

Let us now investigate some of the specific processes by which the excitons can give up their energy. The transition probability for spontaneous emission can be estimated from previously calculated matrix elements<sup>6</sup> to be  $1.6 \times 10^8 \text{ sec}^{-1}$  for the case of an exciton in NaCl. If there is a Stokes' shift of 1 eV between absorption and emission,  $B$  is still of the order of  $10^8 \text{ sec}^{-1}$ , and in the absence of more probable processes strong luminescence should be observed.

In considering the process of  $F$ -center creation one can easily show that the electric field of the vacancy,  $e/Kr^2$ , where  $K$  is the static dielectric constant (5.62 for NaCl), is so strong when the exciton is in a site adjacent to it that it is incorrect to speak of the exciton as being localized in a pure exciton wave function; that is, there does not exist a bound state about the positive hole alone, but the wave function must surround both negative ion sites. Even when the vacancy is a third nearest like neighbor, the excited electron will be pulled away in  $\sim 10^{-14} \text{ sec}$ ; beyond this distance tunneling will occur. The mechanism for forming  $F$ -centers is clearly an exceedingly powerful one, and is effective even though the vacancies be only incipient. Thus the lifetime of an exciton against  $F$ -center creation depends primarily on the time required to get within 3 or 4 negative ion sites of the vacancy, after which the transition will occur within  $10^{-14} \text{ sec}$ . Since the effective mass of the exciton<sup>6</sup> is of the order of the electronic mass, its time of travel from one ion to the next directly after creation is about  $2 \times 10^{-13} \text{ sec}$  in NaCl; after the exciton has become thermalized by collisions with lattice vibrations, the time required is less than this by one or two orders of magnitude. If  $N_v$ , the density of vacancies, is as large as  $10^{20}/\text{cm}^3$  the transition probability is  $\sim 10^{13} \text{ sec}^{-1}$ ; if  $N_v$  is  $10^{19}/\text{cm}^3$  the transition probability is still greater than  $10^{12} \text{ sec}^{-1}$ .

When the exciton first begins to be trapped in the field of the vacancy, at a few atomic distances, the positive hole may diffuse away, eventually to be trapped by, say, an incipient positive ion vacancy, leaving its electron in the  $F$ -center. If the hole does not get away, it will be drawn up to a negative ion site adjacent to the  $F$ -center and form a composite center which one would expect to be stable during optical lifetimes at ordinary temperatures. We shall continue to group these composite centers with the  $F$ -centers, however, and the calculations we present on  $F$ -center annihilation will be applicable in order of magnitude to the composite centers as well.

The probability for  $F$ -center destruction can be calculated from the point of view that an exciton adjacent to an  $F$ -center can undergo a two-center Auger transition; one electron is ejected into the conduction band and the other recombines with the hole. While the exciton and  $F$ -center form a composite center within  $\sim 10^{-15} \text{ sec}$ , we can calculate an approximate value for the probability per second for the transition from  $(2\pi/\hbar) |M|^2$ , where

$$M = (m/\hbar^2 \kappa)^2 \int \psi_{\kappa}^*(1) \psi_F(1) \frac{e^2}{r_{12}} \psi_{3P}^*(2) \psi_{\text{exc}}(2) d\tau_{12}.$$

The largest part of the integral comes from the dipole-dipole part, found by expanding  $1/r_{12}$ . Exchange and other overlap effects are smaller, as was observed for the analogous matrix element which leads to the propagation of the exciton in a perfect lattice.<sup>6</sup> Evaluating  $M$ , we find

$$P_t = (2\pi/\hbar) (m/\hbar^2 \kappa) 4\mu^2 \nu^2 / R^6.$$

Here  $\mu$  is the dipole matrix element of the exciton, and  $\nu^2$  is a mean square dipole matrix element per unit  $\kappa$  (wave number) for the transition from  $\psi_F$  to the continuum, chosen so as to give the correct oscillator strength.  $R$  is the nearest like neighbor distance. Numerically this becomes, using the matrix elements of reference 5,  $P_t \sim 10^{12} \text{ sec}^{-1}$ . Since the probability per second that the exciton reach a negative ion site adjacent to an  $F$ -center has this same magnitude, the total probability that an exciton annihilates an  $F$ -center is still  $\sim 10^{12} \text{ sec}^{-1}$ .

It can now be pointed out why these calculations, though performed for NaCl, should apply quite generally to the alkali halides. That this is so is clear from the similarity of lattice

spacings, and oscillator strengths for the exciton band and for the  $F$ -center continuum transitions in all these salts.

