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Classical cubic model for paramagnetic DySb

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A classical mean-field model, incorporating quadrupolar and bilinear exchange coupling and a strong but finite cubic crystal field, is developed here for DySb at temperatures above the Néel point. Paramagnetic equations of state are derived in simple form for a small magnetic field applied along various principal crystallographic directions. Quantitative comparisons are made with exact crystal-field calculations and with a recent quantum-mechanical mean-field analysis of quadrupolar exchange in DySb. The classical model gives very reasonable overall agreement and shows explicitly how the two cubic components of the quadrupolar exchange are manifested very differently in the magnetic properties for thermal energies small compared to the crystal-field energy.

I. INTRODUCTION

A wealth of experimental information has accumulated on the magnetic and related properties of the cubic (NaCl-structured) rare-earth pnictides. One of the most thoroughly explored of these compounds is DySb. Of particular interest has been its first-order Néel-point transition (at $T_N \approx 9.5$ K) and its field-induced quadrature-spin state, in which the sublattice moments are oriented along two orthogonal $\langle 100 \rangle$-type easy directions closest to the applied field direction, similar to the ferrimagnetic structure of HoP in zero field.[1] Both of these and many other unusual features of the magnetic phase diagrams of DySb are well documented by magnetic and neutron diffraction measurements[2–6] and have been attributed to strong quadrupolar interactions.[7,8] The existence of such interactions, of magnetoelastic and intrinsic exchange origin, has been shown to explain the elastic-constant softening observed ultrasonically in this compound as its temperature is lowered to T_N.[7,9–12] Recently, our detailed analysis of magnetization data for DySb above T_N has also disclosed the significant presence of quadrupolar interactions.[13,14] However, unlike the elastic-constant results which were fitted with temperature-independent quadrupolar coupling coefficients, our magnetization results indicated that these coefficients vary drastically (even changing in sign) as the temperature approaches very close to T_N.

This possible discrepancy, as well as a general need for clearer understanding, has motivated us to examine the basis of our data analysis. Essentially, this analysis[13–15] consisted of a comparison of the measured isotherms of magnetization M vs H (the field applied along a principal crystallographic direction, corrected for demagnetization) with the corresponding isotherms of M vs H_{eff} (the total effective field in the same direction) which were calculated from an experimental knowledge of the crystal-field states of DySb.[16] The difference $H_{\mathrm{eff}}-H$ at the same M was taken as the net exchange field H_{exch} on each Dy^{3+} ion. The dependence of H_{exch} on M was found to contain not only a linear term, which is isotropic, temperature independent, and readily ascribable to a bilinear exchange coupling, but also a substantial M^3 term (plus terms of still higher order) which is highly anisotropic and variable with temperature. This cubic term was fitted successfully at each temperature and field direction by incorporating a mean-field quadrupole-quadrupole coupling of cubic symmetry into the model calculations. The results of these fits showed that the two quadrupolar coupling coefficients are very different from each other in magnitude, as well as highly temperature dependent near T_N, as mentioned earlier.

At all stages of this analysis, we implicitly assumed that a paramagnetic DySb crystal remains structurally cubic even when subjected to a magnetic field. Thus, any magnetoelastic effects, which could provide an additional mechanism for quadrupolar coupling, were not explicitly included. However, even without these effects, the computer calculations involving the crystal-field states of cubic DySb were quite complicated, and the introduction of additional processes would be difficult. For this reason, we considered it advantageous to develop a simplified crystal-field model for cubic paramagnetic DySb, which would include bilinear and higher-order exchange interactions and for which the later inclusion of various magnetoelastic effects would be relatively easy to achieve.

With suitable modification, the model that lends itself readily to this purpose is the so-called "cubic model," as applied to rare-earth pnictides with strong cubic crystal fields.[17] According to this model, the crystal-field states of paramagnetic DySb would be considered to have sixfold degeneracy in zero field, corresponding to projections of the magnetic moments along the six $\langle 100 \rangle$-type easy directions of magnetization. Effectively, the small (~ 9 K) separation between the lowest lying Γ_6 doublet and Γ_8 quartet of the actual crystal-field levels of DySb[16] would be neglected. As a further simplification, since the total angular momentum number J of Dy^{3+} is already very high ($\frac{15}{2}$), we will take this model to the classical limit while allowing the cubic anisotropy to be finite but large compared to the thermal energy. Bilinear and higher-order exchange interactions will be included within the mean-field approximation. In Sec. II, this model will be used in deriving, in explicit form, the paramagnetic equations of state of a DySb crystal in an external field parallel to various principal directions. In Sec. III, these equations will be applied to our experimental $M(H,T)$ data, and the numerical results for the interaction coefficients will be compared to those obtained previously by exact computer calculation.

