PHYSICAL REVIEW VOLUME 94, NUMBER 5 JUNE 1, 1954

Antiferromagnetic $H-T$ Boundaries and Apparent Molecular Fields for $MnCl_2 \cdot 4H_2O$ and $MnBr_2 \cdot 4H_2O$

WARREN E. HENRY
United States Naval Research Laboratory, Washington, D. C.

(Received December 18, 1953; revised manuscript received March 3, 1954)

Experimental study and analysis have been made of non-Brillouin magnetic moments of two hydrated manganous salts of similar structure. The moment (M) was measured as a function of field at constant temperature (T) and as a function of temperature at constant field (H). From the former, analysis of the extent of the nonsuperposition of $M(H/T)$ for different temperatures gave apparent molecular fields of 14 000 gauss and 18 000 gauss, respectively, for manganous chloride tetrahydrate and manganous bromide tetrahydrate. The Van Vleck antiferromagnetic exchange coefficient γ is experimentally determined, corresponding to antiferromagnetic exchange energy densities of the order of 10^6 ergs/cm^3. The constant field measurements gave points on antiferromagnetic transition curves such that H_m/T_N was about 8000 gauss per degree for each salt. If the constant temperature moment is plotted against the Van Vleck parameter $(H-\gamma M)/T$ instead of the usual Brillouin parameter H/T there is superposition of isotherms for points in the H-T plane outside the antiferromagnetic region, thus giving experimental support to the Van Vleck model for simple antiferromagnetics. The method of measurement is the same as for our previous measurements. The temperature range was 1.3°−4.2°K and magnetic fields up to 58 000 gauss were applied, the greater part of the range being such as to prevent antiferromagnetic ordering.

INTRODUCTION

THE magnitude of magnetic interaction has been estimated from high field magnetization measurements on $Mn^{++}(^6S_{\frac{5}{2}}$ state for the free ion) in two manganous salts in which only a small effect of the crystalline electric field is to be expected and in which the anisotropy energy is small. This estimation is based on observation of the departures from a Brillouin function since previous measurements[1] of magnetization of salts with small interionic interactions have shown the applicability of the free spin Brillouin function for magnetic moments up to over 99.5 percent saturation for Cr^{+++}, Fe^{+++}, and Gd^{+++}. The Brillouin moment is given by

$$M=Ng\mu\left[(2S+1)\coth\frac{(2S+1)\mu H}{kT}-\coth\frac{\mu H}{kT}\right], \quad (1)$$

where N is the number of paramagnetic ions, g (having been taken as 2 for free spin and $J=S$) is the Landé factor, μ is the Bohr magneton, S is the spin, H is the magnetic field, k is the Boltzmann constant, and T is the absolute temperature. It can be noted from Eq. (1) that a necessary though not sufficient condition for the applicability of the formula is that M be a function of H/T, implying superposition of magnetic moment isotherms. It has been observed both from adiabatic[2] and isothermal[3] moment measurements that copper sulphate pentahydrate is characterized by nonsuperposition of moment isotherms. This immediately suggests the possibility of using the extent of nonsuperposition of isotherms to estimate molecular fields.[4] A choice of substance to be used for study is based not only on the requirement that the ground state be simple but also on two other necessary but opposing conditions, namely (1) that the magnetization be carried out isothermally, which limits measurements to the range above 1°K and (2) that the effective field, H_{eff} (the difference between the applied field and the molecular field projection) be large enough to produce saturation. This latter condition can be ascertained by estimating the magnitude of the molecular field: If one equates the magnetic energy to the thermal energy, one obtains

$$\mu H_m \sim kT_N, \quad (2)$$

where H_m is the molecular field, T_N is the Néel (antiferromagnetic transition) temperature, μ is the Bohr magnetion, and k the Boltzmann constant. Thus $MnCl_2 \cdot 4H_2O$ was selected because a reasonable Néel temperature[5] had been determined to be about 1.6°K. $MnBr_2 \cdot 4H_2O$ was selected because it has a similar structure.

