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Anisotropic Curie Temperature*

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In an anisotropic ferromagnet the Curie temperature is a function of the direction of the magnetization. The Curie temperature is high in easy directions, and can drop quite low in harder directions for an anisotropy energy comparable to the exchange energy. Magnetization curves as a function of temperature also depend upon the orientation. In sufficiently hard directions, the magnetization drops from a large value precipitously to zero at the Curie temperature.

I. INTRODUCTION

IN another paper,[1] there is discussed from a perturbation theory viewpoint the variation of the magnitude of the magnetization as it is rotated with respect to the crystal axes in an anisotropic material. Briefly, it results that at constant temperature the magnetization is larger in easier directions than in hard, because the anisotropic forces tend to compress the spin cone in easy directions, and spread it in hard ones; in an easy direction the magnetization will drop off from saturation more slowly (as a higher power of the temperature) than in an isotropic material and in a hard direction somewhat faster. However, when perturbation theory is employed, the Curie temperature is independent of the orientation of the magnetization.

In this paper we consider a case in which the anisotropy energy can be comparable to the exchange. Our model is a quantum-mechanical internal field Hamiltonian with a one ion anisotropic term of uniaxial symmetry, which we treat exactly.

To simplify evaluation of our final equation and to avoid an additional parameter we do not keep an external field term in the Hamiltonian, and this requires some explanation. To rotate the magnetization away from the easiest direction, an external field is required, a very large one in highly anisotropic materials. This field of course will markedly affect the magnitude of the magnetization at high temperatures, and will eliminate the Curie point entirely, if the magnetization has any component along the field. In any case, because of domain and saturation effects it is practical to use strong aligning fields. One then makes measurements at a number of field strengths, and extrapolates to zero field.

II. CALCULATION

Consider the magnetization to lie in the ζ direction at an angle θ with the z axis. The component of the moment of an ion along the magnetization is $g\mu_B S_\zeta$. The magnetization per unit volume is $ng\mu_B\langle S_\zeta\rangle$ and the internal field is $\gamma\mathbf{M}$, if n is the number of ions per unit volume and γ the internal field constant. In a uniaxial material the anisotropic term can be conveniently expressed in the form

$$v=(\lambda a/\beta)[S_z{}^2-\tfrac{1}{3}S(S+1)]. \tag{1}$$

$\lambda a/\beta$ is the microscopic anisotropy coefficient of the term with P_2 symmetry; if it is positive the z axis will be the hard direction. Let

$$a=\beta(g\mu_B)^2n\gamma, \tag{2}$$

with $\beta=1/kT$, and $(g\mu_B)^2n\gamma$ the exchange energy. Then the Hamiltonian per ion is

$$h=-(a/\beta)\langle S_\zeta\rangle S_\zeta+(\lambda a/\beta)(S_z{}^2-\tfrac{2}{3})+(a/2\beta)\langle S_\zeta\rangle^2. \tag{3}$$

The constant part of the anisotropic term serves to give the Hamiltonian a vanishing trace. Because it is temperature-dependent, the Hamiltonian must contain the third term $(a/2\beta)\langle S_\zeta\rangle^2$. The origin of this term is discussed in reference 1. This term is important in the free energy; however, insofar as we use the Hamiltonian only to calculate thermal expectation values, this term is a constant which factors out and cancels in the density matrix. We consider a spin-one system, as this is the lowest order spin algebra that can support P_2 symmetry.

The magnetization is determined implicitly by

$$\langle S_\zeta\rangle=\frac{\operatorname{tr}(e^{-\beta h}S_\zeta)}{\operatorname{tr}(e^{-\beta h})}. \tag{4}$$

Equation (3) for h is to be substituted into Eq. (4). It is convenient to work in a basis in which S_z is diagonal. The operator to be diagonalized is

$$-\frac{\beta h}{a}=\begin{bmatrix} \langle S_\zeta\rangle\cos\theta-\frac{1}{3}\lambda & \langle S_\zeta\rangle(\cos\Omega_{\zeta x}-i\cos\Omega_{\zeta y})/\sqrt{2} & 0 \\ \langle S_\zeta\rangle(\cos\Omega_{\zeta x}+i\cos\Omega_{\zeta y})/\sqrt{2} & \frac{2}{3}\lambda & \langle S_\zeta\rangle(\cos\Omega_{\zeta x}-i\cos\Omega_{\zeta y})/\sqrt{2} \\ 0 & \langle S_\zeta\rangle(\cos\Omega_{\zeta x}+i\cos\Omega_{\zeta y})/\sqrt{2} & -\langle S_\zeta\rangle\cos\theta-\frac{1}{3}\lambda \end{bmatrix}. \tag{5}$$

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* A preliminary report on this work was presented at the *Sixth Annual Conference on Magnetism and Magnetic Materials, New York, 1960* [J. Appl. Phys. **32**, 221S (1961)].

