[14] E. I. Zornberg, Phys. Rev. B 1, 244 (1970).
[15] H. A. Mook, Phys. Rev. 148, 495 (1966).
[16] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. 152, 505 (1966).
[17] M. Blume, Phys. Rev. 124, 96 (1961).
[18] M. Diana, G. Mazzone and J. J. DeMarco, Phys. Rev. 187, 973 (1969).

PHYSICAL REVIEW B VOLUME 7, NUMBER 3 1 FEBRUARY 1973

Relaxation Time of Superparamagnetic Particles with Cubic Anisotropy

Amikan Aharoni*
Department of Electronics, The Weizmann Institute of Science, Rehovoth, Israel

(Received 6 August 1971)

The superparamagnetic relaxation time is calculated for spherical particles with cubic magnetocrystalline anistropy, whose easy axis is either [100] or [111] in zero applied field. Results are reported for relatively small particles only, in which no anomaly is found. It is concluded that the experimentally observed anomaly in this size region must be due to incoherent magnetization reversals.

I. INTRODUCTION

A magnetized ferromagnetic particle has to overcome an energy barrier before the direction of its magnetization can be changed. Since this barrier is proportional to the volume of the particle, the probability of a spontaneous flip of direction, by thermal agitation, is negligibly small for relatively large particles. However, if the particles are very small, thermal agitation can cause many changes in the direction of the magnetization in each particle during the time of measurement. An assembly of such particles will therefore reach a thermal equilibrium for the statistical distribution of magnetization orientations, and its measured magnetic properties will be similar to those of an ensemble of paramagnetic atoms. This phenomenon is called "superparamagnetism" and has been observed by many workers.[1]

The usual theoretical study of the relaxation time associated with these thermal fluctuations[1] is based on the assumption that the magnetic moments of the particles are always in one of the two energy minima, and do not spend any time in between. Such a discrete orientation model leads to a relaxation time τ which can be approximated by

$$\tau = f_0^{-1} e^{E_B/kT}, \tag{1}$$

where T is the temperature, k is Boltzmann's constant, and E_B is the barrier energy. Different authors use different values for the parameter f_0, but it is just taken as a constant, which varies roughly between 10^{10} and 10^9 sec^{-1}.

This vague approach has been put on a much sounder basis by Brown,[2] who considered the magnetization vector in each particle as changing its direction continuously, in response to some random forces. Brown still kept the conventional assumption that each particle is a "single domain," namely, that the magnetization vector is constant within each particle during all the stages of its reversal. But he did not use any other arbitrary assumption. By using the theory of stochastic processes for a white spectrum of agitation forces, he wrote a rigorous Fokker–Planck-type differential equation which yields the relaxation time as its eigenvalue. He also showed that for the case of a uniaxial anisotropy in zero applied field, the asymptotic value of the relaxation time (in the limit of a very large barrier compared to kT) is given by Eq. (1) in which f_0 is *not* a constant. Rather,

$$f_0 = 2K\gamma_0(\alpha/\pi)^{1/2}/M_s, \tag{2}$$

where K is the anisotropy constant, γ_0 is the gyromagnetic ratio, M_s is the saturation magnetization, and

$$\alpha = KV/kT, \tag{3}$$

where V is the volume of the particle. This asymptotic formula was later shown to be a very good approximation to the actual eigenvalue in uniaxial ferromagnets, down to α of the order of 1, without,[3] or even with[4] an applied magnetic field. This result is often quoted as a proof for the constancy of f_0, which is not quite the case, although the difference is not always very significant.[5]

For materials with cubic anisotropy, no rigorous computations of the relaxation time have ever been tried; this seems necessary after many experimental studies of superparamagnetism in cubic materials have been published in recent years, in which the results are still analyzed by (1) with a *constant* f_0. Moreover, in a recent experiment[6] a case was found in which τ is not a monotonically increasing function of the particle radius. This effect was explained as resulting from incoherent rotation of the magnetization in the particle,[6] which might or might not be an adequate explanation, but its theory is based on Eq. (1) with a constant f_0 (besides other rough approximations to be discussed in Sec. IV). Therefore, it seems particularly interesting to investigate the more rigorous relaxation time, as obtained from Brown's differential equation, for this case of a cubic anisotropy, even though this equation is limited only to the case of coherent rotations of the magnetization.