Van Vleck's generalized treatment[6] provides for an effective field which is less than the applied field because of the opposition of a molecular field contribution (determined by neighboring ions) which acts in the opposite sense of Weiss fields.[7] If one assumes the simplest case of one type of neighbor, i.e., two sublattices, and if one uses the simplified Van Vleck[8] treatment of this case, one has

$$H_{\text{eff}}=H_0-\gamma M, \quad (3)$$

where H_0 is the applied field, M is the magnetization and γ, the Van Vleck antiferromagnetic exchange

---

[1] W. E. Henry, Phys. Rev. **88**, 559 (1952).

[2] T. H. Gaballe and W. F. Giauque, J. Am. Chem. Soc. **74**, 3513 (1952).

[3] W. E. Henry, Phys. Rev. **87**, 1133 (1952).

[4] W. E. Henry, Phys. Rev. **90**, 492 (1953).

[5] S. A. Friedberg and J. D. Wasscher, Physica **19**, 1072 (1953).

[6] J. H. Van Vleck, J. Chem. Phys. **9**, 85 (1941); also see L. Néel, Ann. Phys. **17**, 64 (1932); **5**, 256 (1936); F. Bitter, Phys. Rev. **54**, 79 (1937).

[7] P. Weiss, J. phys. et radium **6**, 667 (1907).

[8] J. H. Van Vleck, J. phys. et radium **12**, 282 (1951).

coefficient, is given by

$$\gamma = ZA/(Ng^2\beta^2), \tag{4}$$

where Z is the number of neighbors, $A/2$ is the antiferromagnetic exchange integral, N is the density of magnetic ions, g the Landé factor, and β is the Bohr magneton. The first part of the investigation involved experimental investigation of magnetic moments of manganous chloride tetrahydrate and manganous bromide tetrahydrate as a function of magnetic field at selected constant temperatures. This enables one to plot M against H/T, and to determine the dispersion in the magnetic moment isotherms; by analysis of the data over a considerable range, one may obtain a limiting molecular field contribution at saturation. This is taken as the apparent molecular field. This molecular field can now be used to obtain γ, the Van Vleck antiferromagnetic exchange coefficient in Eq. (3) since γM_0 at saturation is the apparent molecular field. From γ and the constants in Eq. (4) one can calculate ZA, which is the antiferromagnetic exchange energy density. To test the applicability of the Van Vleck model for simple antiferromagnetics, one may plot M as a function of the Van Vleck parameter, $(H-\gamma M)/T$, instead of the Brillouin parameter, H/T to see if the magnetic moment isotherms are brought into superposition. It should be pointed out that although substitution of the Van Vleck parameter in the moment equation [Eq. (1)] in the place of H/T results in an equation which is not explicit in H and T, no hardship is imposed, for one can arrive at the true moment by successive approximation. For the first approximation, one starts with the Brillouin moment (explicit in H, T) in the Van Vleck expression for the effective field Eq. (3). The moment so calculated is then used in the effective field for the second approximation, and so on. The second approximation is sufficient for the average case. It is of interest to attempt an experimental determination of the antiferromagnetic exchange energy. This can be done relatively easily if one has the exchange energy density and the magnetic structure which determines the number of neighbors. The exchange energy is determined from the experimental value of γ and the magnetic structure can be obtained by a method such as that of Shull and Smart.[9]

The second part of the experiment consisted in measuring moments as a function of temperature at fixed constant fields. From these measurements one can obtain the field dependence of the antiferromagnetic transition temperatures. The transition temperature is taken to be the temperature at which

$$\left(\frac{\partial M}{\partial T}\right)_H = 0. \tag{5}$$

That is to say, from the Van Vleck theory,[8] the left member of Eq. (5) is negative for all values of T when the theory embodied in Eq. (3) is applicable. If the theory is not applicable, i.e., if γ is not a constant but becomes sufficiently larger as T is lowered, then the left member of Eq. (5) can go through zero and become positive. This represents a breakdown of the theory for the paramagnetic phase and therefore the appearance of a transition point. These critical temperatures corresponding to various sufficiently low fields can be plotted in the H-T plane to look for a transition curve predicted by Sauer and Temperley[10] and Garrett's extension[11] of the Van Vleck model and implied by Garrett's adiabatic experiments[12] on cobalt ammonium sulphate below 1°K. The advantage of using manganous salts here chosen is that isothermal conditions can be maintained and the H intercept in the H-T plane is taken as the molecular field by assuming that no spontaneous antiparallel alignment takes place at the absolute zero in an applied field greater than the aligning molecular field. Also, from the Van Vleck theory, if $H > H_m$, there is no failure of the theory. The T intercept of the transition curve may be obtained by extrapolation of the curve to zero field. This is permissible since the points in this range fall on practically a straight line.