[1] E. R. Callen and H. B. Callen, J. Phys. Chem. Solids **16**, 310 (1960).

The eigenvalues are the roots of the cubic

$$x^3 - c_1 x + c_0 = 0, \tag{6}$$

in which the quadratic term vanishes because

$$\textstyle\sum_k x_k = 0. \tag{7}$$

The coefficients are

$$\begin{aligned} c_0 &= \tfrac{1}{3}\lambda(3\cos^2\theta - 1)\langle S_\zeta\rangle^2 - (2/27)\lambda^3, \\ c_1 &= \langle S_\zeta\rangle^2 + \tfrac{1}{3}\lambda^2. \end{aligned} \tag{8}$$

As the operator of Eq. (5) is hermitean, the eigenvalues are real, the discriminant of the cubic is negative, and the roots are given by

$$x_k = 2\left(\frac{c_1}{3}\right)^{\frac{1}{2}} \cos\left(\frac{\phi}{3} + \frac{2\pi k}{3}\right), \quad k = 0, 1, 2. \tag{9}$$

where

$$\cos\phi = \frac{-c_0/2}{(c_1/3)^{\frac{3}{2}}}. \tag{10}$$

To evaluate the numerator of Eq. (4), rather than rotate S_ζ to the diagonal basis, it is simpler to rewrite Eq. (4) in the form

$$\langle S_\zeta\rangle = \sum_k \frac{\partial x_k}{\partial\langle S_\zeta\rangle} e^{ax_k} \Big/ \sum_k e^{ax_k}. \tag{11}$$

It will be seen that if $\lambda = 0$, this expression reduces to the familiar spin 1 Brillouin function. Equation (11), together with the expressions for the roots, specifies the magnetization ($\langle S_\zeta\rangle$) as a function of the temperature ($1/a$), for all values of the ratio of anisotropy to exchange energy (λ) and the orientation of the magnetization ($\cos\theta$).

A. Magnetization Along the *z* Axis

It is helpful to consider first a special case in which Eq. (11) simplifies. When $\cos\theta = 1$, the roots of the cubic are

$$-\tfrac{1}{3}\lambda + \langle S_\zeta\rangle, \quad \tfrac{2}{3}\lambda, \quad \text{and} \quad -\tfrac{1}{3}\lambda - \langle S_\zeta\rangle. \tag{12}$$

Equation (11) then becomes

$$\langle S_\zeta\rangle = \frac{e^{a\langle S_\zeta\rangle} - e^{-a\langle S_\zeta\rangle}}{e^{a\langle S_\zeta\rangle} + e^{a\lambda} + e^{-a\langle S_\zeta\rangle}}. \tag{13}$$

It is convenient to consider the right side, r, of Eq. (13), as a function of $\langle S_\zeta\rangle$. The solution of Eq. (13) is that value of $\langle S_\zeta\rangle$ for which $r = \langle S_\zeta\rangle$. $\langle S_\zeta\rangle = 0$ is a solution for all λ and a.

$$\lim_{a\to\infty} r = \frac{e^{a\langle S_\zeta\rangle}}{e^{a\langle S_\zeta\rangle} + e^{a\lambda}}, \quad \langle S_\zeta\rangle \neq 0. \tag{14}$$

Here, for $\lambda < 1$, there is a self consistent solution $\langle S_\zeta\rangle = 1$, but for $\lambda \geqslant 1$ the only solution is $\langle S_\zeta\rangle = 0$. Thus for $\lambda > 1$, the only solution of Eq. (13) at all temperatures, is $\langle S_\zeta\rangle = 0$. And for $\lambda < 1$, $\langle S_\zeta\rangle$ starts out as 1 at $a = \infty$ and drops off to zero at some finite a_c. Expand r for small $\langle S_\zeta\rangle$:

$$r \cong \frac{a}{1 + \frac{1}{2}e^{\lambda a}} \left[\langle S_\zeta\rangle + \frac{a^2}{2}\left(\frac{1}{3} - \frac{1}{1 + \frac{1}{2}e^{\lambda a}}\right)\langle S_\zeta\rangle^3 + \cdots \right]. \tag{15}$$

Equation (15) suggests several regions of behavior of Eq. (13).

i. $\lambda \leqslant 0$.