It is also clear from the value of the lifetime for emission (of order  $10^{-8} \text{ sec}$ ) that luminescence will be overshadowed in the evaporated layers by these other processes, which occur within  $10^{-12} \text{ sec}$ . In addition to these effects, one might be tempted to consider "self-trapping,"<sup>7</sup> but this should not be important for the alkali halides in the time available. This may be seen from the estimate given for the time taken for the exciton to travel from one ion to another ( $\approx 10^{-13} \text{ sec}$ ), which is so rapid that the nuclear readjustment required for self-trapping is improbable.<sup>8</sup> These qualitative conclusions may not be applicable to annealed single crystals where the density of incipient vacancies may be as low as  $10^{15} \text{ cm}^{-3}$ , and the density of isolated vacancies even more negligible in number.<sup>8</sup>

The authors wish to thank Professor F. Seitz and Drs. Apker, Taft, Hebb, and Krumbansl for illuminating discussions of the experiments.

\* Research supported by the ONR.

<sup>1</sup> L. Apker and E. Taft, Phys. Rev. **79**, 964 (1950); **81**, 698 (1951); **82**, 814 (1951); **83**, 479 (1951); M. H. Hebb, Phys. Rev. **82**, 701 (1951).

<sup>2</sup> F. Seitz, Revs. Modern Phys. (to be published).

<sup>3</sup> Estermann, Leivo, and Stern, Phys. Rev. **75**, 627 (1949).

<sup>4</sup> R. Hilsch, private communication.

<sup>5</sup> D. L. Dexter, Phys. Rev. **83**, 435, 1044 (1951).

<sup>6</sup> W. R. Heller and A. Marcus, Phys. Rev. (to be published).

<sup>7</sup> J. Franck and E. Teller, J. Chem. Phys. **6**, 861 (1938); F. Seitz, Trans. Faraday Soc. **35**, 84 (1939).

<sup>8</sup> F. Seitz, private communication.

## $\text{O}_2^+$ and H in the Auroral Spectrum\*

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(Received August 21, 1951)

A TWO-PRISM Littrow spectrometer using a 1P21 photomultiplier tube as detector has recently been built. The spectrum from 3800 to 7000 Å is scanned in about five minutes by a synchronous motor drive which slowly rotates the Littrow mirror. Resolution is about 10 Å in the blue and 40 in the red. Incident light is chopped at 90 cycles and the spectrum presented on a recording meter. Wavelength measurements can be made to about 10 Å except at the red end.

An excellent spectrum of a red type  $B$  aurora was secured on June 20, 1951, at LaRonge, Saskatchewan. Three strong bands were prominent: a double-peaked band in the range 5900 to 6000 Å, and two others at 5560 and 5250 angstroms. These are attributed to the first negative system of  $\text{O}_2^+$ : (0, 0)6026, (1, 1)5973, (1, 0)5632, and (2, 0)5296 angstroms. Our wavelength values are low because measurements were made to the blue side of the bands, while the heads are to the red. The (0, 1) band (6418 Å) is seen at 6420, though the instrument is not very sensitive in this region.

It is suggested that some of these bands are responsible for the red color of the type  $B$  aurora. This is supported by the fact that conventional spectrograms show them only weakly. Only a small fraction of the long exposure required would ordinarily be to red aurora. Our instrument covered the region from 5577 to 6500 angstroms in about two minutes, and we were lucky enough to encounter a brilliant red aurora for all of this period. The red first positive bands of  $\text{N}_2$  found by Vegard<sup>1</sup> in type  $B$  aurora would not be recorded by our instrument unless they were very strong, since their wavelength is too long. However, they would also have to be very strong to have much effect on the eye, which loses sensitivity even faster than our spectrometer.

This observation suggests that the red lower border occurs when an aurora penetrates from the region of atomic to the region of molecular oxygen. For the light to appear red or purple, the intensity of the green line would have to be rather small. Unfortunately, this line goes off scale on our spectrogram; however, since

our field of view is  $2^\circ$  in the vertical direction and hence will include more than the lower red border, and also since we may have been looking up through the red aurora to green aurora behind it, this is not surprising.

The night of July 1, 1951, there was considerable aurora at Saskatoon. A very steady homogeneous arc appeared about  $15^\circ$  above the southern horizon from 10.15 to 1.00 Mountain Standard Time. A line at 4860A was prominent in its spectrum the whole time. This is presumably  $H\beta$  (4861). Many spectra were taken during this same period of very bright active forms with ray structure in the rest of the sky, none of which showed any sign of this line. The results of Meinel are similar; he reports<sup>2</sup> that hydrogen emissions are seen only in homogeneous arcs, though his conclusions are less definite because of the longer exposure times of around 15 minutes required with his conventional spectrograph.