EXPERIMENTAL PART

The relative moments were measured on a spherical aggregate of small crystals; the technique employed in our previous measurements[1] was used. The temperature of the sample was kept at desired points in the liquid helium range (1.3°−4.2°K) with the help of a metal Dewar for liquid helium. The magnetic field was produced by a Bitter type magnet which gave fields to over 58 000 gauss. The moment was measured by a differential fluxmeter which consisted of a ballistic galvanometer, a coil system, and a precision lift[13] for motion of the sample with respect to the coil system. Since manganous bromide tetrahydrate is more unstable than the chloride, extra precautions were taken. First, the salt is recrystallized from water at a temperature slightly above room temperature, to insure production of the proper hydrate; then the crystals are kept in a moist atmosphere until just before the experiment is performed. The remainder of the experiment is carried out with the usual care with respect to loss of water of hydration.

INTERPRETATION OF RESULTS

The results are obtained for $MnCl_2 \cdot 4H_2O$ and $MnBr_2 \cdot 4H_2O$ from the measurement of moments as a

---

[9] C. G. Shull and J. S. Smart, Phys. Rev. **76**, 1256 (1949).

[10] J. A. Sauer and H. N. V. Temperley, Proc. Roy. Soc. (London) **A176**, 203 (1940).

[11] C. G. B. Garrett, J. Chem. Phys. **19**, 1154 (1951).

[12] C. G. B. Garrett, Proc. Roy. Soc. (London) **A206**, 242 (1951).

[13] W. E. Henry, National Bureau of Standards Circular No. 519, 1952 (unpublished), p. 237.

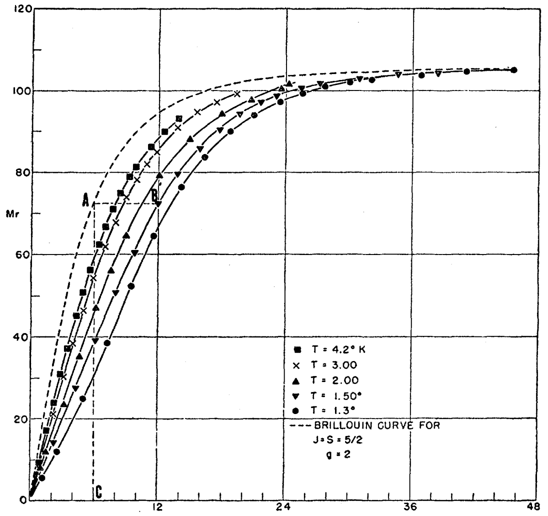

FIG. 1. Plot of relative magnetic moment (M_r) against H/T for manganous chloride tetrahydrate.

function of field at constant temperatures and as a function of temperature at constant fields.

Manganous Chloride Tetrahydrate

Field Dependence of Moment for Fixed Temperatures

Figure 1 shows magnetic moment plotted against H/T. It is seen that

$$\left(\frac{\partial M}{\partial H}\right)_T \rightarrow 0 \tag{6}$$

at the high fields and low temperatures so that saturation is being approached. By estimating the saturation moment (very little different from the highest measured moment) one can draw a Brillouin curve from Eq. (1) with $S=J=5/2$ and $g=2$. Now it is seen from Fig. 1 that the isotherms do not superpose and that no isotherm falls on the theoretical Brillouin curve using the applied field in the argument. If it is assumed that an effective field is constructed from the applied field and a molecular field contribution, then the displacement of the experimental curve for a given temperature from the Brillouin curve is used to estimate the apparent molecular field as follows: An arbitrary test point is chosen on any of the five isotherms. From this arbitrary point, say point B (Fig. 1) on the 1.50°K isotherm, one follows a constant moment line, BA, to the point A on the Brillouin function where the value of H/T is read at the point C. This value of H/T, when multiplied by T (1.50°K in this case), gives the effective field, H_{eff}. The difference between the applied field and the effective field is taken as the contribution of the molecular field. This process is repeated for many arbitrary points on each isotherm. With these data, one is in position to apply the Van Vleck model for the effective field [Eq. (3)] and if one assumes γM to be the contribution of the molecular field,