At large a the function $r(\langle S_\zeta\rangle)$ starts at small $\langle S_\zeta\rangle$ with slope a, and with positive third derivative. As a decreases, the crossing moves downward. At $a = 3$, the initial slope of r is still greater than 1, and the third derivative becomes negative. The Curie point is reached when the initial slope of r is one, with negative third derivative:

$$a_c = 1 + \tfrac{1}{2}e^{\lambda a_c}. \tag{16}$$

At $\lambda = 0$ we regain the limiting condition of the Brillouin function,

$$a_c = \tfrac{3}{2}.$$

In Fig. (1) we plot Eq. (16), which is more conveniently written as

$$\lambda = (\ln 2)(a_c - 1)/a_c, \tag{17}$$

for all values of a_c, though we shall see shortly that this equation loses validity for $\lambda > 0.4621$.

ii. $0 < \lambda \leqslant 0.4621$

At large a there are two crossings of the 45° line by r, the upper one being significant. With decreasing a there is only one crossing, the slope rises to some maximum value and then decreases, and the third derivative changes sign as a drops below 3. The Curie point is determined by the smaller solution of condition (16). At the upper end of the range, when $\lambda = 0.4621$, $a_c = 3$. The third derivative is zero at the lower tangency.

iii. $0.4621 < \lambda \leqslant 0.4631$

For $\lambda > 0.4621$ the third derivative remains positive for all a down to the Curie temperature. At large a there are two crossings of the 45° line. After a goes through the upper solution of Eq. (17), there is only one solution of Eq. (13). Then r rises above unit slope to a maximum slope, and with further decreasing a, r drops again to the lower solution of Eq. (17), but still with positive third derivative. There are again two solutions of (13), the larger being significant. It is helpful to look for small $\langle S_\zeta\rangle$ solutions of Eq. (13) by substituting Eq. (15) for the right side of (13). In addition to the $\langle S_\zeta\rangle = 0$ solution, one finds

$$\langle S_\zeta\rangle = \left[\frac{1 + \frac{1}{2}e^{\lambda a} - a}{\frac{1}{2}a^3\left[\frac{1}{3} - (1 + \frac{1}{2}e^{\lambda a})^{-1}\right]} \right]^{\frac{1}{2}}. \tag{18}$$

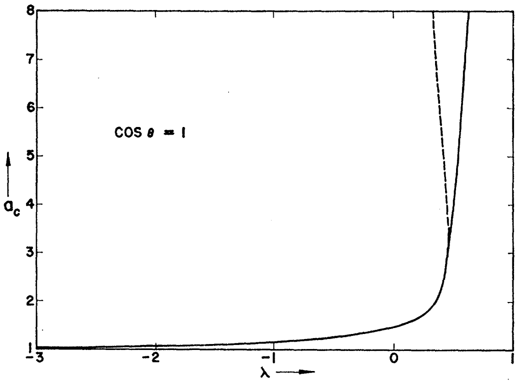

FIG. 1. a_c, which is inversely proportional to the Curie temperature, vs λ, along the z axis. The solid line, which is the correct solution, is determined by the "initial tangency condition" up to $a_c=3$. The dashed line is the continuation of Eq. (16) above $a_c=3$.

For $\lambda \leqslant 0.4621$ both numerator and denominator are negative, and there are small, real $\langle S_\zeta\rangle$ solutions. However, for $\lambda > 0.4621$, the denominator (the third derivative) remains positive as a decreases, and $\langle S_\zeta\rangle$ *drops discontinuously to zero* from some value at which the small $\langle S_\zeta\rangle$ expansion is invalid. For a slightly greater than the lower solution of Eq. (17), r rises with slope less than unity and crosses the 45° line twice. The limiting a_c is that one for which r rises to just touch the 45° line. There does not appear to be a simple explicit expression for a_c in this range, but a is plotted vs λ in Fig. 1.

iv. $0.4631<\lambda<1$

r starts with small positive slope and third derivative, at large a. There are two crossings, approaching $\langle S_\zeta\rangle=1$ as $a\longrightarrow\infty$. As a decreases, r rises in initial slope, but never reaches slope one. The upper crossing moves down to a finite value at which the r curve just touches the 45° line. This determines a_c. As λ approaches one, a becomes infinite, and the Curie temperature goes to 0°K.

v. $1\leqslant\lambda$

When the anisotropy energy exceeds the exchange energy the only solution of Eq. (13) is $\langle S_\zeta\rangle=0$, as previously discussed.

B. Discussion of the cosθ = 1 Case

In Fig. 1 we show the solution of Eq. (16) over the entire range of positive a. This curve gives the correct Curie point a_c up to $a_c=3$. Above this value we also plot the correct solution for a_c vs λ. For large negative λ, a_c approaches 1, that is, kT_c approaches the exchange energy. As λ rises to zero, the anisotropy energy becomes less helpful in holding the spins together, and the Curie temperature drops to $kT_c=\frac{2}{3}\cdot$exchange energy at $\lambda=0$. Positive λ corresponds to harder directions. Here the anisotropy tends to spread the spins apart, and the spontaneous ordering disappears at a lower thermal energy. As the hard anisotropy approaches the exchange energy ($\lambda\longrightarrow 1$), the Curie temperature drops to 0°K.