II. THEORY

It is assumed that the magnetization in each particle is always a constant, so that its direction is defined by the two polar angles θ and ϕ measured from one of the easy axes. For a cubic anisotropy in zero applied field with [100] an easy axis, the energy density for each particle can then be written as

$$F=\tfrac{1}{4}K(\sin^2 2\theta+\sin^4\theta\sin^2 2\phi), \tag{4}$$

where $K>0$, and the second-order anisotropy is neglected. If the easy axis is [111], the same expression can be used, with $K<0$. Substituting in Brown's differential equation for the stochastic process,[2] using the same transformation for the probability function as in all other calculations,[2-4] and assuming that the dissipation constant assumes its value[2] which minimizes the eigenvalue λ, Brown's differential equation becomes

$$(\lambda+\Lambda)\Phi+\alpha(A-B-C)\frac{\partial\Phi}{\partial\phi}-\alpha(A+B-C)\sin\theta\frac{\partial\Phi}{\partial\theta}=0. \tag{5}$$

Here Φ is proportional to the probability density distribution function, α is as defined in (3), and the other notations are

$$A=\tfrac{1}{2}\cos\theta\,(7\cos^2\theta-3), \tag{6a}$$

$$B=\tfrac{1}{2}\sin^2\theta\sin 4\phi, \tag{6b}$$

$$C=\tfrac{1}{2}\sin^2\theta\cos\theta\cos 4\phi, \tag{6c}$$

$$\Lambda=\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\,. \tag{6d}$$

The relaxation time τ is related to the *smallest* nonvanishing eigenvalue λ of (5) according to

$$\lambda=2VM_s/(\gamma_0 kT\tau). \tag{7}$$

In order to solve (5), Φ is expanded in the eigenfunctions of the operator Λ,

$$\Phi(\theta,\phi)=\sum_{l,m}a_{l,m}P_l^m(\cos\theta)\,e^{im\phi}, \tag{8}$$

where P_l^m are the associated Legendre functions of the first kind, $a_{l,m}$ are complex numbers, and $l\geqslant m\geqslant 0$ are integers.

Substituting Eq. (8) in (5), and shifting m indices, the dependence on ϕ can be made of the form

$$\sum_m F_m(\theta)\,e^{im\phi}=0, \tag{9}$$

which can be fulfilled for every m only if each F_m vanishes. Similarly, by shifting indices and using the recurrence relations between the associated Legendre functions, the θ dependence is only through a single P_l^m, so that its coefficient should vanish. This leads, then, to an infinite set of algebraic equations:

$$\sum_{k=-4}^{4}[A_k(l,m)a_{l+k,m+4}+B_k(l,m)a_{l+k,m}+C_k(l,m)a_{l+k,m-4}]=0, \tag{10}$$

which should hold for every integral l and m, provided $l\geqslant m\geqslant 0$. The values of the 27 coefficients A_k, B_k, and C_k are listed in the Appendix. It should be noted particularly that λ and α appear only in B_0, all the other coefficients being constant numbers.