$$\mathbf{H}_m=\gamma\mathbf{M}, \tag{7}$$

with γ a constant, then the molecular field projection divided by the moment should be a constant over the range of applicability. We use the apparent molecular field contribution obtained by the graphical analysis mentioned previously, and find that

$$\mathbf{H}_m^{(i)}/\mathbf{M}^{(i)}=\text{constant}\pm 10\,\text{percent}, \tag{8}$$

over a very large range of temperatures and fields, corresponding to quadrupling H/T. The value of $\mathbf{H}_m^{(i)}$ corresponding to $\mathbf{M}_0$ (the saturation moment) is the apparent molecular field. As saturation is approached, the error becomes large and indeterminable but one may use the value of the constant in Eq. (8) to extrapolate the $\mathbf{H}_m^{(i)}$ to saturation to obtain an apparent molecular field of about 14 000 gauss. From this value of the molecular field we compute an antiferromagnetic exchange energy density from the Van Vleck model[8] for simple antiferromagnetics as follows: We take the experimental molecular field as γM_0, where M_0 is the saturation moment (5 Bohr magnetons). The computed γ is now substituted into Eq. (4) to compute ZA (the antiferromagnetic exchange energy density). If N in Eq. (4) is taken to be 6×10^{21} ions/cm^3 for manganous

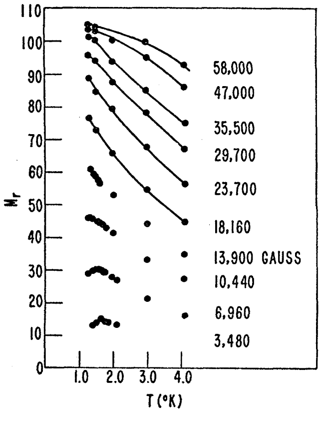

FIG. 2. Plot of relative magnetic moment (M_r) against temperature (T) for fixed fields (H) for manganous chloride tetrahydrate.

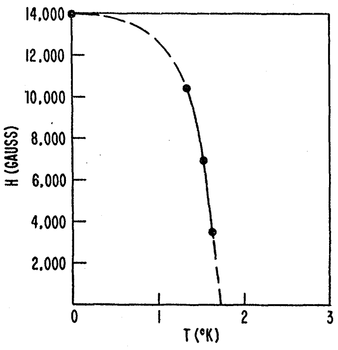

FIG. 3. Plot of critical field (H) against temperature (T) for manganous chloride tetrahydrate.

chloride tetrahydrate,[14] ZA turns out to be 0.6×10^6 ergs/cm^3, $A/2N$ being the exchange integral and of the order of 2.5 cm$^{-1}/Z$ where Z is the number of nearest neighbors.

Temperature Dependence of Moment for Fixed Fields

The dependence of magnetic moment on temperatures for fixed fields is shown in Fig. 2. For low fields it is seen that a change in sign of the slope takes place in the temperature range used. Following the convention of Bizette, Squire, and Tsai[15] of looking for the maximum in susceptibility for monotonic change in temperature, we call the temperature at which Eq. (5) holds the transition temperature for the field H. Thus, by measuring the moment as a function of temperature for various fixed fields it is possible to obtain the field dependence of the antiferromagnetic transition temperature. While one cannot in practice obtain the moment for $T=0$ or $H=0$, it is possible to get these two intercepts (H and T intercepts) as follows: The apparent molecular field is taken as the critical field at absolute zero on the assumption that no spontaneous antiparallel alignment can take place in applied fields greater than the aligning field, namely, the molecular field. This is in accord with the Van Vleck model. Extrapolation of the experimental curve to zero field (the experimental curve seems to approach a straight line in this region) gives a critical temperature in zero field. Thus, one can plot a complete curve (Fig. 3) which serves as a boundary between the paramagnetic and antiferromagnetic regions in the H-T plane. Having this separation between the antiferromagnetic and paramagnetic regions we can see whether or not this separation has a relation to the region of applicability of certain aspects of the Van Vleck theory of antiferromagnetic exchange. That is, we can now use a theoretical curve based on the Van Vleck parameter, $(H_0-\gamma M)/T$, as opposed to the Brillouin parameter, H/T to test the applicability of the Van Vleck model. We do this by plotting M against the Van Vleck parameter to obtain a theoretical curve. Now, all points in the H-T plane not enclosed by the antiferromagnetic transition boundary fall on the theoretical curve Fig. 4.

