

value of this quantity, i.e., the Wigner energy of  $\sim 25$  ev.<sup>8</sup>

A more complete report of this work is in preparation, and it will include results of experiments outlined in parts (b) and (c).

<sup>1</sup> P. Rappaport, Phys. Rev. **94**, 1409(A) (1954).

<sup>2</sup> E. Klontz, Purdue University dissertation, 1948 (unpublished).

<sup>3</sup> P. Rappaport, Phys. Rev. **93**, 246 (1954).

<sup>4</sup> A. Rose, RCA Rev. **12**, 362 (1951).

<sup>5</sup> R. N. Hall, Phys. Rev. **87**, 387 (1952).

<sup>6</sup> W. Shockley and W. R. Read, Phys. Rev. **87**, 835 (1952).

<sup>7</sup> The work was done on a Type AD2 machine at the High Voltage Engineering Corporation in Cambridge, Massachusetts. The authors wish to thank Mr. A. John Gale, who supervised the adaptation of the machine for these experiments.

<sup>8</sup> F. Seitz, Discussions Faraday Soc. **5**, 271 (1949).

### Alternative Explanation of the Waymouth-Bitter Experiments

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WAYMOUTH and Bitter<sup>1</sup> have reported some significant experiments on electroluminescence excited by field pulses of known time constant with certain cubical ZnS:Cu, Pb phosphors. They found that if the electroluminescent lamp was first irradiated with infrared to bring it to a consistently reproducible initial state, then there was practically no luminescence when the field was applied, but luminescence would occur when the field was removed. It was suggested<sup>1,2</sup> that this might be due to ionization of the activator centers, with the field holding the electrons at the positive side of the working portion of the crystal, with luminescence occurring by recombination when the field was released.

An alternative explanation is now proposed. The electrons are assumed to come from donor levels of low energy, say 0.2 ev, and hence either come from initially ionized donors or are released by low fields. These electrons will accordingly migrate to the positive side of the working portion of the crystal at low fields, too low to accelerate the electron to the 2 ev or so energies necessary for impact excitation of the activator. Thus when the field reaches its full value, there will be no electrons that it can accelerate across the working part of the crystal. The electrons will have all gone over slowly to the positive side.

When the applied field is removed, however, the maximum reverse field due to polarization of the crystal will occur at, or close to, the instant of removal of the field. The electrons will therefore begin to move back to their donors in a high field, becoming accelerated to energies high enough for excitation of any activator atoms encountered along the way. Luminescence will thus occur when the field is removed.

The foregoing is true if the applied field is removed shortly after it reaches its maximum value. The electrons will be largely untrapped and free to return to their donors. The longer the applied field is maintained, however, the more electrons will become trapped, and the traps in zinc sulfide, particularly with lead present, will be deeper than the donor levels, for example about 0.5 ev. The electrons held in these traps will not all be released with the collapse of the applied field, and hence the luminescence on removal of the applied field will be reduced.

On the reapplication of the field, however, the electrons will no longer all be free to move at low fields, but will not be released from their traps until the field reaches a higher value, high enough to then accelerate the electrons sufficiently for impact ionization. Thus, if the field is initially applied, maintained for a time, and then removed, luminescence will occur on reapplication of the field. This is in accord with the experimental results of Waymouth and Bitter.

As the time interval between removal and reapplication of the field is increased, more electrons will escape from traps before reapplication and hence the luminescence on reapplication of the field will be smaller.

Irradiation by infrared to empty the traps will also reduce the luminescence on reapplication of the field, all these results being in accord with the Waymouth-Bitter experimental findings.

The reason for the trapping of electrons when the applied field is maintained for a long enough period is presumably the fact that the dielectric material in which the phosphor particles are embedded has a definite, though extremely small, resistance, so that a small direct current will flow through the device, some electrons from the direct flow being trapped as they pass through the working portion of the crystal, and being compensated for by electrons leaving the positive side and passing into the dielectric.

<sup>1</sup> J. F. Waymouth and F. Bitter, Phys. Rev. **95**, 941 (1954).

<sup>2</sup> L. Burns, J. Electrochem. Soc. **100**, 572 (1953).

### Average Crystal Potential

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IN this note, we will discuss the calculation of the average potential in an infinite nonionic crystal, and show that the Frenkel-Bethe formula<sup>1</sup> can be obtained from the Fourier representation of the total crystal potential. In what follows, the Fourier transform  $\Gamma(\mathbf{n})$  of a function  $G(\mathbf{r})$  is given by

$$\Gamma(\mathbf{n}) = \mathcal{F}(G(\mathbf{r})) = \int G(\mathbf{r}) \exp(-2\pi i \mathbf{n} \cdot \mathbf{r}) d\mathbf{r} / v_a, \quad (1)$$

where  $\mathbf{n}$  and  $\mathbf{r}$  are running vectors in Fourier and crystal space respectively, magnitudes  $\eta$  and  $r$ , and  $v_a$  is the volume of the primitive cell.

