chem. Phys. **20**, 240 (1952).

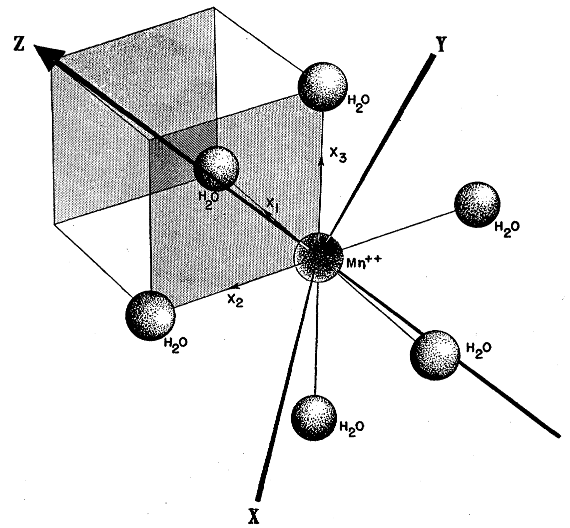

FIG. 1. This shows the trigonal Z axis and the cubic axes (X_1, X_2, X_3). The axes Z, X_3, and Y are assumed to be coplanar.

Now since $\mathcal{H}_0$ is independent of nuclear spin operators, one sees that in the second term of (6) only the a term survives, and this contribution proves to be quite small compared to the first term in (7) since $a/6\cong 10^{-4}$ cm^{-1}. The deviations from the Brillouin free-spin theory in the neighborhood of 1°K will come mostly from the D term. The hyperfine coupling term A will not affect the result until second order, i.e., (βA).[2] The magnetic moment can be calculated in two parts as follows:

$$\mu=\mu^{(0)}+\mu^{(2)},$$

where

$$\mu^{(0)}=\frac{1}{\beta}\frac{\partial}{\partial H_z}\log \mathrm{Sp}\exp(-\beta\mathcal{H}_0),$$

$$\mu^{(2)}=\frac{1}{\beta}\frac{\partial}{\partial H_z}\log(1+\Lambda),$$

$$\Lambda=\frac{1}{\mathrm{Sp}\exp(-\beta\mathcal{H}_0)}\Bigg[-\frac{a}{6}\beta\,\mathrm{Sp}\{\exp(-\beta\mathcal{H}_0)\cdot(S_1^4+S_2^4+S_3^4)\}+\frac{\beta^2}{2}\int_0^1 ds_1\,\mathrm{Sp}\{\exp(-\beta(1-s_1)\mathcal{H}_0)\cdot\mathcal{H}_1\cdot\exp(-\beta s_1\mathcal{H}_0)\cdot\mathcal{H}_1\}\Bigg]. \quad (8)$$

The first part $\mu^{(0)}$ will now be calculated; one introduces for convenience:

$$\theta=g\beta\beta_0H_z;\ \lambda=\beta D;\ \mathcal{H}_0=\theta S_z+\lambda S_z^2, \quad (9)$$

where the constant operator $(D/3)S(S+1)$ can be dropped, since it commutes with each term in $\mathcal{H}$, and it

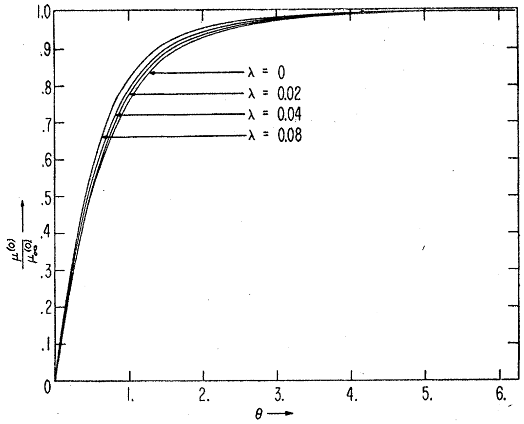

FIG. 2. This shows how for each temperature the magnetic moment per ion deviates from the Brillouin free spin theory.

does not survive the operation $(\partial/\partial H_z)$ log in Eq. (2).

$$\mathrm{Sp}_{NE}\exp(-\theta S_z-\lambda S_z^2)=(2I+1)\sum_{m=-S}^{+S}\exp\{-m\theta-\lambda m^2\}. \quad (10)$$