The actual (complex) values of $a_{l,m}$ do not have any physical significance, and all one is interested in are the eigenvalues λ for which a nonvanishing solution of the set of Eqs. (10) exists. The necessary and sufficient condition for the existence of such a solution is that the (infinite) determinant of the coefficients of $a_{l,m}$ in (10) vanishes. The problem can thus be reduced to a conventional diagonalization of a complex matrix, if the two indices l and m are reduced to a single one by an appropriate ordering procedure. The order chosen was to count all the allowed values of m for a given l before jumping to the next value of l. This means that each pair (l,m) is replaced by the single index

$$n=\tfrac{1}{2}l(l+1)+1+m. \tag{11}$$

III. COMPUTATIONS AND RESULTS

The diagonalization of the infinite matrix was carried out by diagonalizing some finite-order matrix, then increasing the order and repeating the computations until a further increase in the order of the matrix made a negligible change in the value of the smallest nonvanishing eigenvalue λ. For such a computation the choice of Eq. (11) was very convenient, because standard methods for matrix diagonalization could be used (the actual calculation was done using subroutines available in the computer library). However, this choice of (11) is rather wasteful in terms of computer memory requirements, because it calls for defining large complex matrices, which take many memory cells, although most of these matrix elements are zeros, and the real and imaginary parts are actually separate. The computer on which these computations were done (ICL 1906A) could satisfactorily handle a complex matrix only up to an order of about 100.

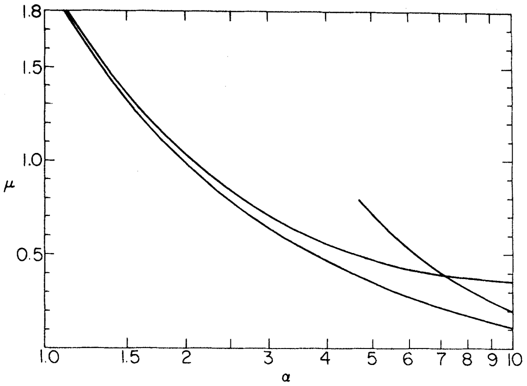

FIG. 1. Parameter μ which is inversely proportional to the theoretical superparamagnetic relaxation time τ, according to Eq. (12), for cubic anisotropy with [100] the easy axis, i.e., Eq. (4), with $K > 0$. The abscissa α is defined in Eq. (3), and is proportional to the energy barrier.

This enabled the computations of eigenvalues with the absolute value of the parameter α, defined in Eq. (3), not exceeding about 10. Even for these, the standard accuracy of the 1906A was not sufficient, and certain parts of the computations had to be done with double precision. Some computations were done with a matrix order up to 135, but it was not easy to push the computer that far, and it would not be pushed further. Therefore, for larger values of $|\alpha|$ this method is not practical, and some transformation of the matrix must be used.

In plotting the results it seems more appropriate to plot $\mu = \lambda/|\alpha|$, rather than λ, since this μ is better related to the relaxation time. Actually, according to (3) and (7),

$$\mu = 2M_s/(\gamma_0|K|\tau). \tag{12}$$

The results for this parameter as a function of α are plotted in Fig. 1 for a positive α (i.e., with the easy axis along [100]), and in Fig. 2 for a negative α (i.e., with the easy axis along [111]). In both cases the three lowest eigenvalues are shown in order to reveal the basic computational difficulty inherent to this region of small $|\alpha|$ values, namely, that the eigenvalues are rather close together. This causes difficulties in most numerical methods for matrix diagonalization, and is evidently the reason for strange behavior in earlier attempts[7] to solve this problem. Moreover, the experimental results should also, in principle, be analyzed in this region in terms of more than one relaxation time. Although generally it is only the smallest value of $1/\tau$ which affects the measurements, the case of two nearly equal eigenvalues is different, and they both should be taken into account. If this is ignored, the results might seem somewhat strange, even though from Figs. 1 and 2 it does not seem likely that they could yield a relaxation time τ which is not a monotonically increasing function of $|\alpha|$.

As has been mentioned in the foregoing, computations beyond the region plotted in Figs. 1 and 2 call for impractically large matrix order. However, some values were computed, and from them it seems that the *lowest* eigenvalue continues to decrease smoothly, and there is no crossover similar to the one seen in the two *upper* eigenvalues in Fig. 1. At any rate, even if such a crossover does occur eventually, it can lead only to an incontinuous derivative of the smallest eigenvalue, which will still be a monotonically decreasing function of α.