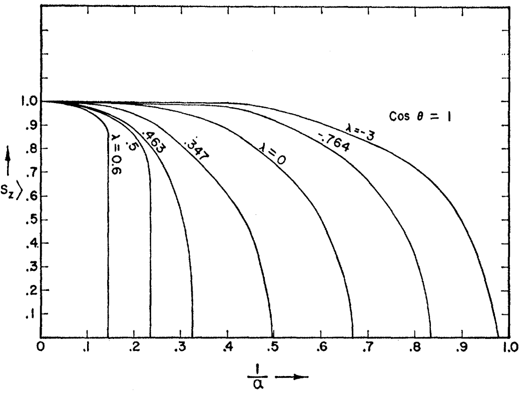

FIG. 2. Magnetization as a function of temperature in the z direction, for various values of λ.

In Fig. 2 we plot magnetization curves for a number of values of λ. For any particular exchange energy, rising $1/a$ corresponds to increasing temperature. For λ less than 0.4621 the magnetization drops smoothly to zero, but in the region in which λ is greater than 0.4621, the magnetization drops abruptly to zero.

C. Curie Temperature

The analysis of the relatively simple case in which the magnetization is along the z axis shows that the Curie temperature is determined by the usual lowest order condition (tangency at the origin) only for λ less than a particular value. In this range of λ for which this tangency condition is valid it is possible to derive an expression for the dependence of the Curie temperature on orientation which reduces to Eq. (16) for $\cos\theta=1$. Let

$$p\equiv 9\langle S_\zeta\rangle^2/\lambda^2, \tag{19}$$

and

$$P_2\equiv 3\cos^2\theta-1, \tag{20}$$

and expand $\cos\phi$ in Eq. (10). This leads to

$$\phi^2\cong p(1+P_2)+p^2\left[\frac{(1+P_2)^2}{12}-\frac{(\frac{5}{6}+P_2)}{2}\right], \tag{21}$$

and

$$\cos(\phi/3)\cong 1-\frac{p}{18}(1+P_2)+p^2\left[\frac{(\frac{5}{6}+P_2)}{36}-\frac{(1+P_2)^2}{3^5}\right]. \tag{22}$$

In Eq. (9) we find

$$x_0\cong\frac{2\lambda}{3}\left[1+\frac{p}{9}(1-\tfrac{1}{2}P_2)+\frac{p^2}{3^5}(-1+\tfrac{5}{2}P_2-P_2^2)\right]. \tag{23}$$

From Eq. (9),

$$x_1=-\tfrac{1}{2}x_0-\sqrt{3}(-\tfrac{1}{3}c_1)^{\frac{1}{2}}\sin(\phi/3), \tag{24}$$

and

$$x_2 = -\tfrac{1}{2}x_0 + \sqrt{3}\left(-\tfrac{1}{3}c_1\right)^{\frac{1}{2}} \sin(\phi/3), \tag{25}$$

So that we must find the approximate expansion for $\sin(\phi/3)$ from Eq. (21) this is

$$\sin(\phi/3) \cong \tfrac{1}{3}(1+P_2)^{\frac{1}{2}} p^{\frac{1}{2}}. \tag{26}$$

From these equations we get

$$x_1 \cong \frac{-\lambda}{3}\left[1 + \left(\frac{1+P_2}{3}\right)^{\frac{1}{2}} p^{\frac{1}{2}} + \frac{p}{9}\left(1-\tfrac{1}{2}P_2\right) + \frac{p^2}{3^5}\left(-1+\tfrac{5}{2}P_2 - P_2^2\right)\right], \tag{27}$$

$$x_2 \cong \frac{-\lambda}{3}\left[1 - \left(\frac{1+P_2}{3}\right)^{\frac{1}{2}} p^{\frac{1}{2}} + \frac{p}{9}\left(1-\tfrac{1}{2}P_2\right) + \frac{p^2}{3^5}\left(-1+\tfrac{5}{2}P_2 - P_2^2\right)\right]. \tag{28}$$

It is our intention to expand up to the lowest order terms in p and to substitute into Eq. (11), in the more convenient form

$$\sum_k e^{ax_k} = \sum_k \frac{1}{\langle S_\zeta\rangle} \frac{\partial x_k}{\partial\langle S_\zeta\rangle} e^{ax_k}. \tag{29}$$

This will lead to an equation of the form

$$A(\lambda,a,P_2)p^2 + B(\lambda,a,P_2)p + C(\lambda,a,P_2) = 0 \tag{30}$$

in analogy with (15). But now the equation is too complicated to allow of the easy analysis of section A, so we content ourselves with the determination only of the Curie point $a_c(\lambda,P_2)$ without investigation of the region of validity of Eq. (30). Hence in our expansions in Eq. (29) we need only find the constant term $C(\lambda,a,P_2)$.