II. CUBIC MODEL ANALYSIS

A. General considerations

For a rare-earth pnictide such as DySb with total angular momentum $\vec{J}$ and Landé factor g per rare-earth ion, with a cubic crystal field (coefficients: B_4, B_6), isotropic bilinear exchange (coefficient: I), and cubic quadrupolar exchange (coefficients: K, L), in an external field $\vec{H}$, the mean-field magnetic Hamiltonian may be written[18]

$$\begin{aligned} H_m = {} & B_4 O_4 + B_6 O_6 - g\mu_B \vec{H}\cdot\vec{J} \\ & - I\langle\vec{J}\rangle\cdot\vec{J} - K(\langle O_2^0\rangle O_2^0 + 3\langle O_2^2\rangle O_2^2) \\ & - 3L(\langle P_{xy}\rangle P_{xy} + \langle P_{yz}\rangle P_{yz} + \langle P_{zx}\rangle P_{zx}) \ , \end{aligned} \tag{1}$$

where the quadrupolar operators, $O_2^0 = 3J_z^2 - J^2$, $O_2^2 = J_x^2 - J_y^2$, and $P_{\alpha\beta} = J_\alpha J_\beta + J_\beta J_\alpha$. The crystal-field operators can be expressed in a cubic representation as follows[19]:

$$\begin{aligned} O_4 &= O_4^0 + 5O_4^4 = 20R_4 + \text{const} \ , \\ O_6 &= O_6^0 - 21O_6^4 \\ &= 616R_6 - 280(3J^2 - 7)R_4 + \text{const} \ , \end{aligned}$$

where $R_n = J_x^n + J_y^n + J_z^n$. In the classical limit, the operators in Eq. (1) all commute, and we have for the magnetic energy (within an additive constant):

$$\begin{aligned} E_m = {} & -(D_4/\mu^4)(\mu_x^4 + \mu_y^4 + \mu_z^4) \\ & -(D_6/\mu^6)(\mu_x^6 + \mu_y^6 + \mu_z^6) - \vec{H}\cdot\vec{\mu} \\ & -\lambda\langle\vec{\mu}\rangle\cdot\vec{\mu} - \lambda_1'(\langle\mu_x^2\rangle\mu_x^2 + \langle\mu_y^2\rangle\mu_y^2 + \langle\mu_z^2\rangle\mu_z^2) \\ & -2\lambda_2'(\langle\mu_x\mu_y\rangle\mu_x\mu_y + \langle\mu_y\mu_z\rangle\mu_y\mu_z + \langle\mu_z\mu_x\rangle\mu_z\mu_x) \end{aligned} \tag{2}$$

where $\vec{\mu}\,(=g\mu_B\vec{J})$ is the rare-earth ionic moment, $D_4 = -20J^4[B_4 - 14(3J^2-7)B_6]$, $D_6 = -616J^6B_6$, $\lambda = I/g^2\mu_B^2$, $\lambda_1' = 6K/g^4\mu_B^4$, and $\lambda_2' = 6L/g^4\mu_B^4$. Note that if $\lambda_1' = \lambda_2'$ (i.e., $K = L$) the quadrupolar exchange terms in Eq. (2), taken together, form the mean-field version of an isotropic biquadratic exchange term.

In determining the various thermal-average quantities, such as $\langle\mu_z^2\rangle$, we will ultimately consider that the crystal-field energy dominates over the thermal energy (kT) and that the latter dominates over the Zeeman and exchange energies. In this regime of approximation, which corresponds to the physical situation of our magnetization measurements on DySb above the Néel point, the states of any appreciable thermal population are those for which the rare-earth moments are oriented closely parallel to the six cube-edge easy directions ($\pm x$, $\pm y$, $\pm z$). For the case where $\mu_x \approx \pm\mu$, we obtain from Eq. (2) to second order in μ_y and μ_z,

$$\begin{aligned} E_m(\pm x) = {} & -D_4 - D_6 + (D/\mu^2)(\mu_y^2 + \mu_z^2) \mp (H_x + \lambda\langle\mu_x\rangle)[\mu - (\mu_y^2 + \mu_z^2)/2\mu] \\ & -(H_y + \lambda\langle\mu_y\rangle)\mu_y - (H_z + \lambda\langle\mu_z\rangle)\mu_z - \lambda_1'[\langle\mu_x^2\rangle(\mu^2 - \mu_y^2 - \mu_z^2) + \langle\mu_y^2\rangle\mu_y^2 + \langle\mu_z^2\rangle\mu_z^2] \\ & -2\lambda_2'[\pm\langle\mu_x\mu_y\rangle\mu\mu_y + \langle\mu_y\mu_z\rangle\mu_y\mu_z \pm \langle\mu_z\mu_x\rangle\mu\mu_z] \ , \end{aligned} \tag{3}$$

where $D = 2D_4 + 3D_6 = -8J^4[5B_4 + 7(3J^2+70)B_6]$. Permutation of x,y,z in this equation gives $E_m(\pm y)$ and $E_m(\pm z)$, corresponding to $\mu_y \approx \pm\mu$ and $\mu_z \approx \pm\mu$, respectively. For convenience, we define the related quantity,