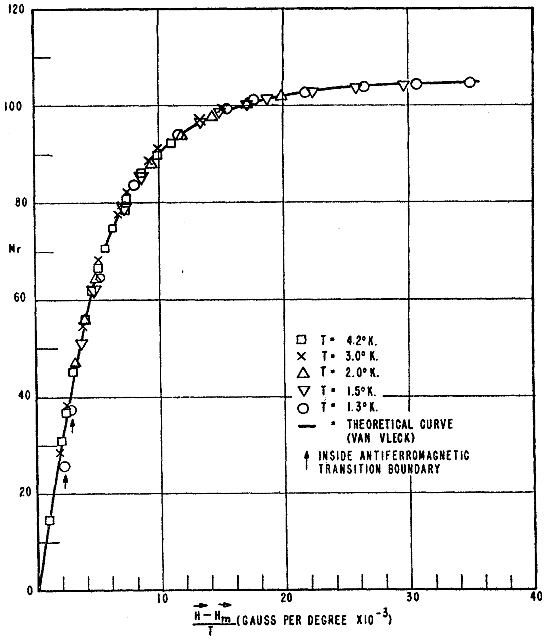

FIG. 4. Plot of relative magnetic moment (M_r) against the Van Vleck parameter $(H_0-\gamma M)/T$ for manganous chloride tetrahydrate. Points well inside the antiferromagnetic transition boundary are indicated by arrows.

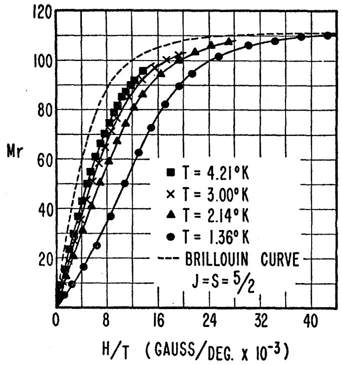

FIG. 5. Plot of relative magnetic moment (M_r) against H/T for manganous bromide tetrahydrate.

Manganous Bromide Tetrahydrate

Field Dependence of Moment for Fixed Temperatures

A graphical representation of the field dependence of moment for fixed temperatures is shown for $MnBr_2\cdot4H_2O$ in Fig. 5. Although the highest moments for manganous bromide tetrahydrate do not come as near to exhibiting a vanishing slope as the chloride, saturation is sufficiently near to make a good approximation for the saturation moment and thus to construct a

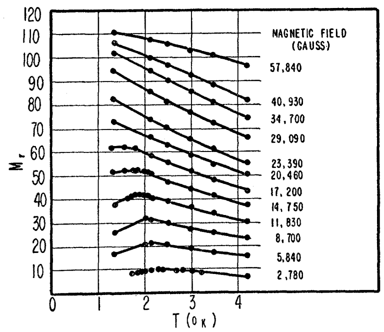

FIG. 6. Plot of relative magnetic moment (M_r) against temperature (T) for fixed fields (H) for manganous bromide tetrahydrate.

---

[14] National Research Council, *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1926), Vol. I, p. 127.

[15] Bizette, Squire, and Tsai, Compt. rend. **207**, 449 (1938).

Brillouin curve. The same graphical technique is used here as for the chloride and a limiting molecular field of about 18 000 gauss is obtained.

Temperature Dependence of Moment for Fixed Field

Figure 6 shows a plot of magnetic moment against temperature for fixed fields. It is noticed that the moment reaches a maximum for the lower fields just as in the case of the chloride, but that there is a greater range of fields and temperatures in the antiferromagnetic region for the bromide than for the chloride. This makes a more detailed examination possible for the bromide. It is noticed that slopes of the curves at temperatures below the maxima are different for different fields, and lends support to the suggestion of Van Vleck[8] that the ratio of the average susceptibility at absolute zero to the susceptibility at the critical temperature is field dependent and might be expected in some cases to vary from $\frac{2}{3}$ to unity as higher and higher fields are applied.