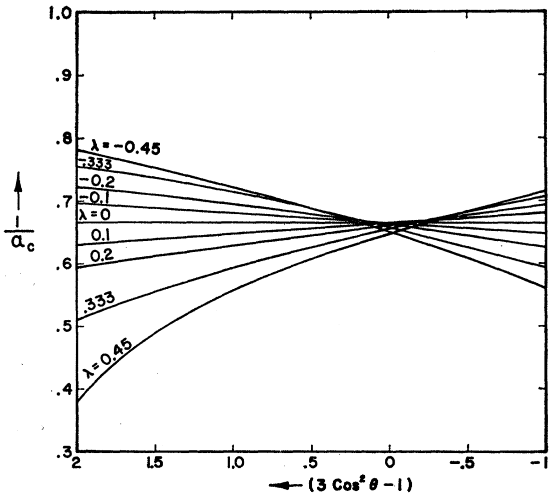

FIG. 3. Curie temperature as a function of direction in the "initial tangency" region, for various λ.

To this approximation, from (24), (25), (27), and (28),

$$\sum_k e^{ax_k} \cong e^{2\lambda a/3} + 2e^{-\lambda a/3}, \tag{31}$$

and

$$\frac{1}{\langle S_\zeta\rangle}\frac{\partial x_0}{\partial\langle S_\zeta\rangle} \cong \frac{3}{\lambda}\frac{4}{9}\left(1-\tfrac{1}{2}P_2\right),$$

$$\frac{1}{\langle S_\zeta\rangle}\frac{\partial x_1}{\partial\langle S_\zeta\rangle} \cong -\frac{3}{\lambda}\left[\left(\frac{1+P_2}{3}\right)^{\frac{1}{2}} p^{-\frac{1}{2}} + \frac{2}{9}\left(1-\tfrac{1}{2}P_2\right)\right], \tag{32}$$

$$\frac{1}{\langle S_\zeta\rangle}\frac{\partial x_2}{\partial\langle S_\zeta\rangle} \cong -\frac{3}{\lambda}\left[-\left(\frac{1+P_2}{3}\right)^{\frac{1}{2}} p^{-\frac{1}{2}} + \frac{2}{9}\left(1-\tfrac{1}{2}P_2\right)\right],$$

Expanding the exponentials up to terms of order $\frac{1}{2}$ in p, and multiplying by (32), gives

$$\sum_k \frac{1}{\langle S_\zeta\rangle}\frac{\partial x_k}{\partial\langle S_\zeta\rangle} e^{ax_k} \cong e^{2\lambda a/3}\left[\frac{4}{3\lambda}\left(1-\tfrac{1}{2}P_2\right)\right] + e^{-\lambda a/3}\left[-\frac{6}{\lambda}\right]\left[\frac{2}{9}\left(1-\tfrac{1}{2}P_2\right) - \frac{\lambda a}{3}\left(\frac{1+P_2}{3}\right)\right]. \tag{33}$$

Substituting (31) and (33) into (29) yields

$$\left(\frac{1+P_2}{3}\right)a_c - \left[\frac{1}{2} - \frac{2}{3\lambda}\left(1-\tfrac{1}{2}P_2\right)\right]e^{\lambda a_c} = 1 + \frac{2}{3\lambda}\left(1-\tfrac{1}{2}P_2\right). \tag{34}$$

This equation determines a_c as a function of λ, the ratio of anisotropy to exchange, and P_2, the direction of the magnetization. When the magnetization is along the z axis, $P_2=2$, and Eq. (34) reduces to Eq. (16). The upper bound on λ for which this "initial tangency" condition (34) indeed determines the Curie point has not been investigated. But in Fig. 3 we plot $1/a_c$ as a function of $P_2(\cos\theta)$ for a number of values of λ within the range of validity of Eq. (16). It is seen that for positive λ, when the z axis is the hard direction, the Curie temperature is lower than in an isotropic material ($\lambda=0$). As the magnetization is rotated toward the easy direction, T_c rises, for any particular exchange interaction, reaching the isotropic value near $P_2=0$, for small λ, and rising to a maximum in the easy direction.

