PARAMAGNETIC HYSTERESIS

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Communicated by A. H. Wilson

Received 3 August 1939

In this paper we attempt to give a theoretical account of some curious results on the heating of iron ammonium alum by alternating magnetic fields, obtained recently by Shire and Barkla (1). The experiments were carried out at temperatures of the order of 0·2° on the magnetic scale. The following are the principal experimental results:

(1) The heating effect is proportional to the square of the amplitude of the A.C. field, at any rate until it reaches 10 gauss.

(2) The heating effect is linearly proportional to the frequency of the A.C. field.

(3) The heating effect is very sensitive to temperature, and is much increased by the application of a steady magnetic field of the order of 100 gauss. The law describing the variation of the heating with temperature and field is approximately of the form H^2/T^3.

(4) Experiments with a very impure specimen seem to show that the effect is not primarily due to ferromagnetic impurities.

From the theoretical point of view, the fact that the effect is linearly proportional to the frequency is very striking indeed. It is well known that any explanation in terms of a relaxation time leads to a heating effect which is a function of the frequency squared, and this is also true of any explanation in terms of eddy currents. The linearity suggests that the effect is really some kind of hysteresis, but then we are confronted by the difficulty that our temperatures are at least twice that found by Simon (2) for the Curie point. It is evident that this new hysteresis effect must be quite different from the ordinary hysteresis of ferromagnetic metals.

A theory of the behaviour of paramagnetic salts at low temperatures, developed by Sauer and Temperley (3), shows that at low temperatures and small fields the ionic magnets tend to set themselves in rows, consisting of magnets pointing in the same direction, but with alternate rows pointing in opposite directions. This structure can be destroyed by applying a field of the order of 200 gauss. These properties may be traced to the peculiar form of the interaction between magnetic dipoles. If we have a pair of dipoles pointing in the same direction along the line joining them, and wish to reverse both of them, there is no way of doing so without supplying a finite amount of energy. In other

https://doi.org/10.1017/S0305004100017023 Published online by Cambridge University Press

words, there is a potential barrier between the two states of equal energy. In iron alum the height of this potential barrier for even a single pair of nearest neighbours corresponds to a field of the order of 100 gauss. It is clear that similar effects will show themselves in a large assembly of ions such as a crystal. This idea was applied by Ewing (4) in an attempt to explain hysteresis in ferromagnetic metals. Owing to the fact that ferromagnetism in metals is due to exchange forces, which do not have this peculiar "directional" property, the explanation is inadequate, since no energy is required to reverse two spins pointing in the same direction if they are coupled only by exchange forces.

Since we know so little about the properties of a three-dimensional lattice of small magnets, it is very difficult to give a satisfactory theory of its behaviour, but it does seem possible to give an account of the hysteresis effects observed by Shire and Barkla in iron alum at temperatures above the Curie point. If we suppose that a certain fraction α of the spins are "locked" and unable to follow small variations of the field, so that, at every change of the A.C. field from zero to its maximum value or vice versa, the assembly only travels a fraction $1-\alpha$ of the way towards true equilibrium, it is quite easy to show that we get a hysteresis loop whose area is of the order of magnitude

$$W \sim \tfrac{1}{2}\alpha(1-\alpha)\frac{\partial I}{\partial H}(\Delta H)^2, \tag{1}$$

where W is the work lost per cycle, I is the intensity of magnetization, and ΔH is the amplitude of the A.C. field. For T above the Curie temperature and H not too large, we have

$$\frac{\partial I}{\partial H} \sim \beta\frac{N\mu^2}{kT}. \tag{2}$$

The factor β will be 7/15 for iron alum (magneton number 5), and will vary between unity and 1/3 for other salts according to the magneton number of the particular salt. Thus we have the problem of calculating α as a function of H and T.