Carrying out the sum for our Mn^{++} ion ($S=5/2$) and substituting into Eqs. (8) leads to the following result:

$$\mu^{(0)}=g\beta_0\times\frac{(\frac{5}{2})\sinh(\frac{5}{2}\theta)+(\frac{3}{2})e^{4\lambda}\sinh(\frac{3}{2}\theta)+\frac{1}{2}e^{6\lambda}\sinh(\frac{1}{2}\theta)}{\cosh(\frac{5}{2}\theta)+e^{4\lambda}\cosh(\frac{3}{2}\theta)+e^{6\lambda}\cosh(\frac{1}{2}\theta)}. \quad (11)$$

Now it is conventional to normalize to the saturation value $\mu_\infty^{(0)}$ approached by $\mu^{(0)}$ as $\theta\to\infty$; i.e., $\mu_\infty^{(0)}=5/2g\beta_0$, so that finally:

$$\frac{\mu^{(0)}}{\mu_\infty^{(0)}}=\frac{1}{5}\frac{5\sinh(5\theta/2)+3e^{4\lambda}\sinh(\frac{3}{2}\theta)+e^{6\lambda}\sinh(\frac{1}{2}\theta)}{\cosh(5\theta/2)+e^{4\lambda}\cosh(\frac{3}{2}\theta)+e^{6\lambda}\cosh(\frac{1}{2}\theta)}. \quad (12)$$

For $\lambda=0$ (i.e., no Stark splitting) one obtains of course Brillouin's function:

$$\left(\frac{\mu^{(0)}}{\mu_\infty^{(0)}}\right)_{\lambda=0}=B_{5/2}(\theta)=\frac{6}{5}\coth 3\theta-\frac{1}{5}\coth\frac{\theta}{2}. \quad (13)$$

It is instructive to relate Eq. (12) to Brillouin's function for small λ. One way of doing this without using Schwinger's formula is to expand $\exp(-\lambda m^2)$ in Eq. (1.11) in a power series as follows: Define

$$f(\theta,\lambda)=\sum_{m=-S}^{+S}\exp\{-m\theta-\lambda m^2\}=\sum_{n=0}^{\infty}\frac{(-)^n\lambda^n}{n!}\sum_{m=-S}^{+S}m^{2n}e^{-m\theta}. \quad (14)$$

One then uses the known result,

$$\sum_{m=-S}^{+S}e^{-m\theta}=\frac{\sinh[(S+\frac{1}{2})\theta]}{\sinh(\frac{1}{2}\theta)}\equiv Z(\theta),$$

so that

$$f(\theta,\lambda)=\sum_{n=0}^{\infty}\frac{(-)^n\lambda^n}{n!}Z^{(2n)}(\theta), \quad (15)$$

where $Z^{(2n)}(\theta)$ is the $2n$th derivative of $Z(\theta)$ with respect to θ. The first term $n=0$ gives Brillouin's function, namely:

$$\frac{\mu^{(0)}}{\mu_\infty^{(0)}}=\frac{1}{S}\frac{Z^{(1)}}{Z}=\frac{2S+1}{2S}\coth(S+\tfrac{1}{2})\theta-\frac{1}{2S}\coth\frac{\theta}{2}\equiv B_s(\theta). \quad (16)$$

The result up to and including $n=1$ yields [this also follows from Eq. (7)]:

$$\frac{\mu^{(0)}}{\mu_\infty^{(0)}}=\frac{1}{S}\frac{Z^{(1)}-\lambda Z^{(3)}}{Z-\lambda Z^{(2)}}, \quad (17)$$

which by the use of the previous result (16) leads, to order λ, to the following relation:

$$\frac{\mu^{(0)}}{\mu_\infty^{(0)}}=B_s(\theta)\left[1-\lambda\left\{2SB_s^{(1)}(\theta)+\frac{B_s^{(2)}(\theta)}{B_s(\theta)}\right\}\right]. \quad (18)$$

One can immediately see, since $D=-0.01$ cm^{-1}, $S=5/2$, and the slope of $B_{5/2}(\theta)$ can be of order unity, that of 1°K($kT\approx\frac{2}{3}$ cm^{-1}), $\lambda=-0.02$, and one can expect deviations of about 5 percent. Actually, the second derivative term $B_s^{(2)}(\theta)$ cuts this down to a few percent. For numerical purposes, it is easier to plot the closed result (12). Figure 2 and Table I show three such typical curves based on Eq. (12) for the value $T=1, \frac{1}{2}, \frac{1}{4}$°K, $D=-0.013$ cm^{-1}, and how they compare with the corresponding Brillouin function. One notes the interesting fact that there is a different curve for each temperature, since D is assumed to be constant in this range (this could be checked experimentally).