IV. DISCUSSION

Afanas'ev *et al.*[6] have measured at different temperatures the fraction of stable and superparamagnetic particles for various samples of fine particles made of the Fe-Ni alloy with 37-at.% Ni. The fraction of superparamagnetic particles usually decreases with increasing particle size, but they find that in changing from an average diameter of 120 to 190 Å, there is an *increase* in the fraction of superparamagnetic particles at several temperatures. This increase is quite small, being hardly above the reported experimental accuracy. It *might* be just a manifestation of slightly different physical properties of the samples with 120- and 190-Å average diameters, since these properties are very sensitive to the exact composition of the alloy[8] in the vicinity of 37-at.% Ni. It is also possible that the increase is due to a somewhat different shape of the particles in the two samples, because they cannot all be quite spherical, and elongation is known[9] to cause a very significant change in the fraction of superparamagnetic particles. However, a very similar anomaly has already been observed by Weil in fine particles of Ni as one of the earliest

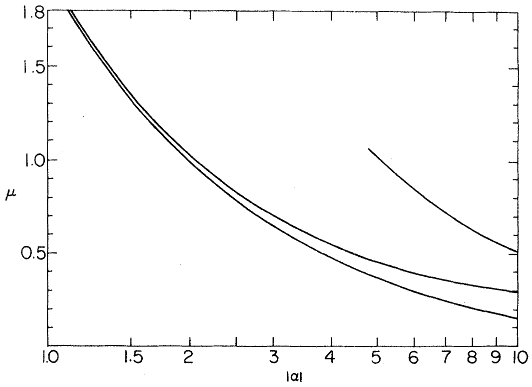

FIG. 2. Same as Fig. 1 for the case of a cubic anisotropy with the easy axis along [111], i.e., Eq. (4), with $K < 0$.

studies of superparamagnetism.[10] The results were then interpreted in terms of a gap in the distribution function of particle sizes, which is of course possible but somehow does not seem very likely. When asked about that strange distribution in the discussion, Weil[10] claimed that it was "undoubtedly" due to the particular sample preparation and that it would be interesting to study differently prepared Ni particles by the same method. In the meantime, another and more pronounced gap in the distribution was found necessary in order to account for the superparamagnetic behavior of some nickel-lead alloys.[11] Again, it is possible that such a gap exists, but it seems more reasonable to assume, as Afanas'ev *et al.* do, that the distribution function is smooth, but that there is a region in which τ decreases with increasing particle volume. This will cause certain small particles to behave as if they were much larger, and will lead to the experimental results of Weil[10] or Müller[11] without the gap in the distribution function.

For the alloy with 37-at.% Ni, Afanas'ev *et al.*[6] report a positive K, of the order of 10^4 erg/cm^3. Even though by comparing to data[8] on similar alloys one expects this K to vary quite considerably with temperature, the region in which the anomaly was observed must be within the region plotted in Fig. 1. Since the theoretical curve does not show this anomaly, it must be caused by something neglected in the theory, and the *argument* of Afanas'ev *et al.* about the reversal of the magnetization by the curling mode seems very plausible. It is known[12] that for a sphere whose radius is small enough, the state of lowest free energy, in zero applied field, is that of a uniform magnetization. But this does not mean that *during the magnetization reversal* the state of uniform magnetization is conserved, and thermal agitation might excite some nonuniform state before causing a complete reversal. This has also been noted by Dunlop and West[5] who realize that magnetization curling, or other nonuniform processes, might take place in a certain size region, although their[5] conclusion is that this range is sufficiently narrow so that its effect is usually not very great. Still, the *treatment* of this problem by Afanas'ev *et al.* is not satisfactory because they assume (1), with a constant f_0, which is a very poor approximation to Fig. 1. Moreover, in order to use (1) they express the energy barrier in terms of the anisotropy constant K to which they transfer the exchange and magnetostatic terms by using the formulas for static nucleation. This can hardly do in the dynamic problem of a random walk, and the *linearized* theory of nucleation cannot be used to calculate an energy barrier since such a barrier is mainly determined by its maximum at which the linearization might not hold.[13] One thus needs a more rigorous theory for the energy barrier for incoherent reversals, preferably worked out together with the stochastic processes[14] involved.

