LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Relations between Hall Effect and Resistance

Measurements of the Hall effect have been made on sputtered gold films, while the films were heated in air from room temperature to 110°C. These show a relation between the Hall e.m.f. and resistance like that obtained for tellurium films (Phys. Rev. **30,** 673 (1927)). During the first heating after the film was sputtered, the Hall e.m.f. and resistance alike underwent a rapid decrease, in one case to values of both Hall e.m.f. and resistance only one-tenth that of the initial values. This relation is then a property of metals and not a peculiarity of tellurium. Wait and Mackeown have previously shown the Hall e.m.f. to be independent of resistance during aging of the film, and the tellurium films showed two types of aging; (1) a decrease in resistance independent of the Hall effect, and (2) a decrease in Hall e.m.f. in proportion to resistance, similar to the proportionality to resistance, (3) when the latter decreased with increase in temperature. This proportionality also held (4) when the resistance increased with increase in temperature. Processes (3) and (4) are reproducible.

Wait explained process (1) by showing that the measured e.m.f. should be the sum of the e.m.f.'s across the granules. This measured e.m.f. should be constant, while the decrease in resistance was due to the elimination of the interstices between the granules.

If we assume that the decrease in resistance on heating, in the case of metals and films which have a negative temperature coefficient of resistance, is due not to the increase in the number of so-called "free" electrons, but to the increase in the ease with which the electron passes from one atom to another, the proportionality between Hall e.m.f. and resistance in processes (2), (3), and (4) is readily accounted for. In the initial non-reproducible decrease of resistance and Hall e.m.f. there is undoubtedly a coalescence of particles, decreasing the difficulty with which the electron can pass from atom to atom. The thermal agitation should occasionally bring an electron of one atom near to the orbit of another atom so that the electron in passing from atom to atom climbs over a smaller potential hill. Again, greater thermal agitation may cause greater obstruction to the drift of the electron from atom to atom in the current stream, giving the usual positive temperature coefficient of resistance. Since e.m.f. is work per electron, the Hall e.m.f., on this basis, should be proportional to the resistance in each of the three stages; (2) the initial decrease of Hall e.m.f. and resistance; (3) when the temperature coefficients of resistance and of Hall e m.f. are negative; and (4) when the coefficients are positive.

With the increase in ease with which an electron passes from atom to atom there is probably also an increase in the number of electrons separating from atomic centers and taking part in conduction, giving the same result as above described in processes (3) and (4) but not accounting for process (2), if the number of "free" electrons depends only on temperature.

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February 25, 1931.

Note on the Structure of Groups in Crystals

In the February 15th number of the Physical Review, (**37**, 447, 1931) is published a letter to the Editor from Mr. M. L. Huggins, which was based upon a short abstract of a paper given by me at the Chicago Meeting of American Physical Society last year. I find it rather unfortunate that Mr. Huggins has based his letter on this abstract, as I am now preparing for publication a full account of the results I have obtained during my investigations of the last 3 years on groups $(XO_3)^{-m}$ in crystals. It seems necessary to me to give a few comments on Mr. Huggins' letter.

In the letter is stated that I, in agreement with earlier work on the crystal structure of $NaClO_3$ and $NaBrO_3$ (Kolkmeijer, Bijvoet, and Karssen,[1] Dickinson and Goodhue[2]) describe the XO_3-group in these crystals as tetrahedral groups with one corner missing. This passage obviously must give the reader the false impression that these earlier investigators already had determined the structure of these interesting groups. This is not the case as every one familiar with the above papers can ascertain. I have shown that the structure proposed by the Dutch investigators for $NaClO_3$ and $NaBrO_3$, as well as that proposed by Vegard,[3] is incorrect.[4] The structure given by Dickinson and Goodhue is inaccurate, and their results therefore do not allow conclusions to be drawn with regard to a possible nonplanar XO_3-group. Dickinson and Goodhue were as a matter of fact themselves aware of the inaccuracy, and only remark about the XO_3-group that the halogen lies nearly in the plane of the oxygens, indicating that they are considering the XO_3-group to be a coplanar group. There is thus a rather wide step from this conception of the XO_3-group to mine. The first description of "tetrahedral" groups XO_3 in crystals was given by me in 1928,[4] and has been dealt with also in other of my papers on these groups.[5]