We wish to acknowledge the encouragement and interest of Dr. W. Petrie. One of us (C.E.D.) was aided by a studentship from the National Research Council of Canada.

\* This research has been supported by the Geophysics Research Division of the Air Force Cambridge Research Center.

<sup>1</sup> L. Vegard and E. Tonsberg, *Geofys. Publik.* 11, No. 16 (1937).

<sup>2</sup> A. B. Meinel, Conference on Auroral Physics, London, Ontario (July, 1951).

### Interatomic Distances and Ferromagnetism in Spinel

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(Received August 24, 1951)

EXCELLENT agreement exists between the experimental saturation moments of ferromagnetic spinels determined by Gorter<sup>1</sup> and the values predicted by Néel.<sup>2</sup> The essence of Néel's theory was to assume that strong negative (antiferromagnetic) interactions exist between the unpaired spins of cations occupying the tetrahedral voids amidst close-packed oxygens in the spinel lattice and the unpaired spins of cations occupying octahedral voids. Thus, in the series of inverse spinels<sup>3</sup>  $\text{Fe}^{+++}\text{MeFe}^{+++}\text{O}_4$  (where the metal  $\text{Me} = \text{Mn}, \text{Fe}^{++}, \text{Co}, \text{Li}_2\text{Fe}_4^{+++}, \text{Ni}, \text{Cu}^+, \text{or Mg}^+$ ), since one  $\text{Fe}^{+++}$  occupies tetrahedral interstices and ( $\text{Me}$  plus the other  $\text{Fe}^{+++}$ ) share octahedral interstices, the saturation moment is simply that corresponding to the unpaired spins of  $\text{Me}$ . Néel also showed that spin interactions operate through the oxygens separating the metal ions ("superexchange"), and Anderson<sup>5</sup> has shown that the antiferromagnetism of  $\text{MnO}$  is to be explained similarly.

The author wishes to point out a new hypothesis by means of which the following may be accomplished: (1) the *ad hoc* assumption of Néel that the strongest spin interaction in inverse spinels is between tetrahedrally situated cations ( $\text{Me}_t$ ) and octahedrally situated cations ( $\text{Me}_o$ ) rather than between  $\text{Me}_t$  and  $\text{Me}_t$  or between  $\text{Me}_o$  and  $\text{Me}_o$  may be rationalized; (2) the nonoccurrence of ferromagnetism in normal spinels such as  $\text{NiCr}_2\text{O}_4$  may be explained; and (3) a quantitative relationship may be shown to exist between Curie temperature and interatomic distance in the ferromagnetic spinels and in the rock-salt structure antiferromagnetics. The hypothesis is simply that spin interaction is inversely proportional to the distance from a metal ion to a nearest neighbor, i.e., an oxygen, and thence to another metal ion. This is similar to the assumption of Zener<sup>6</sup> that direct spin interaction decreases continuously with increasing distance between adjacent atoms in metals.

Geometrical calculations show that in spinels the distance  $\text{Me}_t\text{-O-Me}_o$  is smaller than the distance  $\text{Me}_t\text{-O-Me}_t$  or the distance  $\text{Me}_o\text{-O-Me}_o$ , provided that the lattice parameter  $u$  is less than  $31/80$  (0.388). Verwey and Heilman<sup>3</sup> have found  $u$  to be about 0.380 for inverse spinels. If  $u$  is greater than 0.388, however,  $\text{Me}_o\text{-O-Me}_o$  is now the closest cation-oxygen-cation distance. Verwey and Heilman<sup>3</sup> found  $u$  to be greater for most normal spinels

TABLE I. Exchange energy for ferromagnetic spinels.

Spinel	$a_0, \text{ \AA}$	$kT \text{ exp., ergs}$	$kT \text{ calc., ergs}$	% difference
$\gamma\text{-Fe}_2\text{O}_3^a$	8.32	$1.31 \times 10^{-12}$	$1.32 \times 10^{-12}$	- 0.8
$\text{MnFe}_2\text{O}_4$	8.55	0.798	0.786	+ 1.5
$\text{Fe}_3\text{O}_4$	8.39	1.19	1.17	+ 1.7
$\text{CoFe}_2\text{O}_4$	8.36	1.096	1.15	- 4.9
$\text{Li}_2\text{Fe}_4\text{O}_4$	8.31	1.19	1.32	-10.9
$\text{NiFe}_2\text{O}_4$	8.35	1.18	1.006	+14.7
$\text{CuFe}_2\text{O}_4^b$	8.37	0.943	0.798	+15.4
$\text{MgFe}_2\text{O}_4^b$	8.36	0.826	0.710	+14.0

<sup>a</sup>  $T$  experimental, extrapolated. See Michel and Chaudron, *Compt. rend.* 201, 1191 (1935).