D. Range of Validity

We have envisioned a series of measurements in which an external aligning magnetic field is reduced in magnitude, and the resultant moment extrapolated to zero field. But if the anisotropy energy is larger than the exchange, in relatively hard directions, the presence of the external field will have a critical effect on the magnetization, and its omission leads to troubles with the second law of thermodynamics. In this section we wish to consider the limits on λ, for any particular orientation, within which the magnetization behaves properly at zero temperature. For λ outside this range, our treatment would lead to a reduced magnetization less than one, and a nonzero entropy at zero degrees. The inclusion of the external field is then essential.

In Eq. (11), if x_0 specifies the largest root, which must be greater than zero by Eq. (7), it will be seen that as $T\rightarrow 0$,

$$\langle S_\zeta\rangle \xrightarrow[T\rightarrow 0]{} \frac{\partial x_0}{\partial\langle S_\zeta\rangle}. \tag{35}$$

From Eq. (6), differentiating with respect to $\langle S_\zeta\rangle$ and collecting terms,

$$x'=\frac{c_1'x-c_0'}{3x^2-c_1}, \tag{36}$$

where the prime designates differentiation with respect to $\langle S_\zeta\rangle$. Then from Eq. (35), to have $\langle S_\zeta\rangle_{T\rightarrow 0}\rightarrow 1$, we require that

$$3x_0^2-c_1=c_1'x_0-c_0' \tag{37}$$

in the limit. Solving for x_0, and substituting the appropriate values of the coefficients from Eq. (8),

$$x_0=\frac{1+\frac{5}{6}\lambda P_2+\frac{1}{3}\lambda^2-\frac{1}{3}\lambda^3}{1+\lambda P_2+\lambda^2}. \tag{38}$$

It will be seen that when $P_2=2$, this reduces to the root $x=1-\frac{1}{3}\lambda$, of Eq. (12). We must now ensure that this root of unit derivative is indeed the largest root. For example, in the case $P_2=2$, with one root equal to $1-\frac{1}{3}\lambda$, the cubic can be factored, and the next largest root is found to be equal to $\frac{2}{3}\lambda$. Setting

$$1-\tfrac{1}{3}\lambda>\tfrac{2}{3}\lambda, \tag{39}$$

we find our solution to be acceptable only if

$$\lambda<1, \tag{40}$$

which is the limit previously discussed.

In general, utilizing the relations

$$\begin{gathered}\textstyle\sum_k x_k=0,\\ x_0x_1+x_1x_2+x_2x_0=-c_1,\\ \textstyle\prod_k x_k=-c_0,\end{gathered} \tag{41}$$

we solve for the next largest root, x_1, which is the larger solution of

$$x_1^2+x_0x_1-c_0/x_0=0, \tag{42}$$

and of

$$x_1^2+x_0x_1+x_0^2-c_1=0.$$

Setting

$$x_1\leqslant x_0, \tag{43}$$

the limiting conditions become

$$x_0\geqslant (c_0/2)^{\frac{1}{3}}\big|_{\langle S_\zeta\rangle=1}, \tag{44a}$$

$$x_0\geqslant (c_1/3)^{\frac{1}{2}}\big|_{\langle S_\zeta\rangle=1}, \tag{44b}$$

with x_0 given by Eq. (38) and c_0 and c_1 by (8). The more restrictive of conditions (44) must be satisfied. It is cumbersome to solve these for λ as a function of $P_2(\cos\theta)$.

In the case of $P_2(\cos\theta)=2$, both conditions reduce to Eq. (40). In the case $P_2(\cos\theta)=0$, condition (44a) becomes

$$1+\tfrac{1}{3}\lambda+\tfrac{1}{3}\lambda^2>0,$$

which is satisfied for all λ, while condition (44b) becomes

$$\lambda<0.797$$

In the case $P_2(\cos\theta)=-1$, inequality (44b) becomes

$$-9<\lambda.$$

Thus, if we restrict λ to be less than 0.797 and greater than -1, we are able to consider experiments in which the magnetization is rotated in direction, at any temperature, without fear of violation of the requirements of thermodynamics, and without explicit inclusion of the external field.