Again taking the antiferromagnetic transition temperature corresponding to a given field as the point at which the slope of the moment curve goes through zero, we obtain a series of transition temperatures for the bromide. If the temperatures so obtained are plotted against the fields, one obtains a plot shown in Fig. 7, which represents the antiferromagnetic transition boundary in the H-T plane for manganous bromide tetrahydrate. The apparent molecular field of 18 000 gauss is taken as the critical field for the suppression of antiparallel alignment at the absolute zero. It is of interest that Fig. 7 (as well as Fig. 3) shows the same qualitative features as the critical field curve for the suppression of superconductivity.[16] That is, in both cases, fields exceeding the appropriate critical fields prevent the spontaneous ordering which would otherwise occur. Let us assume that there exists an analytical expression for the two types of ordering of the form

$$H_c = H_0[1-(T/T_0)^n], \tag{9}$$

where H_c is the critical field corresponding to a given temperature T, H_0 is the limiting critical field at $T=0$°K, and T_0 is the critical temperature in zero field. Now, whereas for the superconductor, n is of the order of 2 to fit many data in the literature, the value of n for the antiferromagnetic ordering transition is about 5.3 for the two substances here studied.

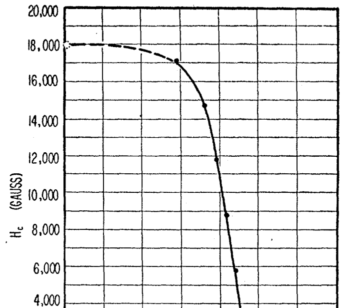

FIG. 7. Plot of critical field (H) against temperature (T) for manganous bromide tetrahydrate.

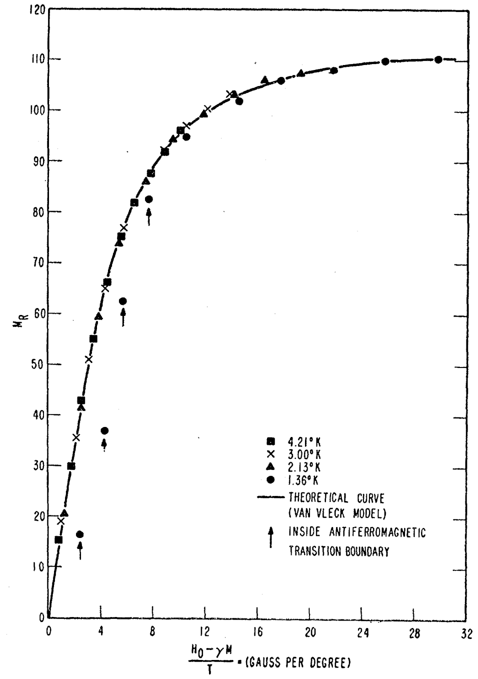

FIG. 8. Plot of relative magnetic moment (M_r) against the Van Vleck parameter $(H_0-\gamma M)/T$ for manganous bromide tetrahydrate. Points well inside the antiferromagnetic transition boundary are indicated by arrows.

Since manganous bromide tetrahydrate has a larger area in the antiferromagnetic region of the H-T plane, one may see in bold relief the difference between the antiferromagnetic and paramagnetic regions with respect to the use of the Van Vleck parameter for the calculation of the moment; one uses the method of successive approximation and the product of the Van Vleck antiferromagnetic exchange coefficient and the Brillouin moment is taken as the first approximation to the molecular field contribution. Figure 8 is a plot of magnetic moment against the Van Vleck parameter, and it is seen that for all points outside of the antiferromagnetic transition boundary, the experimental points for all isotherms fall on the theoretical curve calculated from the Van Vleck model. If the points are well inside the antiferromagnetic transition boundary of Fig. 7, the points do not fall on the theoretical curve as illustrated in the points associated with arrows, but these points deviate more, percentagewise, the greater the distance inside the antiferromagnetic transition boundary.

---

[16] D Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), p. 9.