<sup>b</sup>  $s_t s_o$  computed from experimental data of reference 1.

<sup>c</sup> From reference 3, wherever possible.

than for inverse ones. For example,  $\text{NiCr}_2\text{O}_4$  (in which Ni occupies tetrahedral voids and 2 Cr's occupy octahedral voids) had  $u = 0.388 \pm 0.003$ . For this substance our hypothesis correctly predicts the absence of ferromagnetism, while if strong tetrahedral-octahedral spin interactions were present, ferromagnetism with a saturation magnetic moment of 4 Bohr magnetons would be expected.

The following semi-empirical equation was developed to correlate spin exchange energy as measured by  $kT$  with the supposed variables:

$$kT = c_1 s_t s_o e^{-c_2 d}, \quad (1)$$

where  $k$  = Boltzmann's constant,  $T$  is the Curie temperature in  $^\circ\text{K}$ ,  $s_t$  and  $s_o$  are respectively the number of unpaired spins on  $\text{Me}_t$  and  $\text{Me}_o$ ,  $d$  is the distance  $\text{Me}_t\text{-O-Me}_o$  in  $\text{ \AA}$  ( $= 0.470a_0$ , where  $a_0$  is the lattice constant of a spinel with  $u = 0.388$ ). With  $c_1 = 5.04 \times 10^{-3}$  erg and  $c_2 = 7$ , the data of Table I were obtained. The agreement ( $\pm 16$  percent) between observed and calculated exchange energies is reasonable, since (1) an error of 0.01A in  $a_0$  (which is less than the disagreement between published values for a given spinel) would cause an error of 5 percent in  $kT$ , (2)  $u$  values may vary slightly from 0.380 for certain of the spinels,<sup>3</sup> and (3) the value of  $s_t s_o$  is not precisely known for  $\text{CuFe}_2\text{O}_4$  and  $\text{MgFe}_2\text{O}_4$ .

An equation similar to (1) but with  $c_1 = 6.5 \times 10^7$  ergs and  $c_2 = 12$  holds for the antiferromagnetic oxides  $\text{MeO}$  ( $\text{Me} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ) to  $\pm 27$  percent. The difference in  $c_2$  for the 2 structures shows that (1) does not account for all the factors involved. Indeed, Anderson<sup>5</sup> has shown that as a consequence of superexchange a strong directionality exists such that the strongest interaction is between magnetic ions on opposite sides of an oxygen. The angle  $\text{Me-O-Me}$  is  $180^\circ$  for the rock salt structure and  $126^\circ$  for  $\text{Me}_t\text{-O-Me}_o$  in inverse spinels with  $u = 0.380$ .

<sup>1</sup> E. W. Gorter, *Compt. rend.* 230, 192 (1950).

<sup>2</sup> L. Néel, *Ann. Physik* 3, 137 (1948).

<sup>3</sup> E. J. Verwey and E. L. Heilmann, *J. Chem. Phys.* 15, 174 (1947).

<sup>4</sup>  $\text{CuFe}_2\text{O}_4$  and  $\text{MgFe}_2\text{O}_4$  are intermediate between normal and inverse spinels. See reference 1.

<sup>5</sup> P. W. Anderson, *Phys. Rev.* 79, 350 (1950).

<sup>6</sup> C. Zener, *Phys. Rev.* 83, 299 (1951).

### Evidence for Non-Additivity of Nucleon Moments\*

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(Received August 24, 1951)

THE existence of a change in the nucleon intrinsic moments due to the interaction with other nucleons has for some time been rather well established by the  $\text{H}^2$ ,  $\text{He}^3$  moment anomaly. It has been pointed out<sup>1</sup> that this change will lead both to a modification of the magnetic moments of most nuclei and to marked changes in the lifetimes for nuclear magnetic dipole transitions. A possible connection between the deviations of magnetic moments from the Schmidt lines and non-additivity of the nucleon moments has recently been emphasized by Miyazawa,<sup>2</sup> de-Shalit,<sup>3</sup> and Bloch.<sup>4</sup>