E. Magnetization in an Arbitrary Direction

When the magnetization is in other than the z direction, the operators in the Hamiltonian no longer commute, the cubic does not factor, and the solution of Eq. (11) is something of a chore though the qualitative nature of the solutions turns out to be much the same. With the aid of the NOL 704 computer, we have obtained solutions for several values of λ, varying both a and the angle θ. In Fig. 4 we plot a few representative curves of the magnetization, $\langle S_\zeta\rangle$, as a function of orientation, for particular choices of reduced temperature and anisotropy ratio λ. Both the continuous and discontinuous curves occur. The most dramatic results are to be found at low a values, at temperatures close below the Curie temperature in the easy direction. For example, in the case of $\lambda=0.5$, $a=1.75$, when the magnetization lies in the basal plane, $\langle S_\zeta\rangle$ is about 0.7. As the magnetization is rotated toward the z axis its

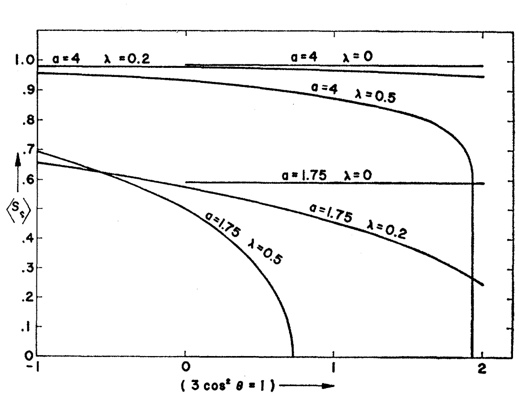

FIG. 4. Magnetization as a function of direction for various temperatures and λ.

magnitude drops, going to zero when $(3\cos\theta-1)$ is equal to 0.72. For comparison, the values of $\langle S_\zeta \rangle$ for no anisotropy, for the two particular temperatures selected, are shown on the figure.

III. DISCUSSION

We have diagonalized exactly the Hamiltonian of a spin 1 ferromagnet with uniaxial anisotropy, in the internal field approximation. The results, first of all, confirm an earlier perturbation calculation[1] on the orientation dependence of the magnetization. The magnetization drops off with increasing temperature more slowly (as a higher power of T) than the isotropic magnetization, in easier directions, and more rapidly (lower power of T) in harder directions. This is consistent with observations which have been made in easy directions on several metals. For example, Behrendt, Levgold, and Spedding[2] have found the saturation moment of dysprosium to follow a T^2 rather than a $T^{\frac{3}{2}}$ law, in the easy direction, which is in the basal plane. Niira[3] has carried out an anisotropic spin-wave calculation, for this case, which agrees with experiment. Recently Argyle and Pugh[4] have measured the temperature dependence of the magnetization of nickel, and find a 1.6 power law to be approximately correct. It would be worthwhile to measure the temperature dependence of the magnetization in the hard direction of a sufficiently anisotropic material, to see if it indeed drops off as a lower power of the temperature than the three halves. It is interesting that in dysprosium Behrendt, Levgold, and Spedding find that, with the magnetic field parallel to the c_0 axis, the magnetic moment is a linear function of the field, as is true of the moment in the basal plane above the Néel temperature. The paramagnetic Curie temperature obtained for the field in the hard direction is 121°K, while that in the basal plane is 169°K. The complicated spin arrangements now being uncovered in the rare earths disqualify most of them for a direct application of the present analysis.

Charap[5] has also considered the effect of magnetic anisotropy on the magnetization. As the isotropic states he uses spin waves, and the perturbation, which is taken as pseudodipolar coupling, is carried to second order, to arrive at an anisotropic magnetization with cubic symmetry, which is the case Charap treats. The result here is exactly the opposite of our own; the magnetization is reduced in easy directions and enhanced in hard ones. This interesting result comes about by the nature of second order perturbation theory, Charap points out.

However, Charap's treatment is restricted to the low-temperature range, in which spin-wave theory is valid, while our molecular field treatment is reasonably good in the neighborhood of the Curie temperature, with which this paper is primarily concerned.

While the present expanded version of this research was in progress there appeared a related analysis of an antiferromagnet with uniaxial anisotropy. The author, Cooper,[6] investigates the temperature dependence of the sublattice magnetization in the easy direction only, and finds, in agreement with the present work, that the reduced sublattice magnetization is shifted noticeably upward from the Brillouin function. Where the present work is restricted to the internal field approximation, Cooper also considers the effect of spin correlations.

For very anisotropic materials the shapes of the magnetization vs temperature curves depart markedly from the Brillouin function, even dropping discontinuously to zero from quite large values of the reduced moment. Dwight and Menyuk[7] have measured the magnetic properties of a single crystal of Mn_3O_4 as a function of temperature. They find the c axis to be the hard direction, with an anisotropy field of about 10^5 oersteds, and with large anisotropy, about 10^4 oersteds in the basal plane. The Curie temperature is about 42°K. Analysis of their data leads Dwight and Menyuk to the conclusion that canted spin arrangements exist in this material. Thus some of the spins find themselves in hard directions which may be why the authors find magnetization curves more "square" than a Brillouin function, though again our analysis of a simple ferromagnet can at best be only qualitatively applied to a complex spin arrangement.