In the first place, let us suppose that there is no field present. Since we are above the Curie point, it is clear that the antiparallel structure is destroyed and that there is no long-range order. On the other hand, there will be a certain amount of ordering of neighbours at all temperatures, which will tend to build up an antiparallel structure, similar to the state of lowest energy of the whole crystal, but on a small scale. Now, if such a structure builds up to any extent, potential barriers will be set up and we shall get the "locking effect", some ions being immobilized. Owing to the long-range nature of the magnetic forces, it is probable that quite a considerable ordered nucleus will have to be built up around a particular ion, before it can be said to be immobilized. To a first approximation, we may assume that a particular ion is immobilized if all its nearest neighbours are "right", i.e. if all of them help to build up the antiparallel structure. The

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chance of this is $\{e^{M/kT}/(e^{M/kT}+1)\}^z$, where z is the number of nearest neighbours, and M is a quantity of the order of magnitude μ^2/a^3 and thus is a measure of the interaction between the magnets.

We have also to consider that certain ions, so far from being "locked" in a potential "valley", actually have energy to spare, so that they will tend to turn over even without the application of an A.C. field. If such a "super-mobile" ion is near an immobile or "locked" ion, the energy required to turn the "locked" ion over can be supplied by the "super-mobile" ion, by the spin-spin coupling effect (5, 6). (This is very rapid compared with any of the frequencies used, so it would not of itself lead to any heating effects.) We may assume, again as a first approximation, that the condition for an ion to be "super-mobile" is that all its nearest neighbours are "wrong", the chance of which is $(e^{M/kT}+1)^{-z}$. Since each super-mobile ion will destroy the effect of one locked ion, the quantity α will be given by the *net* number of locked ions, which gives

$$\alpha \sim \frac{e^{zM/kT}-1}{(e^{M/kT}+1)^z}. \tag{3}$$

For T large this is of the asymptotic form $\alpha \sim zM/2^z kT$, but, as T decreases, the variation with T becomes more and more rapid, until M/kT approaches unity, when this tendency is reversed, and the rate of change becomes less, finally tending to zero as α tends to the asymptotic value unity at absolute zero temperature.

If we apply a steady magnetic field as well as the A.C. field, the position becomes more complex. For a large field we can deduce by an analogous kind of argument a formula of the type

$$\alpha \sim \frac{e^{2\mu Hz/kT}-1}{(e^{2\mu H/kT}+1)^z}, \tag{4}$$

since the field causes an excess of the ions to point along it and thus sets up a degree of order, which again gives rise to the "locking-effect". However, the field tends to turn all the magnets along it, while the interaction M tends to set up an antiparallel structure. In the region of small H the correct expression for α is probably very complex. Since α is always small compared with unity, we deduce from (1), (2), (3) and (4),

$$\left.\begin{aligned} W &\sim \frac{N\mu^2}{kT}\frac{7}{30}\frac{e^{zM/kT}-1}{(e^{M/kT}+1)^z} \quad (H=0), \\ W &\sim \frac{N\mu^2}{kT}\frac{7}{30}\frac{e^{2\mu Hz/kT}-1}{(e^{2\mu H/kT}+1)^z} \quad (2\mu H > M), \end{aligned}\right\} \tag{5}$$

where W is the energy lost per A.C. cycle. We have assumed M to be of the order of magnitude μ^2/a^3 and z to be the number of nearest neighbours (or at any rate

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of this order of magnitude). Since we have a good idea of the order of magnitude of both these parameters and M does not enter the second expression, the situation is that of having a single adjustable constant. If we take M to be $0{\cdot}33\ k$ then we get the best agreement with experiment if we take $z = 12$. The experimental features are well reproduced, W being approximately proportional to H^2/T^3 in the region studied experimentally, in agreement with the facts. The only discrepancy is that W seems to increase too rapidly for H large and T small, but the effect is very sensitive to a slight alteration in the temperature scale, which is imperfectly known in this region, only "magnetic" temperatures being measured. A table of calculated values is compared with values from Shire and Barkla's curves.