Now that one has the largest part of μ, namely, $\mu^{(0)}$, which at $T=0.25$°K shows a maximum deviation of about 8 percent, one can proceed to calculate $\mu^{(2)}$. One can certainly neglect the last two nuclear terms in (1). Then in the expression for Λ one can drop the D term in $\mathcal{H}_0$, and $\mathcal{H}_1$ (in Λ) can be taken as $A\mathbf{I}\cdot\mathbf{S}$, since everything else will yield results smaller by at least one order of magnitude. Such considerations are based on the assumption that the Pryce constants, D, A and a sift out the various orders of terms independent of the values of the spurs which they multiply (i.e., the latter spurs which lead to closed functions of θ are assumed to have a maximum value which does not alter the order of magnitude of the result). The calculation of Λ would then require the following:

$$\Lambda=\frac{1}{\mathrm{Sp}\exp(-\theta S_z)}\bigg[-\tfrac{1}{6}\beta a\,\mathrm{Sp}\{\exp(-\theta S_z)\cdot(S_1^4+S_2^4+S_3^4)\}+\tfrac{1}{2}(\beta A)^2\int_0^1 ds_1 \times\mathrm{Sp}\{\exp(-\theta(1-s_1)S_z)\cdot(\mathbf{I}\cdot\mathbf{S})\cdot\exp(-s_1\theta S_z)\cdot(\mathbf{I}\cdot\mathbf{S})\}\bigg]. \quad (19)$$

The first term is laborious to compute because of the two systems of axes involved. One can express the coordinates (1, 2, 3) or (x_1, x_2, x_3) in terms of (x, y, z), by two successive rotations through angles of $\cos^{-1}(1/\sqrt{3})$ and $\pi/4$ about the x axis and the new $\bar{y}$ axis, respectively, if one originally chooses the y axis to lie in the plane of (z, x_3). (See Fig. 1.) One has

$$S_1=\frac{1}{\sqrt{2}}S_x-\frac{1}{\sqrt{6}}S_y+\frac{1}{\sqrt{3}}S_z,$$
$$S_2=\sqrt{\tfrac{2}{3}}S_y+\frac{1}{\sqrt{3}}S_z, \quad (20)$$
$$S_3=-\frac{1}{\sqrt{2}}S_x-\frac{1}{\sqrt{6}}S_y+\frac{1}{\sqrt{3}}S_z.$$

One can then express $(S_1^4+S_2^4+S_3^4)$ in terms of S_x, S_y, S_z and carry out the many spurs. This will not be carried out here since this contribution to μ is unimportant until one reaches $T\sim 0.01$°K, which is probably outside the range of temperatures at which experiments of the type being considered here are possible. The second-order hyperfine coupling contribution is similarly small but far more tractable. The details of this calculation are similar to one carried out by Simon-Rose-Jauch[10] in another connection, so only a sketch of the result will be given here. Using the same notation as the above authors, namely,

$$S_\pm=\frac{1}{\sqrt{2}}(S_x\pm S_y);\quad S_0=S_z;$$
$$S_\pm S_\mp=\tfrac{1}{2}[S(S+1)-S_z^2\mp S_z]; \quad (21)$$
$$S_0S_0=S_z^2,$$

and similarly for $(I_\pm, I_0)$, one has to calculate

$$\mathrm{Sp}[\exp\{-(1-s_1)\theta S_z\}I^mS_m\exp\{-s_1\theta S_z\}I^nS_n],$$

where $\mathbf{I}\cdot\mathbf{S}=I^mS_m$ (summed over $m=+,0,-$), and $I^m=I_{-m}$. This is most easily done by commuting the middle two operators by means of the commutation rules:

$$S_\pm S_0=(S_0\mp 1)S_\pm,$$
$$S_\pm\exp\{-s_1\theta S_0\}=\exp\{-s_1\theta(S_0\mp 1)\}S_\pm. \quad (22)$$

[10] Simon, Rose, and Jauch, Phys. Rev. **84**, 1155 (1951).