We consider a crystal in which the total charge density at a typical lattice site, taken as origin, is  $R(\mathbf{r}) = Z[\delta(\mathbf{r}) - R_S(r)]$ , where  $Z$  is the atomic number, and  $R_S(r)$  is a spherically symmetric electron density of content  $+1$ ; there is no net charge at any site. Let  $P(\mathbf{n}) = \mathfrak{F}(R(\mathbf{r}))$ ,  $P_S(\eta) = \mathfrak{F}(R_S(r))$ ,  $\Phi(\mathbf{n}) = \mathfrak{F}(V(\mathbf{r}))$ , where  $V(\mathbf{r})$  is the potential due to  $R(\mathbf{r})$ . Then from Poisson's equation,

$$\Phi(\mathbf{n}) = P(\mathbf{n})/4\pi^2\eta^2 = Z[v_a^{-1} - P_S(\eta)]/4\pi^2\eta^2, \quad (2)$$

where<sup>2</sup>

$$P_S(\eta) = \frac{2\pi}{v_a} \int_0^\infty \frac{J_{\frac{3}{2}}(2\pi\eta r)}{(\eta r)^{\frac{3}{2}}} R_S(r) r^2 dr. \quad (3)$$

The average crystal potential is  $\lim_{\eta \rightarrow 0} \Phi(\eta)$ . Using the Taylor expansion<sup>3</sup> of  $J_{\frac{3}{2}}(2\pi\eta r)$  in (1)-(3), we have

$$\begin{aligned} \Phi(\eta) = Z(4\pi^2 v_a \eta^2)^{-1} & \left[ 1 - 4\pi \int_0^\infty R_S(r) r^2 dr \right. \\ & \left. + \frac{8\pi^3}{3} \eta^2 \int_0^\infty R_S(r) r^4 dr - O(\eta^4) \right]. \quad (4) \end{aligned}$$

The first integral in (4) is  $(4\pi)^{-1}$  by the normalization, so

$$\Phi(000) = \frac{2\pi Z}{3v_a} \int_0^\infty R_S(r) r^4 dr = \frac{2\pi}{3v_a} Z \langle r^2 \rangle_{av}, \quad (5)$$

which is the Frenkel-Bethe result. If the crystal has a basis, (5) must be summed over each species present.

Thus the contribution of one type of particle to the average crystal potential can be directly determined from the appropriate atomic scattering factor,  $f(\sin\vartheta/\lambda) = ZP_S(\eta)$ . Near  $\eta=0$ ,

$$ZP_S(\eta) = [Z/v_a - 4\pi^2\Phi(000)\eta^2 + O(\eta^4)]. \quad (6)$$

Since the largest contribution to  $P_S(\eta)$  at small  $\eta$  comes from the outer or valence electrons,<sup>4</sup> the average crystal potential is primarily determined by the valence electron density. Crystal binding will of course greatly distort the valence electrons from their configuration in the free atom. Hence in general one cannot use the *free* atom scattering factors to determine the average crystal potential, unless accurate x-ray Fourier synthesis of the crystal electron density shows that the same scattering factors apply to the atom bound in the crystal.

For an ionic crystal the net charge at each site,  $P(000)$ , is not zero so it is not clear that this analysis should apply. If, however, the excess or deficiency of charge is treated separately from the neutral complex of core plus compensating charge,<sup>5</sup> then (5) can apply to the neutral complex, while the excess density makes no contribution. We hope to discuss the average crystal potential again at a later date.

The author wishes to thank Professor P. P. Ewald with whom he has discussed many questions concerning crystal potentials. The comments of Dr. D. R. Frankl and A. Lempicki have been most helpful.

<sup>1</sup> J. Frenkel, *Z. Physik* **59**, 649 (1930); H. Bethe, *Ann. Physik* **87**, 55 (1928), see footnotes 1 and 2 on p. 106 and Eq. (85) on p. 109.

<sup>2</sup> S. Bochner and K. Chandrasekharan, *Fourier Transforms* (Princeton University Press, Princeton, 1949), p. 67 ff.

<sup>3</sup> G. N. Watson, *Bessel Functions* (The Macmillan Company, New York, 1945), second edition, p. 15.

<sup>4</sup> R. W. James, *The Optical Principles of the Diffraction of X-rays* (G. Bell and Sons, Ltd., London, 1950), pp. 125-129.

<sup>5</sup> J. L. Birman, *Phys. Rev.* **97**, 897 (1955); see also erratum, *Phys. Rev.* **98**, 1871 (1955). Note that in *both* (4.2) and (4.3) the average potential is made equal to zero, which is a consequence of the use of the sums  $\psi^{(1)}(\mathbf{r}; \alpha)$  and  $\psi^{(2)}(\mathbf{r}; \alpha)$ .

## Magnetic Susceptibility of $\alpha$ Manganese at Low Temperatures\*

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RECENT measurements of the specific heat in  $\alpha$  manganese<sup>1</sup> at liquid helium temperatures yield a value for the electronic term that is very large compared to other elements of the first transition series. This implies a very high density of states at the Fermi surface of the  $3d-4s$  band which could on the band picture lead to strong magnetic effects. To investigate this, measurements of the magnetic susceptibility were undertaken in the range of temperature between 1.8°K and room temperature. Previous measurements of the susceptibility of  $\alpha$  Mn by Serres<sup>2</sup> and Kriessman and McGuire<sup>3</sup> show a maximum in the susceptibility in the neighborhood of 150°K but these measurements were only taken down to liquid nitrogen temperatures. Shull<sup>4</sup> has studied this material by means of neutron diffraction and finds evidence for a feeble antiferromagnetism at low temperature which disappears at approximately 100°K. Since the completion of this work, more recent measurements by Kriessman and McGuire to lower temperatures<sup>5</sup> have come to our attention and in these a marked increase in susceptibility is reported.

The measurements were made by an induction technique<sup>6</sup> in which a disk-shaped sample is translated between two detecting coils connected in series opposition. The magnetic moment is obtained by measuring the dc current that must be supplied to a third coil, that is wound on the sample and which rides with the sample, in order to balance out the detected signal. The entire coil and sample assembly is suspended in a Dewar designed to eliminate the need for liquid nitrogen in the field-sensitive region<sup>7</sup> and sits between the pole pieces of an A. D. Little electromagnet. With this