$$W(\pm\xi) = -[E_m(\pm\xi) + \lambda_1'\mu^2\langle\mu_z^2\rangle + D_4 + D_6] \ , \tag{4}$$

where $\xi = x, y,$ or z. Thus, for a typical thermal average, we have

$$\langle q \rangle = [Y_x(q) + Y_y(q) + Y_z(q)](Z_x + Z_y + Z_z)^{-1} \ , \quad (5)$$

where we have defined, for $\beta = 1/kT$,

$$Y_x(q) = \int\int q\,(e^{\beta W(+x)} + e^{\beta W(-x)})\, d\mu_y\, d\mu_z \ ,$$

$$Z_x = \int\int (e^{\beta W(+x)} + e^{\beta W(-x)})\, d\mu_y\, d\mu_z \ ,$$

and similarly by permutation of x,y,z. In general, we can write

$$\beta W(+x) = C_0 + C_1\mu_y/\mu + C_2\mu_z/\mu + C_3\mu_y\mu_z/\mu^2 + C_4\mu_y^2/\mu^2 + C_5\mu_z^2/\mu^2 - \beta D(\mu_y^2 + \mu_z^2)/\mu^2$$

and similar expressions for $\beta W(-x)$, $\beta W(+y)$, etc., in each of which the C's depend on the direction of the applied field $\vec{H}$ and can be expressed in terms of the following dimensionless quantities:

$$\begin{aligned} \rho_0 &= \beta\mu(H + \lambda\langle\mu\rangle) \ , \\ \rho_1 &= \tfrac{1}{2}\beta\lambda_1'\mu^2(\mu^2 - 3\langle\mu_z^2\rangle) \ , \\ \rho_2 &= 2\beta\lambda_2'\mu^2\langle\mu_y\mu_z\rangle \ , \\ \rho_3 &= 2\beta\lambda_2'\mu^2\langle\mu_x\mu_y\rangle \ , \end{aligned} \quad (6)$$

where $\langle\mu\rangle$ is the average moment in the direction of $\vec{H}$. Since all these quantities are taken to be much smaller than βD, then for μ_y and μ_z small compared to μ,

$$e^{\beta W(+x)} = e^{C_0}[\,1 + C_1\mu_y/\mu + C_2\mu_z/\mu + (C_3 + C_1C_2)\mu_y\mu_z/\mu^2 + (C_4 + \tfrac{1}{2}C_1^2)\mu_y^2/\mu^2 + (C_5 + \tfrac{1}{2}C_2^2)\mu_z^2/\mu^2]\exp[-\beta D(\mu_y^2 + \mu_z^2)/\mu^2] \ ,$$

and similarly for the other exponentials in the above integrals. Furthermore, since the limits of integration can be safely extended to $\pm\infty$, the integrals take on a readily determinable form.

In what follows, H will be considered parallel to each of the principal cubic directions. In each case, expressions will be given for $\beta W(\pm\xi)$, where $\xi = x,\ y,$ or z, and for the various thermal-average quantities as they emerge interrelated from the integrations. An equation of state will then be derived in the form of an expansion for small H.

B. Field parallel to ⟨100⟩

We first consider the case of $\vec{H} = \hat{z}H$, for which $\langle\mu_z\rangle = \langle\mu\rangle$, $\langle\mu_x\rangle = \langle\mu_y\rangle = 0$, $\langle\mu_x^2\rangle = \langle\mu_y^2\rangle = \tfrac{1}{2}(\mu^2 - \langle\mu_z^2\rangle)$, and $\langle\mu_y\mu_z\rangle = \langle\mu_z\mu_x\rangle$, from symmetry. From Eqs. (3) and (4), we obtain

$$\beta W(\pm x)\mu^2 = \rho_1\mu^2 \pm \rho_3\mu\mu_y + (\rho_0 \pm \rho_2)\mu\mu_z + \rho_2\mu_y\mu_z - \rho_1\mu_z^2 - \beta D(\mu_y^2 + \mu_z^2),$$

$$\beta W(\pm y)\mu^2 = \beta W(\pm x)\mu^2$$

with μ_y replaced by μ_x,

$$\beta W(\pm z)\mu^2 = \pm\rho_0\mu^2 \pm \rho_2\mu(\mu_x + \mu_y) + \rho_3\mu_x\mu_y + (\mp\tfrac{1}{2}\rho_0 + \rho_1 - \beta D)(\mu_x^2 + \mu_y^2) \ ,$$

where the ρ's are defined as given in Eq. (6). Performing the appropriate integrations, as described above, and defining $\alpha = (2\beta D)^{-1}$, we find

$$\langle\mu\rangle = \mu Z^{-1}\{\,[\,1 - \alpha(1 - 2\rho_1 - \rho_2^2)]\sinh\rho_0 - \alpha\rho_0\cosh\rho_0 + 2\alpha\rho_0 e^{\rho_1}\} \ , \quad (7a)$$