The region plotted in Figs. 1 and 2 is only that where the energy barrier (which is[15] $\frac{1}{4}KV$ for $K > 0$, and $\frac{1}{12}|K|V$ for $K < 0$) is far from being large with respect to kT. Therefore, one does not expect the asymptotic formula (1) to hold, even approximately, and in fact it does not hold. However, one can use for this region a much simpler formula for the relaxation time. Actually, for $|\alpha| \lesssim 1$ the eigenvalue λ is 2 to a very good approximation, both for the cubic anisotropy discussed here and for uniaxial anisotropy which was treated[3] before. Therefore one obtains from (12) and (3) that in this region the relaxation time is

$$\tau = M_s V/(\gamma_0 kT). \tag{13}$$

Here as before, γ_0 is the gyromagnetic ratio (typically about 2×10^7 G^{-1} sec^{-1}) and M_s is the saturation magnetization. The anisotropy constant does not enter at all.

The region of validity of (13) is outside all practical magnetic measurements for which the "measurement time" is[15] of the order of 10^2 sec. For the Mössbauer effect, for which the measurement time which counts is[16] very close to 10^{-8} sec, Eq. (13) might well be applicable. In fact, in the region of the Afanas'ev *et al.* experiment, (13) should be a much better approximation than (1). But the experiment for which (13) should be especially applicable is the one mentioned by Roth[17] and discussed before in this context,[3] namely, to study the magnetic scattering of neutrons from fine ferromagnetic particles. In this case, if one considers neutrons whose velocity is 5000 m/sec, they spend 10^{-12} sec in a particle with a 50-Å diameter. The theoretical relaxation time, inasmuch as noncoherent rotations can be neglected, is then just (13).

However, when such short measurement times are concerned, one should be careful not to push this theory too far. Formally, the theoretical relaxation time in (13) tends to zero when the particle volume V approaches zero. But this should not be taken too literally because the theory starts with the basic assumption[2] that the response time of the spin system is very long in comparison with the correlation time of the random forces responsible for the fluctuation from the mean. Therefore, if this theory does not break down before, due to some other reasons, it will certainly break down when the time approaches the value for which the spectrum of the thermal agitation forces can no more be considered as "white." According to the estimation of Brown,[2] this spectrum may be considered as "white" down to correlation times of the order of 10^{-13} sec.

The problem of noncoherent rotations discussed before is probably not important for the very small particles. However, for these one should be careful in using the concept of the saturation magnetization M_s. Since its value at a given temperature is obtained by averaging some spin amplitude, this averaging might not be allowed for the thermal processes giving rise to superparamagnetism, for which the instantaneous rather than the average value should be used. According to a recent estimation,[18] Brown's theory, assuming a constant M_s, is valid for low temperatures but not for relatively high ones.

It is thus not clear at all if one can actually enter into the region of validity of (13) without the whole theory breaking down beforehand. In order to find that out, it should be particularly interesting to try and do the neutron-scattering experiment, as suggested by Roth, which has never been done as far as this author could find out.

ACKNOWLEDGMENTS

The early stages of this work were done with the active cooperation of R. Bijaoui, who worked hard on trying to solve Eq. (5) in a different way than the one described here, which unfortunately did not prove successful.