It surprises me somewhat to learn that Mr. Huggins finds it necessary to point out the elementary fact that the two displaced electrons in the XO_3-group can be correlated to a Lewis electron pair. I thought the interpretation of e.g. the ClO_3-ion according to the Lewis hypothesis was familiar to everyone. So far the application of the principles of shared electron pairs on the atomic arrangement in inorganic crystals has proved unsuccessful, while considerations of the crystal structure from point of view of ions, ionic dimensions, ionic polarizability, and crystal energy in the hands of such men as W. L. Bragg, K. Fajans, V. M. Goldschmidt, F. Hund, L. Pauling, A. E. van Arkel, J. A. Wasastjerna, and others have given very valuable and important results.

Until one is able to treat the quantization of the electrons in polyatomic groups completely on the basis of wave mechanics, we must be satisfied with rough approximations. It is obvious that one cannot consider such groups to be purely ionic in character. The point of view I have taken with regard to the groups XO_3 is the familiar one of considering the constituents primarily as ions, and then take into consideration the deformation taking place in the electron clouds. The final continuous distribution of electron density may then be regarded as an approximation to the statistical continuity of density one will get from a quantum mechanical treatment. Judging from the results already obtained by this point of view I see at present no advantage in introducing the conception of shared electron pairs in crystals of this kind.

The most important factor which is independent of the point of view one takes is, of course, the total number of valence electrons in the group. In my paper on the groups XO_3 soon to be submitted I have devoted a chapter to the relation between the number of valence electrons and the symmetry of molecules or groups XY_2 and XY_3. If we limit ourselves to considering groups containing atoms of relatively low atomic number I have showed that the following rule holds for all observations hitherto obtained:

A group or molecule $\left\{\begin{matrix}(XY_2)^{-m}\\(XY_3)^{-m}\end{matrix}\right.$ has a $\left\{\begin{matrix}\text{co-}\\\text{co-}\end{matrix}\right.$ $\begin{matrix}\text{linear}\\\text{planar}\end{matrix}$ structure if the condition $\begin{matrix}\Sigma v=2\times p\\\Sigma v=3\times p\end{matrix}$ is satisfied. Here Σv denotes the total number of valence electrons in the group or molecule, while p is the number of valence electrons in the inert gas following atom Y in the periodic system if the number of valence electrons on the other hand has to be expressed by an equation of the form $\begin{matrix}\Sigma v=2\times p+\Delta\\\Sigma v=3\times p+\Delta\end{matrix}$ the group or

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[1] Kolkmeijer, Bijvoet, Karssen, Proc. Roy. Acad. Amsterdam **23,** 644 (1920).

[2] Dickinson and Goodhue, J. Am. Chem. Soc. **43,** 2045 (1921).

[3] L. Vegard, Zeits. f. Physik **12,** 289 (1922); Norske Vid.-Akad. Skr. Oslo Nr. 16, 1922.

[4] W. H. Zachariasen, Norske Vid.-Akad. Skr. No. 4. p. 143, 1928; Zeits. f. Krist. **71,** 517 (1929).

[5] W. H. Zachariasen, Zeits. f. Krist. **71,** 501 (1929); Paper in print in Phys. Rev.

molecule has an angular or pyramidal structure. The deviation from co-linearity or co-planarity probably increases with increasing Δ. A few examples of the kind of structures we may expect according to this rule may be given.

Co-linear: CO_2, ON_2, CS_2, $(NN_2)^-$, $(HF_2)^-$
Angular (polar): OH_2, SO_2, OO_2? (ozone), SH_2, NO_2, $(NO_2)^-$
Co-planar: $(BO_3)^{-3}$, $(CO_3)^{-2}$, $(NO_3)^-$, SO_3, BH_3, BF_3
Pyramidal (polar): $(PO_3)^{-3}$, $(SO_3)^{-2}$, $(ClO_3)^-$, $(AsO_3)^{-3}$, $(SeO_3)^{-2}$, $(BrO_3)^-$, $(OH_3)^+$, NH_3, PH_3, AsH_3, PF_3, PCl_3 and so on.