$$\langle\mu_z^2\rangle = \mu^2 Z^{-1}\{\,[\,1 - \alpha(2 - 2\rho_1 - \rho_2^2)]\cosh\rho_0 - \rho_0\sinh\rho_0 + 2\alpha e^{\rho_1}\} \ , \quad (7b)$$

$$\langle\mu_x\mu_y\rangle = \mu^2 Z^{-1}(2\alpha\rho_3 e^{\rho_1}) \ , \quad (7c)$$

$$\langle\mu_y\mu_z\rangle = \mu^2 Z^{-1}(2\alpha\rho_2\cosh\rho_0) \ , \quad (7d)$$

where

$$Z = [1 + \alpha(2\rho_1 + \rho_2^2)]\cosh\rho_0 - \rho_0\sinh\rho_0 + [2 - \alpha(2\rho_1 - \rho_0^2 - \rho_2^2 - \rho_3^2)]e^{\rho_1} \ .$$

The averaged quantities, being contained in the ρ's, can be determined self-consistently from these equations. In fact, since ρ_3 and ρ_2 are proportional respectively to $\langle\mu_x\mu_y\rangle$ and $\langle\mu_y\mu_z\rangle$, it follows immediately from Eqs. (7c) and (7d) that $\langle\mu_x\mu_y\rangle = \langle\mu_y\mu_z\rangle = 0$. Hence, in the rest of these equations, we set $\rho_2 = \rho_3 = 0$. Moreover, we expand the hyperbolics and exponentials for small ρ_0 and ρ_1, and let $\rho_1 = b\rho_0^2$. From Eq. (7b), it follows that:

$$b = -\tfrac{1}{3}g_1(1 + \tfrac{2}{3}g_1 - 6\alpha) \ ,$$

to second order in $g_1 = \tfrac{1}{2}\beta\lambda_1'\mu^4$. We then let $\sigma = \langle\mu\rangle/\mu = a_1\rho_0 + a_3\rho_0^3 + \cdots$ in Eq. (7a), determine a_1 and a_3, and find from the inversion of this $\sigma(\rho_0)$ series that

$$\rho_0 = 3\sigma + 2(9\alpha - 3g_1 - 2g_1^2 + 36g_1\alpha)\sigma^3 \ ,$$

which, written out explicitly, is the equation of state,

$$H = \left(3\frac{kT}{\mu^2} - \lambda\right)\langle\mu\rangle + \left[9\frac{kT}{\mu^4}\left(\frac{kT}{D}\right) - 3\lambda_1'\left(1 + \frac{\lambda_1'\mu^4}{3kT} - 6\frac{kT}{D}\right)\right]\langle\mu\rangle^3 \tag{8}$$

valid for small magnetization $\langle\mu\rangle$ and for the condition, $\lambda_1'\mu^4 << kT << D$.

From $\rho_1 = b\rho_0^2 = 9b\sigma^2$ and the expression for b, we also obtain the average quadrupole moment,

$$\begin{aligned}\langle\mu_z^2\rangle - \tfrac{1}{3}\mu^2 &= (1 + \tfrac{2}{3}g_1 - 6\alpha)\mu^2\sigma^2 \\ &= (1 + \lambda_1'\mu^4/3kT - 3kT/D)\langle\mu\rangle^2 \ ,\end{aligned} \tag{9a}$$

which similarly is valid for small $\langle\mu\rangle$ and $\lambda_1'\mu^4 << kT << D$. Note that for the other quadrupole moments,

$$\langle\mu_x\mu_y\rangle = \langle\mu_y\mu_z\rangle = \langle\mu_z\mu_x\rangle = 0 \ . \tag{9b}$$

The fact that the latter are all zero is related, of course, to the fact that λ_2' does not appear in the equation of state.

C. Field parallel to ⟨110⟩

We now consider the case of $\vec{H} = (\hat{x} + \hat{y})H/\sqrt{2}$, for which $\langle\mu_x\rangle = \langle\mu_y\rangle = \langle\mu\rangle/\sqrt{2}$, $\langle\mu_z\rangle = 0$, and as in the previous case, $\langle\mu_x^2\rangle = \langle\mu_y^2\rangle = \frac{1}{2}(\mu^2 - \langle\mu_z^2\rangle)$ and $\langle\mu_y\mu_z\rangle = \langle\mu_z\mu_x\rangle$, from symmetry. Following the same procedure as before, we obtain:

$$\beta W(\pm x)\mu^2 = \pm\rho_0'\mu^2 + \rho_1\mu^2 + (\rho_0' \pm \rho_3)\mu\mu_y \pm \rho_2\mu\mu_z + \rho_2\mu_y\mu_z - \rho_1\mu_z^2 + (\mp\tfrac{1}{2}\rho_0' - \beta D)(\mu_y^2 + \mu_z^2),$$

$$\beta W(\pm y)\mu^2 = \beta W(\pm x)\mu^2$$

with μ_y replaced by μ_x,

$$\beta W(\pm z)\mu^2 = (\rho_0' \pm \rho_2)\mu(\mu_x + \mu_y) + \rho_3\mu_x\mu_y + (\rho_1 - \beta D)(\mu_x^2 + \mu_y^2) \ ,$$