APPENDIX

The matrix elements, as defined in Eq. (10), are

$$A_k = (-1)^k C_k \frac{(l+m+4+k)!}{(l+m)!} \prod_{j=0}^{3-k} (l-m-j),$$

(using the convention that an empty product, for $k=4$, is 1)

$$C_4 = \frac{l+5}{(2l+3)(2l+5)(2l+7)(2l+9)},$$

$$C_3 = \frac{i}{(2l+3)(2l+5)(2l+7)},$$

$$C_2 = -\frac{2l+13}{(2l-1)(2l+3)(2l+5)(2l+7)},$$

$$C_1 = -\frac{3i}{(2l-1)(2l+3)(2l+5)},$$

$$C_0 = \frac{15}{(2l-3)(2l-1)(2l+3)(2l+5)},$$

$$C_{-1} = \frac{3i}{(2l-3)(2l-1)(2l+3)},$$

$$C_{-4} = -\frac{l-4}{(2l-7)(2l-5)(2l-3)(2l-1)},$$

$$C_{-2} = \frac{2l-11}{(2l-5)(2l-3)(2l-1)(2l+3)},$$

$$C_{-3} = -\frac{i}{(2l-5)(2l-3)(2l-1)},$$

$$B_0 = (4/\alpha)\left[\lambda - l(l+1)\right] + \tfrac{2}{5} C_0 \left[3(l-1)l(l+1)(l+2) - 5m^2(6l^2+6l-7m^2-5)\right].$$

For $k>0$,

$$B_k = C_k \frac{(l+m+k)!}{(l+m)!} D_k,$$

with

$$D_4 = 14, \quad D_3 = 14m,$$

$$D_2 = -2\left[l(l+3) - 7m^2\right],$$

$$D_1 = -2m(3l^2 - 7m^2 + 6l - 2).$$

For $k<0$,

$$B_k = C_k D_k \prod_{j=0}^{-1-k} (l-m-j),$$

with

$$D_{-1} = 2m(3l^2 - 7m^2 - 5),$$

$$D_{-2} = 2\left[7m^2 - (l-2)(l+1)\right],$$

$$D_{-3} = -14m, \quad D_{-4} = 14.$$

---

*Work done while the author was on Sabbatical leave at the Department of Metallurgy, Oxford University, England.

[1] I. S. Jacobs and C. P. Bean, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. III, pp. 271–294.

[2] W. F. Brown, Jr., Phys. Rev. **130**, 1677 (1963).

[3] A. Aharoni, Phys. Rev. **135**, A447 (1964).

[4] A. Aharoni, Phys. Rev. **177**, 793 (1969).

[5] D. J. Dunlop and G. F. West, Rev. Geophys. **7**, 709 (1969).

[6] A. M. Afanas'ev, I. P. Suzdalev, M. Ya. Gen, V. I. Gol'danskii, V. P. Korneev, and E. A. Manykin, Zh. Eksp. Teor. Fiz. **58**, 115 (1970) [Sov. Phys.-JETP **31**, 65 (1970)].

[7] R. Bijaoui, M.Sc. thesis (Weizmann Institute of Science, 1971) (unpublished).

[8] R. M. Bozorth, *Ferromagnetism* (Van Nostrand, Princeton, N.J., 1956), pp. 570–571.

[9] T. Tanaka and N. Tamagawa, Jap. J. Appl. Phys. **6**, 1096 (1967).

[10] L. Weil, J. Chim. Phys. **51**, 715 (1954).

[11] K. Müller, Z. Angew. Phys. **30**, 56 (1970).

[12] W. F. Brown, Jr., Ann. N.Y. Acad. Sci. **147**, 461 (1969).

[13] A. Aharoni, Crit. Rev. Solid State Sci. **2**, 121 (1971).

[14] G. Nienhuis, Physica (Utr.) **49**, 26 (1970).

[15] C. P. Bean and J. D. Livingston, J. Appl. Phys. Suppl. **30**, 120 (1959).

[16] L. Pfeiffer, J. Appl. Phys. **42**, 1725 (1971).

[17] W. L. Roth, Acta Crystallogr. **13**, 140 (1960).

[18] Yu. D. Tropin and G. I. Grozovskiy, Phys. Sol. Earth 7, 160 (1971).