One readily obtains the following result:

$$\Lambda=\frac{SI(I+1)}{6}(\beta A)^2\bigg[S\bigg(1-\frac{\sinh\theta}{\theta}\bigg)M_2+\frac{1-\cosh\theta}{\theta}M_1+(1+S)\frac{\sinh\theta}{\theta}\bigg], \quad (23)$$

where the moments M are the usual

$$M_1=\frac{\mathrm{Sp}\{\exp(-\theta S_z)\cdot S_z\}}{S\,\mathrm{Sp}\exp(-\theta S_z)}=-B_S(\theta);$$
$$M_2=\frac{\mathrm{Sp}\{\exp(-\theta S_z)\cdot S_z^2\}}{S^2\,\mathrm{Sp}\{\exp(-\theta S_z)\}}.$$

One then substitutes Eq. (23) into (8) to obtain the hyperfine coupling correction to μ, i.e.,

$$\frac{\mu^{(2)}}{\mu_\infty^{(0)}}=\frac{1}{S}(1+\Lambda)^{-1}\frac{\partial\Lambda}{\partial\theta}=\frac{I(I+1)}{6(1+\Lambda)}(\beta A)^2\bigg[S\bigg(1-\frac{\sinh\theta}{\theta}\bigg)\times\bigg\{2BB^{(1)}+\frac{1}{S}B^{(2)}\bigg\}+\frac{\cosh\theta-1}{\theta}B^{(1)}+\bigg(\frac{\sinh\theta}{\theta^2}-\frac{\cosh\theta}{\theta}\bigg)\{B^{(1)}+SB^2-S-1\}+\bigg(\frac{1}{\theta^2}+\frac{\sinh\theta}{\theta}-\frac{\cosh\theta}{\theta^2}\bigg)B\bigg], \quad (24)$$

where $B^{(1)}\equiv(d/d\theta)B_s(\theta)$, etc. This correction is smaller than 1 percent of the D-term contribution in the immediate vicinity of 1°K, since the bracket term in (24) is of order unity for all θ. The actual values of $\mu^{(2)}/\mu_\infty^{(0)}$ for $A=(-)0.009$, $T=1$, $\frac{1}{2}$, $\frac{1}{4}$°K are given in Table II.

If one now agrees that only the D term in the Hamiltonian contributes to the deviations from the Brillouin

TABLE I. $\mu^{(0)}/\mu_\infty^{(0)}$.

θ	$\lambda=0$	$\lambda=-0.02$	$\lambda=0.04$	$\lambda=0.08$
0	0	0	0	0
0.2	0.2284	0.2371	0.2465	0.2655
0.4	0.4268	0.4414	0.4567	0.4867
0.6	0.5806	0.5980	0.6148	0.6472
0.8	0.6940	0.7096	0.7251	0.7549
1.0	0.7732	0.7869	0.8002	0.8247
1.4	0.8695	0.8788	0.8874	0.9030
1.8	0.9208	0.8267	0.9323	0.9422
2.2	0.9502	0.9540	0.9573	0.9637
2.6	0.9680	0.9702	0.9727	0.9766
3.0	0.9790	0.9807	0.9821	0.9848
3.6	0.9888	0.9896	0.9904	0.9919
4.2	0.9940	0.9944	0.9948	0.9953
4.8	0.9966	0.9986	0.9984	0.9987
5.4	0.9982	0.9992	0.9992	0.9993
6.0	0.9990	0.9995	0.9997	0.9996
7.0	0.9996	0.9998	0.9997	0.9999

TABLE II. $\mu^{(2)}/\mu_\infty^{(0)}$.