where $\rho_0' = \rho_0/\sqrt{2}$. And from the integrations, we find

$$\begin{aligned}\langle\mu\rangle = \sqrt{2}\mu Z^{-1}\{&[1 - \tfrac{1}{2}\alpha(2 + 2\rho_1 - 2\rho_3 - \rho_0'^2 - \rho_2^2 - \rho_3^2)] \\ &\times e^{\rho_1}\sinh\rho_0' + \alpha\rho_0'\} \ ,\end{aligned} \tag{10a}$$

$$\begin{aligned}\langle\mu_z^2\rangle = \mu^2 Z^{-1}\ [&2\alpha e^{\rho_1}\cosh\rho_0' + 1 \\ &- \alpha(2 - 2\rho_1 - \rho_0'^2 - \rho_2^2)] \ ,\end{aligned} \tag{10b}$$

$$\langle\mu_x\mu_y\rangle = \mu^2 Z^{-1}[2\alpha e^{\rho_1}(\rho_0'\sinh\rho_0' + \rho_3\cosh\rho_0')] \ , \tag{10c}$$

$$\langle\mu_y\mu_z\rangle = \mu^2 Z^{-1}(\alpha\rho_2) \ , \tag{10d}$$

where

$$\begin{aligned}Z = 2[1 - \tfrac{1}{2}\alpha(2\rho_1 - \rho_0'^2 - \rho_2^2 - \rho_3^2)]e^{\rho_1}\cosh\rho_0' \\ - 2\alpha\rho_0' e^{\rho_1}\sinh\rho_0' + 1 + \alpha(2\rho_1 + \rho_0'^2 + \rho_2^2) \ .\end{aligned}$$

Since ρ_2 is proportional to $\langle\mu_y\mu_z\rangle$, it follows from Eq. (10d) that $\langle\mu_y\mu_z\rangle = 0$. We then set $\rho_2 = 0$ in the rest of these equations and expand the hyperbolics and exponentials for small ρ_0 and ρ_1. Letting $\rho_3 = c\rho_0^2$ in Eq. (10c), we find that $c = \frac{1}{3}g_2\alpha$, to first order in $g_2 = 2\beta\lambda_2'\mu^4$. Then, letting $\rho_1 = b\rho_0^2$, we find from Eq. (10b) that

$$b = \tfrac{1}{6}g_1(1 + \tfrac{2}{3}g_1 - 6\alpha) \ ,$$

to second order in $g_1 = \frac{1}{2}\beta\lambda_1'\mu^4$. Finally, by letting $\sigma = \langle\mu\rangle/\mu = a_1\rho_0 + a_3\rho_0^3 + \cdots$ in Eq. (10a) and determining a_1 and a_3, we obtain from the inversion of this $\sigma(\rho_0)$ series that

$$\begin{aligned}\rho_0 = 3\sigma + \tfrac{1}{2}\ (&\tfrac{9}{2} - 9\alpha - 3g_1 - 2g_1^2 \\ &+ 36g_1\alpha - 18g_2\alpha^2)\sigma^3 \ ,\end{aligned}$$

which, written out explicitly, is the equation of state,

$$\begin{aligned}H = &\left[3\frac{kT}{\mu^2} - \lambda\right]\langle\mu\rangle \\ &+ \left[\frac{9kT}{4\mu^4}\left(1 - \frac{kT}{D}\right) - \frac{3}{4}\lambda_1'\left(1 + \frac{\lambda_1'\mu^4}{3kT} - 6\frac{kT}{D}\right) - \frac{9}{2}\lambda_2'\left(\frac{kT}{D}\right)^2\right]\langle\mu\rangle^3 \ ,\end{aligned} \tag{11}$$

valid for small $\langle\mu\rangle$ and for $\lambda_1'\mu^4$, $\lambda_2'\mu^4 << kT << D$.

Regarding the average quadrupole moments, we obtain from $\rho_1 = b\rho_0^2 = 9b\sigma^2$ and the expression for b,

$$\begin{aligned}\langle\mu_z^2\rangle - \tfrac{1}{3}\mu^2 &= -\tfrac{1}{2}(1 + \tfrac{2}{3}g_1 - 6\alpha)\mu^2\sigma^2 \\ &= -\tfrac{1}{2}(1 + \lambda_1'\mu^4/3kT - 3kT/D)\langle\mu\rangle^2 \ ,\end{aligned} \tag{12a}$$

and from $\rho_3 = c\rho_0^2 = 3g_2\alpha\sigma^2$,

$$\langle\mu_x\mu_y\rangle = 3\alpha\mu^2\sigma^2 = (3kT/2D)\langle\mu\rangle^2 \ , \tag{12b}$$

and as we have already shown,

$$\langle \mu_y \mu_z \rangle = \langle \mu_z \mu_x \rangle = 0 \quad . \tag{12c}$$

In this case, since $\langle \mu_x \mu_y \rangle \neq 0$, λ_2' does appear in the equation of state, but only by virtue of kT/D being nonzero.