Table of calculated and observed values of the heating effect/cycle/gram-ion/(gauss)²

H	0		65		130		195		260	
T	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
0·07	0·090	—	—	—	—	—	—	—	—	—
0·08	0·062	0·05	—	—	—	—	—	—	—	—
0·09	0·044	0·03	—	—	—	—	—	—	—	—
0·10	0·032	0·03	0·053	0·05	—	—	—	—	—	—
0·11	0·025	0·02	0·039	0·04	0·230	—	0·770	—	—	—
0·12	0·020	0·02	0·031	0·04	0·160	0·18	0·520	0·45	—	—
0·13	0·017	0·02	0·025	0·03	0·118	0·12	0·382	0·30	0·890	—
0·14	0·014	0·01	0·021	0·03	0·088	0·11	0·296	0·24	0·670	0·42
0·15	0·011	0·01	0·017	0·025	0·069	0·09	0·219	0·20	0·519	0·33
0·16	0·010	<0·01	0·014	0·02	0·056	0·07	0·169	0·17	0·405	0·25
0·17	0·008	<0·01	0·012	0·02	0·046	0·06	0·127	0·13	0·311	0·21
0·18	—	—	0·011	0·01	0·037	0·05	0·101	0·11	0·243	0·19
0·19	—	—	0·009	0·01	0·031	0·04	0·083	0·10	0·200	0·17
0·20	—	—	0·005	<0·01	0·027	0·03	0·069	0·09	0·164	0·14
0·25	—	—	—	—	0·014	0·02	0·034	0·05	0·064	0·08
0·30	—	—	—	—	0·009	0·01	0·018	0·02	0·034	0·06

We have not allowed for the approach of saturation, which is appreciable for fields of the order of 200 gauss. We might expect this to lead to different values of W when the steady field is parallel or perpendicular to the A.C. field, because $\partial I/\partial H$ will be different in the two cases. For moderate values of H we should have $\frac{W_\parallel}{W_\perp} \sim \left(\frac{\partial I}{\partial H}\right)_H \Big/ \left(\frac{\partial I}{\partial H}\right)_{H=0}$, since applying a field does not, to a first approximation, affect the magnetization curve for small perpendicular fields. (For large H this ceases to be so, and the problem becomes more complex.) This point has actually been investigated by Shire and Barkla, using a steady field parallel and perpendicular to the A.C. field, and they find that W is less for the parallel case, approximately in the ratio indicated by the above discussion. The number of "locked" ions should be the same in both cases.

https://doi.org/10.1017/S0305004100017023 Published online by Cambridge University Press

SUMMARY

Ewing's original theory of hysteresis, though not admissible for metals, seems to apply to paramagnetic salts. The peculiar form of the interaction between dipoles implies that a certain fraction of them may be incapable of following small changes in the external field. The agreement with experiment is satisfactory, considering the rough nature of the theory.

In conclusion, I should like to thank Messrs E. S. Shire and H. M. Barkla for kindly discussing their results with me before publication, and also Prof. R. H. Fowler, Dr J. D. Cockcroft and Mr A. H. Wilson for helpful discussions. Also I should like to thank the Provost and Fellows of King's College for the award of a studentship, during the tenure of which this work was carried out.

REFERENCES

(1) SHIRE and BARKLA. *Proc. Cambridge Phil. Soc.* 35 (1939), 327.
(2) KÜRTI, LAINÉ and SIMON. *C.R. Acad. Sci., Paris*, 204 (1937), 754.
(3) SAUER and TEMPERLEY. To be published shortly.
(4) EWING. *Proc. Roy. Soc.* 48 (1890), 342.
(5) KRONIG and BOUWKAMP. *Physica*, 5 (1938), 521.
(6) FRÖHLICH and HEITLER. *Proc. Roy. Soc.* A, 155 (1936), 640.

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