$\theta \backslash (\beta A)^2$	$\left(\frac{0.009}{\frac{2}{3}\cdot 1}\right)^2$	$\left(\frac{0.009}{\frac{2}{3}\cdot \frac{1}{2}}\right)^2$	$\left(\frac{0.009}{\frac{2}{3}\cdot \frac{1}{4}}\right)^2$
0.2	0.0000991	0.000394	0.00153
0.4	0.000179	0.000709	0.00276
0.6	0.000234	0.000929	0.00361
0.8	0.000274	0.00109	0.00421
1.0	0.000308	0.00122	0.00473
1.2	0.000344	0.00136	0.00526
1.4	0.000385	0.00153	0.00589
1.6	0.000436	0.00173	0.00664
1.8	0.000497	0.00197	0.00754
2.0	0.000570	0.00225	0.00862
2.2	0.000658	0.00260	0.00991
2.4	0.000763	0.00301	0.0114
2.6	0.000887	0.00350	0.0132
2.8	0.00103	0.00407	0.0153
3.0	0.00121	0.00476	0.0178
3.2	0.00142	0.00556	0.0206
3.4	0.00166	0.00651	0.0242
3.6	0.00195	0.00763	0.0278
3.8	0.00230	0.00894	0.0323
4.0	0.00271	0.0105	0.0374
4.2	0.00319	0.0123	0.0432
4.4	0.00376	0.0144	0.0499
4.6	0.00444	0.0169	0.0574
4.8	0.00524	0.0199	0.0659
5.0	0.00619	0.0233	0.0754
5.2	0.00731	0.0273	0.0858
5.4	0.00864	0.0319	0.0973
5.6	0.0102	0.0372	0.110
5.8	0.0121	0.0433	0.123
6.0	0.0142	0.0503	0.137

free-spin theory near 1°K, one can carry out the calculation of μ when the magnetic field is perpendicular to the trigonal z axis; $\mathbf{H}\cdot\mathbf{S}=H_xS_x$, say.

One has to calculate the following:

$$\mathrm{Sp}\exp(-\theta S_x-\lambda S_z^2), \tag{25}$$

which can be done by first rotating the coordinates through $\frac{1}{2}\pi$, i.e., ($x\rightarrow z$; $z\rightarrow -x$; $S_x\rightarrow S_z$; $S_z^2\rightarrow S_x^2$) and then using Schwinger's formula (7). This will be done here to first order in λ (there is no difficulty in carrying out higher orders). One obtains then:

$$\begin{aligned}\mathrm{Sp}\exp(-\theta S_x-\lambda S_z^2)&=\mathrm{Sp}\exp(-\theta S_z-\lambda S_x^2)\\ &=\mathrm{Sp}\exp(-\theta S_z)-\lambda\,\mathrm{Sp}\{\exp(-\theta S_z)S_x^2\}\\ &\quad+\frac{\lambda^2}{2}\int_0^1 ds_1\,\mathrm{Sp}\{\exp(-(1-s_1)\theta S_z)\cdot S_x^2\\ &\qquad\cdot\exp(-s_1\theta S_z)\cdot S_x^2\}.\end{aligned} \tag{26}$$

Now one has,

$$\begin{aligned}\mathrm{Sp}\{\exp(-\theta S_z)\cdot S_x^2\}&=\sum_{m=-S}^{+S}e^{-m\theta}\langle m|S_x^2|m\rangle\\ &=\sum_{m=-S}^{+S}e^{-m\theta}\left\{\frac{S(S+1)-m^2}{2}\right\}.\end{aligned} \tag{27}$$

Then, to first order in λ, one finds:

$$\begin{aligned}&\mathrm{Sp}\{\exp(-\theta S_x-\lambda S_z^2)\}\\ &\qquad=Z(\theta)-\tfrac{1}{2}\lambda[S(S+1)Z(\theta)-Z^{(2)}(\theta)].\end{aligned} \tag{28}$$

The magnetic moment μ is easily obtained from Eq. (2) and is given by

$$\frac{\mu}{\mu_\infty}=\frac{1}{S}\frac{\partial}{\partial\theta}\left[\log Z\left\{1-\frac{\lambda}{2Z}(S(S+1)Z-Z^{(2)})\right\}\right], \tag{29}$$

or, with some reduction similar to those earlier, one finds finally:

$$\frac{\mu}{\mu_\infty}=B_s(\theta)\left[1+\frac{\lambda}{2}\left\{2SB_s^{(1)}(\theta)+\frac{B_s^{(2)}(\theta)}{B_s(\theta)}\right\}\right]. \tag{30}$$

This differs from the "parallel" case (18) by the substitution $\lambda\rightarrow-\lambda/2$. In this case, then the curves should fall below the Brillouin curve by half as much as the curves in Fig. 2 lie above it. All the above results are for a single crystal.

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