D. Field parallel to $\langle 111 \rangle$

Finally, we consider the case of $\vec{H} = (\hat{x} + \hat{y} + \hat{z})H/\sqrt{3}$, for which $\langle \mu_x \rangle = \langle \mu_y \rangle = \langle \mu_z \rangle = \langle \mu \rangle / \sqrt{3}$, $\langle \mu_x^2 \rangle = \langle \mu_y^2 \rangle = \langle \mu_z^2 \rangle = \frac{1}{3}\mu^2$, and $\langle \mu_x \mu_y \rangle = \langle \mu_y \mu_z \rangle = \langle \mu_z \mu_x \rangle$, from symmetry. Again, following the same procedure, we obtain:

$$\beta W(\pm x)\mu^2 = \pm \rho_0'' \mu^2 + (\rho_0'' \pm \rho_3)\mu(\mu_y + \mu_z) + \rho_3 \mu_y \mu_z + (\mp \tfrac{1}{2}\rho_0'' - \beta D)(\mu_y^2 + \mu_z^2) \quad ,$$

where $\rho_0'' = \rho_0/\sqrt{3}$, and permutation of x,y,z gives $\beta W(\pm y)\mu^2$ and $\beta W(\pm z)\mu^2$. The integrations now yield

$$\langle \mu \rangle = \sqrt{3}\mu Z^{-1}\{ [1 - \alpha(1 - 2\rho_3 - \rho_0''^2 - \rho_3^2)] \times \sinh\rho_0'' + \rho_0'' \cosh\rho_0'' \} \quad , \tag{13a}$$

$$\langle \mu_x \mu_y \rangle = \mu^2 Z^{-1}[2\alpha(\rho_0'' \sinh\rho_0'' + \rho_3 \cosh\rho_0'')] \quad , \tag{13b}$$

where

$$Z = 3[1 + \alpha(\rho_0''^2 + \rho_3^2)]\cosh\rho_0'' - 3\alpha\rho_0'' \sinh\rho_0'' \quad .$$

Expanding the hyperbolics for small ρ_0 and letting $\rho_3 = c\rho_0^2$, we find from Eq. (13b) that $c = \frac{2}{3}g_2\alpha$, to first order in $g_2 = 2\beta\lambda_2'\mu^4$. Then, letting $\sigma = \langle \mu \rangle / \mu = a_1\rho_0 + a_3\rho_0^3 + \cdots$ in Eq. (13a) and determining a_1 and a_3, we obtain from the inversion of this $\sigma(\rho_0)$ series that

$$\rho_0 = 3\sigma + 3(1 - 4\alpha - 4g_2\alpha^2)\sigma^3 \quad ,$$

which, written out explicitly, is the equation of state,

$$H = \left[3\frac{kT}{\mu^2} - \lambda\right]\langle \mu \rangle + \left[3\frac{kT}{\mu^4}\left(1 - 2\frac{kT}{D}\right) - 6\lambda_2'\left(\frac{kT}{D}\right)^2\right]\langle \mu \rangle^3 \quad , \tag{14}$$

valid for small $\langle \mu \rangle$ and for $\lambda_2'\mu^4 << kT << D$.

For the average quadrupole moments, we have from the outset that

$$\langle \mu_z^2 \rangle - \tfrac{1}{3}\mu^2 = 0 \quad , \tag{15a}$$

whereas from $\rho_3 = c\rho_0^2 = 2g_2\alpha\sigma^2$, we obtain

$$\langle \mu_x \mu_y \rangle = \langle \mu_y \mu_z \rangle = \langle \mu_z \mu_x \rangle = (kT/D)\langle \mu \rangle^2 \quad , \tag{15b}$$

which explain, respectively, the nonappearance of λ_1' and the appearance of λ_2' in the equation of state.

III. COMPARISON WITH EXPERIMENT

The three paramagnetic equations of state, Eqs. (8), (11), and (14), have the general form,

$$H = \eta_{hkl}(T)M + \eta'_{hkl}(T)M^3 \quad , \tag{16}$$

where $M = \langle \mu \rangle$, the magnetization per rare-earth ion parallel to $\langle hkl \rangle$, the direction of the external magnetic field $\vec{H}$. Taken together, they have two features of note. The first and most obvious is that

$$\eta_{100}(T) = \eta_{110}(T) = \eta_{111}(T) = 3kT/\mu^2 - \lambda \quad , \tag{17a}$$

which expresses the fact that the initial susceptibility ($\chi_0 = \eta^{-1}$) is isotropic and obeys the Curie-Weiss law with a paramagnetic Curie point proportional to λ, the isotropic bilinear exchange coefficient. Second, the η' functions containing the quadrupolar exchange coefficients (λ_1', λ_2') are anisotropic but obey the simple relationship,

$$\eta'_{100}(T) + 3\eta'_{111}(T) = 4\eta'_{110}(T) \quad , \tag{17b}$$

which presumably reflects the cubic symmetry assumed for the crystal field and for the quadrupolar exchange.

