

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.

Inhomogeneities in Crystals (A Reply)

Dr. R. H. Canfield¹ has published in a letter of the above title some objections to my theory of the mosaic structure of crystals. His arguments are based on a very serious misunderstanding of my considerations.² In order to clear up the case, I shall repeat here the general method which enabled me to find configurations of lower energy than that of the crystallographically ideal crystal. For the sake of an unambiguous illustration, I shall give the energy changes involved for the very specific case of an NaCl crystal.

Using the notations of loc. cit., we have $d_0 = 5.6\text{\AA}$ for the lattice constant of NaCl. The lattice constant of an isolated (100) plane "in equilibrium," which is not sandwiched in between other (100) planes, is $d = 0.94d_0$. The outline of my method for finding the configurations of low energy given in loc. cit. p. 818 is literally this.

" α) Contract (an arbitrary plane 100) II so that its spacing is changed from d_0 to d .

β) Fill the gaps which have been opened by α between the two remaining parts I and II of the crystal.

γ) Rearrange the relative position of I and II in a certain way."

If we disregard the polarizability of the atoms for a moment, then the process α involves an energy change $\epsilon_\alpha = \epsilon_1 + \epsilon_2$, where ϵ_1 represents the (negative) energy of contraction of the plane II under its own forces. ϵ_2 is the positive energy which has to be supplied in order to annihilate the energy of the plane II relative to the remaining parts I and II. It is easily seen that ϵ_2 if taken per cm^2 is approximately equal to $2\sigma = 300$ ergs where σ is the theoretically derived surface energy of NaCl. The value for $\epsilon_1 \cong -220$ ergs/cm² may be obtained from curves published by I. E. Lennard-Jones and B. M. Dent³

for instance. It is $\epsilon_1 + \epsilon_2 > 0$ as Mr. Canfield justly remarks. Otherwise an NaCl crystal would fall apart.

The step β involves a negative energy change which is easily seen to be 12 percent of 2σ approximately. This yields $\epsilon_\beta \cong -36$ ergs/cm². The rearrangement γ in our specific case is a very simple process. Exchange all the positive ions with all the negative ions in part I of the crystal. This leaves the relative energy between I and the plane II unaltered. It involves, however, a small negative change of energy of I relative to II; namely, $\epsilon_\gamma \cong -20$ ergs/cm².

Finally, we have to consider the polarizability of the ions. In the ideal crystallographic configuration, the ions are in locations where the electric field strength is zero. The ions (e) of our II plane, however, are subjected to fields of the order of $E = 4e/d_0^2$ e.s.u. due to the rearrangement γ of the relative position of I and II. We therefore have lowered in this way, the energy of an ion in the II-plane by an amount $|\delta\epsilon_4| = \alpha E^2/2 = 8\alpha e^2/d_0^4$ where α is the polarizability of the ion. The average value of α for the couple Na^+ and Cl^- may be taken equal to that of Ne and A with sufficient accuracy. This results in $\alpha = 10^{-24}$ cm³. We therefore obtain $\delta\epsilon_4 = -1.8 \times 10^{-13}$ ergs/cm². As there are $n = 1.3 \times 10^{15}$ ions per cm², we have $\epsilon_4 = n\delta\epsilon_4 = -230$ ergs/cm². This value has in reality to be multiplied by a factor of the order of three, because of the fact that the ions in the two neighboring planes of II are also subjected

¹ R. H. Canfield, Phys. Rev. **35**, 114 (1930).

² F. Zwicky, Proc. Nat. Acad. Sci. **15**, 816 (1929). Will be referred to as loc. cit.

³ I. E. Lennard-Jones & B. M. Dent, Proc. Roy. Soc. **A121**, 259 (1928).

to the same high fields. In any case the, figures show conclusively that the total change in energy is $\epsilon = \epsilon_\alpha + \epsilon_\beta + \epsilon_\gamma + \epsilon_\delta < 0$ which verifies my general contention for the case of rock-salt.

The principle which led me to the conception of the mosaic structure might be called the *principle of the slight asymmetries in complex configuration* such as atoms, molecules, and crystals. *Indeed, due to the deformability of the atoms and molecules, nature, according to the above, definitely favors configurations which are somewhat asymmetrical.* I owe to Professor O. Stern the remark that this principle might apply to cases like $\text{H}_2\text{O} = (\text{HO}^- + \text{H}^+)$.

The trivial consideration mentioned by Mr. Canfield that under the proper circumstances, certain planes like (111) have a tendency to expand has not escaped my attention. Indeed, I have thought out its consequences long ago. One of them I have mentioned, loc. cit. p. 820, "In regard to the space groups characterizing the primary and the secondary (mosaic) structure, it must be remarked that they are not necessarily the same, etc."

In regard to the experimental evidence which we have secured so far, I can mention here only that it supports my conception of a *spacial* mosaic structure. It is not a surface

phenomenon only as Mr. Canfield seems to think. Moreover, if an indirect argument is wanted, I may mention the quantitative agreement which can be obtained on the basis of my theory with some of the important phenomena related to the *slipping strength* (not the tensile strength). For all further detailed information, I have to refer the reader to several articles by my collaborators and myself which will be published presently. A complete representation of my theory is now in preparation for the *Helvetica Physica Acta*.

Finally, I wish to make a remark in regard to the development of the theory. Mr. Canfield intimates that I had secured direct experimental (optical) evidence for the mosaic structure first, and then developed a theory "resulting in a prediction of the required phenomenon." I can only state that the exact contrary is true, inasmuch as *all* the experimental investigations at this Institute dealing with the mosaic structure have been undertaken at my suggestion to check the theoretical predictions and *all* the evidence obtained is posterior to the development of the essentials of the theory.

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The Effect of Dilution upon the Raman Spectra of Nitric Acid

Photographs of the Raman spectra of dilute and concentrated solutions of nitric acid in water obtained in this laboratory last May show striking differences in the frequencies of the lines scattered in the two cases. Lines which are strong in commercial 70 percent acid become weak and ultimately disappear as the acid is diluted, and other lines, weak in the concentrated acid grow strong, reach a maximum intensity and disappear as the dilution becomes infinite. In a recent note to *Nature* (124, 762 (1929)) I. R. Rao reports similar results. As Rao points out, the effect can be attributed to dissociation. The lines which are strong in the concentrated acid and which disappear upon dilution are very probably due to the HNO_3 molecule. Those which are greatly enhanced by dilution can be attributed to the NO_3^- ion.

Four infra-red frequencies, two forming a doublet, give rise to the strong scattering in

the concentrated acid, and hence may be associated with the HNO_3 molecule. They are 618, 669, 937, and 1293 cm^{-1} . One transition, at 1034 cm^{-1} , grows enormously strong with dilution, reaching its greatest strength, approximately, in mixtures of equal volumes of water and commercial acid. Rao attributes the doublet at 618 and 669 cm^{-1} (given by him as 630 and 689 cm^{-1}) to the NO_3^- ion. On the plates obtained by the author this pair behave exactly as do 937 and 1293 cm^{-1} disappearing completely in a 25 percent solution of the commercial acid. At this dilution 1034 cm^{-1} is still of high intensity. Rao reports, in addition, a Raman frequency at 3319 cm^{-1} and attributes it to the HNO_3 molecule. No such frequency was found on the present plates. The doublet transition 618 and 669 cm^{-1} which is strongly excited by the mercury line 4358 appears only feebly excited by 4046 in concentrated acid. An