In no case is there observed a contradiction to the rule, so it may be used with some confidence for predictions. For a more complete information about my work on the groups I can refer to my paper which is to be published shortly.

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February 28, 1931.

Interpretation of the Spectra of Rare Earth Crystals

From the work of J. Becquerel, Brunetti, Ephraim, Freed and Spedding, and others, it is known that the absorption spectra of rare earth crystals consist of narrow bands which become resolved into sharp lines as the temperature of the crystals is lowered. The lines tend to gather into multiplets, and arise from energy levels which resemble in their behavior the energy levels of atoms subjected to electric and magnetic fields much more than they resemble the levels of molecules. For example, the positions of the lines are but very little influenced by the negative ions present, and such influence amounts only to the expected slight shifting caused by the different electric fields set up by the various ions in the lattice. Furthermore, the lines do not fade out as the temperature is lowered, but are still strong at the temperature of liquid helium. Again, the lines are polarized, as would be the case if the levels were split apart by electric fields.

In a paper which is to be published soon in this journal, Dr. Freed and I have presented a partial energy-level diagram for Gd^{+++} self-consistent within the accuracy we were able to attain (1 cm^{-1} for position, 4 cm^{-1} for resolution), derived from eight sets of data. The data were:[1,2,3] Absorption spectra of $GdCl_3 \cdot 6H_2O$ at ordinary temperatures, and at that of liquid nitrogen and of liquid hydrogen. Gd^{+++} even at room temperatures gives sharp spectra, but as the temperature is lowered the lines shift somewhat owing to changes in the effective electric fields caused by the ingathering of the crystal lattice;[4,5] Absorption spectra of $GdBr_3 \cdot 6H_2O$ at room and liquid nitrogen temperatures;[6,7] Transverse Zeeman effect on the *a* and *b* axis of monoclinic

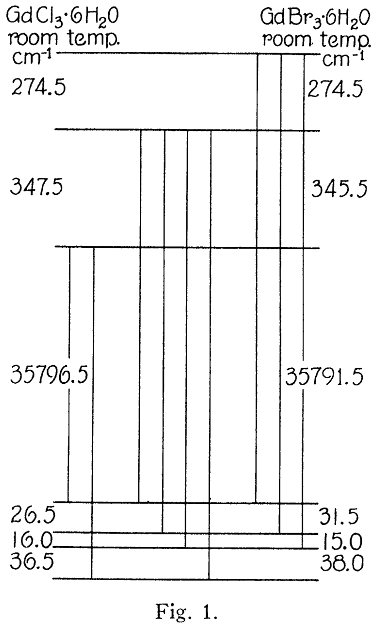

Fig. 1.

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[1] F. Hund, Linien Spektren, Julius Springer, Berlin.

[2] Woltjer and Kammerlingh Onnes, Leiden Comm. No. 167 C.

[3] Giauque, J. Am. Chem. Soc. **49**, 1870 (1929).

[4] (a) H. A. Kramers, Proc. Amst. Acad. **32**, 1176 (1929); **33**, 9 (1930). (b) H. A. Kramers et J. Becquerel, Proc. Amst. Acad. **32**, 1190 (1929). (c) J. Becquerel, W. J. de Haas, et H. A. Kramers, Proc. Amst. Acad. **32**, 1206 (1929). (d) H. A. Kramers, Proc. Amst. Acad. **32**, 1196 (1929) and private conversation.

[5] Freed and Spedding (a) Nature **123**, 525 (1929); (b) Phys. Rev. **34**, 945 (1929); (c) J. Am. Chem. Soc. **52**, 3747 (1930); (d) Phys. Rev. **35**, 1408 (1930).