For fixed temperature, as the magnetization is rotated away from the easy direction, the magnetization drops off in magnitude. In a perturbation calculation the Curie temperature is, however, independent of the magnetization direction. The question of the angular dependence of the Curie temperature was raised by Carr, when the results of the perturbation calculation were first made known. Exact calculation now corroborates this expectation; the anisotropy energy, holding the spins together in the easy direction and spreading them in a hard one, raises the Curie temperature in the former case and lowers it in the latter. This is at least suggestive of the results of Behrendt, Levgold, and Spedding discussed above. To achieve the unusually large values of λ of interest here, the materials must have very low exchange energy, hence a low Curie point, and a large anisotropy, hence usually lower than cubic symmetry.

One such interesting material is ludlamite, which Bozorth and Kramer[8] find to have a Curie temperature of 20°K and a uniaxial anisotropy field greater than 12 500 oersteds, so that λ is in excess of 0.1. Ludlamite,

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which is monoclinic, is ferromagnetic along the easy twofold *b* axis, but paramagnetic behavior was observed in all perpendicular directions.

Another crystal of large anisotropy is pyrrhotite, Fe_7S_8, first studied by Weiss[9] and later by Weiss and Foex.[10] In this hexagonal crystal the *c* axis is hard, but there is also considerable anisotropy in the basal plane. At room temperature the crystal is paramagnetic along the *c* axis, and ferromagnetic in the basal plane. Low-temperature studies are unfortunately not reported.

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Galvanomagnetic Effects and the Band Structure of Antimony*

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The energy band structure of antimony is deduced from room temperature galvanomagnetic measurements and their interpretation in terms of a theoretical model. A systematic series of experiments is performed on oriented single crystals to measure all the 12 components of the isothermal resistivity tensor through second order in the magnetic field. The calculated galvanomagnetic effects assuming simple, independent three-valleyed bands for both the valence and conduction bands and isotropic relaxation times for both holes and electrons, are shown to fit the data by only one set of values for the 9 adjustable parameters in the theory. These parameters are: a set of three principal mobilities μ_i and ν_i, for electrons and holes, respectively; angles of tilt ψ_1 and ψ_2 of one of the principal axes of the electron and hole energy ellipsoids out of the base plane; and the carrier density N, the same for both carriers. The best fit is determined by exploring systematically a large number of possible solutions with the aid of an IBM 650 computer. If the "1" directions refer to binary symmetry axes and the "3" directions to those making angles ψ with the trigonal symmetry axis, the parameters have the values $\mu_1=0.15_4\times10^3$, $\mu_2=4.0_5\times10^3$, $\mu_3=1.1_8\times10^3$, $\nu_1=3.5_6\times10^3$, $\nu_2=3.3_0\times10^3$, $\nu_3=0.13_8\times10^3$ (all in cm^2/volt-sec); $\psi_1=30._7°$, $\psi_2=63._2°$; $N=3.7_4\times10^{19}$ carriers/cm^3$=1.0_5\times10^{-3}$ carriers/atom. The results agree well with Shoenberg's de Haas-van Alphen data if the carriers responsible for the observed susceptibility oscillations are holes.

I. INTRODUCTION

THE general features of the electrical conduction processes in Sb have been known for some time.[1] They are attributed to a small though degenerate carrier population consisting of an equal number of both electrons and holes, with at least one of the overlapping bands multivalleyed. The energy surfaces of each valley are generally represented by ellipsoids tilted with respect to crystal axes.

The purpose of the present work has been to carry out a complete set of low-field room temperature galvanomagnetic (GM) measurements and to interpret these in terms of a general multivalley model for the bands. If the model is qualitatively correct, this procedure will determine the band structure. Partial interpretations of this nature have been worked out before on sets of data which were sufficient to specify only special multivalley structures. In this work the emphasis is on a systematic analysis of an overcomplete set of data permitting determination of all the nine parameters of a general multivalley model.

The presentation falls into three parts: (1) A series of experiments to determine all room temperature GM constants through second order in the magnetic field; (2) The calculation of GM effects for a model containing 9 adjustable parameters; (3) The adjustment of these parameters to obtain a best fit with experiment which then serves to specify quantities related to the band structure.

II. EXPERIMENTAL DESIGN

If the magnetic field dependence of the isothermal resistivity tensor can be expressed as a rapidly convergent series in powers of the field, a relatively small number of low-field measurements suffices to obtain all pertinent GM information for a finite parameter model. The number of independent coefficients appearing in the expansion depends on crystal symmetry, and the identification of these phenomenological constants in the Sb point group $\bar{3}m$, for transport processes characterized

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