SUMMARY

Magnetization data have been obtained for two manganous salts. Analyses of these data for manganous chloride tetrahydrate and manganous bromide tetrahydrate have been carried out by (1) plotting magnetic moments against H/T and observing nonsuperposition of magnetic moment isotherms, (2) construction of Brillouin curves from the saturation magnetization and determining graphically the departures of the moments from the Brillouin moments; from these departures, we obtain molecular fields, Van Vleck antiferromagnetic exchange coefficients and exchange energy densities, (3) plotting magnetic moments against temperature for fixed fields and determining geometrically the transition temperatures corresponding to these fields; this leads to antiferromagnetic transition boundary curves which separate the regions of spontaneous antiparallel alignment from the paramagnetic regions and, (4) subjecting the Van Vleck model for simple antiferromagnetics to critical examination which consisted in plotting magnetic moment against the Van Vleck parameter, $(H_0-\gamma M)/T$; this showed that the model for simple antiferromagnetics gives a quantitative evaluation of the magnetic moment for the group of points in the H-T plane which lie outside the antiferromagnetic transition boundary.

PHYSICAL REVIEW VOLUME 94, NUMBER 5 JUNE 1, 1954

Interpretation of Electroluminescence Effects in an Excited Phosphor*

FRANK MATOSSI
U. S. Naval Ordnance Laboratory, White Oak, Maryland

(Received September 10, 1953; revised manuscript received February 17, 1954)

The consideration of electron transitions between valence band, conduction band, and traps as presented by Randall and Wilkins' theory of luminescence growth is extended by including terms which take into account the emptying of traps by an electric field and the draining off of electrons by field-induced, nonradiative transitions. The result of the mathematical analysis corresponds to effects observed in a ZnS phosphor, embedded in a dielectric matrix, under the influence of a periodic electric field while continuously excited by ultraviolet radiation. These are a momentary illumination, an extinguishing effect, and the superposition of a ripple with twice the frequency of the field, whose amplitude decreases with increasing frequency. Some further observations are discussed qualitatively, utilizing the following assumptions: the draining effect ceases after some time; at low frequencies and for dc fields, a current effect counteracts the draining effect.

INTRODUCTION

THE influence of an electric field on luminescence can be expected to reveal fundamental properties of phosphors. However, in spite of much experimental research in this field, or rather because of the abundance of complex results, the understanding of these processes is still very limited. The present paper attempts a theoretical approach to one particular electroluminescence effect, the change of light output of a continuously excited phosphor by alternating electric fields.

The observations referred to may be briefly summarized as follows:[1] A ZnS(Cu) phosphor, embedded in a dielectric matrix and excited to equilibrium output, is subjected to a sinusoidal electric field while the excitation continues. Then a momentary illumination ("electrically stimulated luminescence" = electric stimulation) is followed by an extinguishing effect ("electric quenching"). After this, the light output recovers slowly to a new equilibrium ("intermediate recovery"). Cutting the field off may stimulate a second momentary illumination ("cut-off stimulation"), after which the original equilibrium is finally attained again ("final recovery").

The essential features of the observations are schematically illustrated in Fig. 1 and Fig. 2. The large time scale of Fig. 2 reveals the superposition, upon the "basic effect" of Fig. 1, of a periodic "ripple" whose frequency is twice the frequency of the field. The amplitude of this ripple decreases with increasing

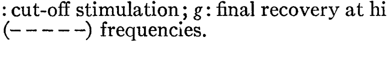

FIG. 1. Basic effect, schematical. I = luminescent output; t = time (in order of minutes); a: field on; b: field off; 0: ultraviolet on; c: electric stimulation; d: electric quenching; e: intermediate recovery; f: cut-off stimulation; g: final recovery at high (———) and at low (-----) frequencies.

---

* Presented at the Rochester Meeting of the American Physical Society, June, 1953 [Phys. Rev. **92**, 846 (1953)]. A preliminary account appeared in Naturwiss **40**, 239 (1953).

[1] G. Destriau and J. Mattler, J. phys. et radium **11**, 529 (1950); F. Matossi and S. Nudelman, Phys. Rev. **89**, 660 (1953). Similar results for decaying phosphors are reported by K. W. Olson, Phys. Rev. **92**, 1323 (1953).