In order to compare our analytical equations of state with the exact crystal-field calculations and the paramagnetic data analysis for DySb described earlier, we will consider that in Eq. (16) under fixed conditions, the applied field is expressible as

$$H = H_{\text{eff}} - H_{\text{exch}} \quad ,$$

where H_{eff} is the total effective field in a crystal-field-only analysis and H_{exch} is the average exchange field. Thus, Eq. (16) can be subdivided into the following two parts:

$$H_{\text{eff}} = \kappa_{hkl}(T)M + \kappa'_{hkl}(T)M^3 \tag{18a}$$

and

$$H_{\text{exch}} = \lambda_{hkl}(T)M + \lambda'_{hkl}(T)M^3 \quad . \tag{18b}$$

According to the equations of state (8), (11), and (14), the coefficients in Eq. (18a) are

$$\begin{aligned} &\kappa_{100} = \kappa_{110} = \kappa_{111} = 3kT/\mu^2 \quad , \\ &\kappa'_{100} = (9kT/\mu^4)kT/D \quad , \\ &\kappa'_{110} = (9kT/4\mu^4)(1 - kT/D) \quad , \\ &\kappa'_{111} = (3kT/\mu^4)(1 - 2kT/D) \quad , \end{aligned} \tag{19a}$$

and the coefficients in Eq. (18b) are

$$\begin{aligned} &\lambda_{100} = \lambda_{110} = \lambda_{111} = \lambda \quad , \\ &\lambda'_{100} = 3\lambda_1'(1 + \lambda_1'\mu^4/3kT - 6kT/D) \quad , \\ &\lambda'_{110} = \tfrac{3}{4}\lambda_1'(l + \lambda_1'\mu^4/3kT - 6kT/D) + \tfrac{9}{2}\lambda_2'(kT/D)^2 \quad , \\ &\lambda'_{111} = 6\lambda_2'(kT/D)^2 \quad . \end{aligned} \tag{19b}$$

The crystal-field calculations previously carried out for Dy^{3+} ($J=\frac{15}{2}$, $g=\frac{4}{3}$) in DySb were based on the parameters, $A_4\langle r^4\rangle/k=60$ K and $A_6\langle r^6\rangle/k=2$ K,[16] and yielded values of M as a function of H_{eff} for different temperatures and field directions.[13] The calculated results, when examined at small M, are found to give isotherms of H_{eff}/M vs M^2 that are linear and which therefore conform to Eq. (18a). The values thus determined for $\mu\kappa_{hkl}$ and $\mu^3\kappa'_{hkl}$ (both in kOe units, where $\mu=gJ\mu_B=10\mu_B$) are plotted versus temperature, for $hkl=100$, 110, and 111, in Fig. 1. The values of $\mu\kappa_{hkl}$, which are isotropic and labeled simply as $\mu\kappa$, vary almost linearly with temperature. For comparison, we have also plotted $\mu\kappa=3kT/\mu$, from the isotropic expression in Eq. (19a), as a dashed line, and there clearly is close agreement. In order to include in our comparison, values of $\mu^3\kappa'_{hkl}$ derived also from expressions in Eq. (19a), we must first arrive at a suitable value for D, the cubic crystal-field parameter. Referring back to our analysis, we note that $D=-8J^4[5B_4+7(3J^2+70)B_6]$. When we substitute into this expression, $B_4/k=-3.55\times10^{-3}$ K and $B_6/k=+2.07\times10^{-6}$ K (corresponding to the above values for $A_4\langle r^4\rangle$ and $A_6\langle r^6\rangle$) and also $J=\frac{15}{2}$, we obtain $D/k=362$ K. With this value of D and the expressions in Eq. (19a), we calculated $\mu\kappa'_{hkl}$ versus temperature for different hkl, and the results are represented in Fig. 1 by long-dashed curves. The agreement with the exact crystal-field calculations is very good in the $\langle 100\rangle$ case, but less so in the $\langle 110\rangle$ and $\langle 111\rangle$ cases, especially at temperatures above 20 K. As an alternative, we have chosen $D/k=200$ K and again calculated $\mu\kappa'_{hkl}$ versus temperature from the expressions in Eq. (19a). These results are represented by short-dashed curves in Fig. 1, and now the agreement with the crystal-field calculations is best in the $\langle 111\rangle$ case and worst in the $\langle 100\rangle$ case. Clearly, a compromise value of about 280 K for D/k would give optimal overall agreement at low temperatures between the classical cubic model and the exact crystal-field calculations for DySb.

With this approximate value for D, the cubic crystal-field parameter of our classical model, we can now use the expressions in Eq. (19b) to convert experimentally derived values for λ'_{100} and λ'_{111} obtained

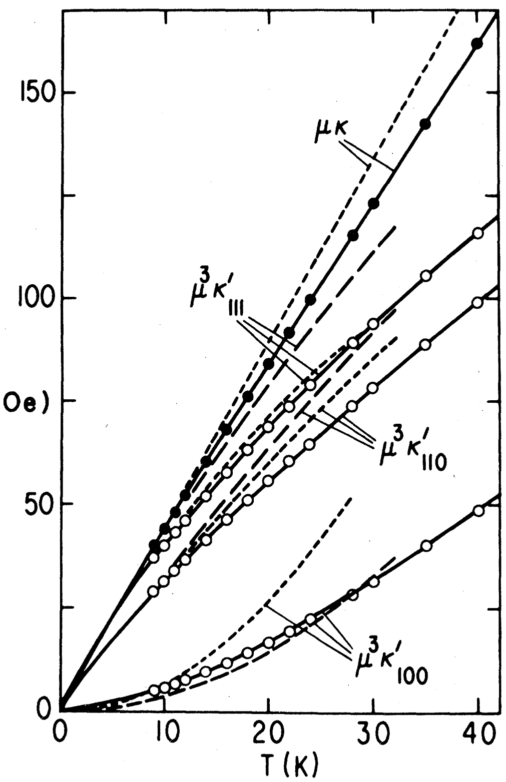

FIG. 1. Values of $\mu\kappa$ (closed circles) and $\mu^3\kappa'_{hkl}$ (open circles), from exact crystal-field calculations for DySb, plotted vs temperature. Dashed line for $\mu\kappa$ vs temperature derived from Eq. (19a). Long-dashed and short-dashed curves for $\mu^3\kappa'_{hkl}$ vs temperature derived from Eq. (19a) with $D/k=362$ and 200 K, respectively.

for DySb at various temperatures into corresponding values for the quadrupolar exchange coefficients, λ'_1 and λ'_2, respectively. The latter can then be related, respectively, to K and L, the quadrupolar interaction coefficients in Eq. (1), the quantum-mechanical mean-field Hamiltonian of the problem. This Hamiltonian, in fact, was previously applied to paramagnetic DySb with no further approximation, whereby exact self-consistent calculations[14] were employed in fitting the experimental λ'_{100} and λ'_{111} values listed in Table I and thus determining K and L. The values of

TABLE I. Quadrupolar coupling coefficients for DySb. (λ'_{100} and λ'_{111} in units of Oe/μ_B^3; K/k and L/k in units of 10^{-4} K.)

T(K)	λ'_{100}	λ'_{111}	K/k[a]	L/k[a]	K/k[b]	L/k[b]
12	0.0	+15.2	0.00	+107.8	0.00	+488.1
14	+4.3	+6.7	+0.82	+49.2	+0.69	+158.1
18	+14.7	−5.0	+2.81	−41.0	+2.47	−71.3
22	+22.9	−10.5	+4.34	−79.7	+4.17	−100.3

[a] Values derived from exact mean-field calculations in Ref. 14.

[b] Values derived from Eq. (19b) with $D/k=280$ K.

the latter (divided by k) are also listed in Table I, for the same temperatures above the Néel point (~ 9.5 K).

Starting with the same values for λ'_{100} and λ'_{111} and using $D/k = 280$ K, we have calculated λ'_1 and λ'_2 from the simple expressions in Eq. (19b) and converted these directly, through the same proportionality factor ($\frac{1}{6}g^4\mu_B^4$, where $g=\frac{4}{3}$), into K and L, respectively. Our results for K/k and L/k are also listed in Table I, and in the case of the former there is remarkably close agreement with the K/k values previously deduced from the more exact analysis. In the case of L/k, the corresponding agreement is not close, but our present results do show a similar contrast with the much smaller absolute values of K/k, despite the lack of such a contrast between the experimental values for λ'_{100} and λ'_{111}. In this context, our present analysis gives an explicit explanation for the contrast between K and L. Namely, in Eq. (19b), we note that λ'_2 (which gives L) is related to λ'_{111} through the factor $(D/kT)^2$ which is of order 10^2 for DySb over the temperature range of interest, whereas the relationship between λ'_1 (which gives K) and λ'_{100} contains no such enhancement factor. This phenomenon is related to the fact that in the $\langle 111 \rangle$ case the quadrupole moments have to be thermally excited into existence against the strong crystal field, as indicated by Eq. (15b), whereas this is not so in the $\langle 100 \rangle$ case, as shown by Eq. (9a).

Thus, in summary, our classical analysis does capture, in simple explicit form, all the salient magnetization properties of paramagnetic DySb related to its quadrupolar interactions as interpreted on the basis of a cubic crystal field. At this stage, magnetoelastic distortions of the crystal and their effects on the quadrupolar coupling have been totally neglected. Such effects are known to play an important role in DySb, as we mention at the start, and they may well be the physical origin of the peculiar behavior we have deduced for the effective quadrupolar coupling in DySb just above the Néel point. Fortunately, the simplicity of our model makes it relatively easy to incorporate any magnetoelastic mechanisms and study their various property effects in detail, and we are presently carrying out an investigation of this kind.

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