

to the  $\varphi$  value required to keep the reflexion at a maximum. The plot of the  $\varphi$  variations against the crystal length corresponded quite well with the photographic record obtained with the multiple exposure technique previously described, and gave the twist in degrees per mm, regardless of the geometry of the system.

The precision obtained was ten times that of the photographic method, since by centring the crystal with great care, the error involved was always less than  $\pm 0.01$  degree. Fig. 2(a) and (b) compare the results obtained by the two above methods from a strongly twisted specimen.

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## The Electron Density in the Hydrogen Atom of the Bifluoride Ion: a Comparison of Theory and Experiment

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A simple calculation shows that the experimentally determined electron density in the bifluoride ion is not incompatible with a theoretical model having a charge of  $+\frac{1}{2}$  on the hydrogen atom, as was previously believed.

In a previous communication (McDonald, 1960), the author presented the results of an experimental determination of the electron density in the bifluoride ion which, at the time, were thought to be at variance with the theoretical charge distribution of  $+0.56$  on H and  $-0.78$  on F (Hamano, 1957). It is now realized that the disagreement between theory and experiment was, in fact, largely illusory. Further calculations show that the experimental and theoretical electron densities agree quite well up to a distance of about  $0.5 \text{ \AA}$  from the centre of the hydrogen atom, if allowance is made for the effects of thermal vibrations in the crystal, and if a reasonable value is assumed for the temperature factor. Beyond this limit, we are not justified in making any comparison, because of the relatively large experimental error and for other reasons mentioned below.

The results of Hamano's LCAO-SCF-MO treatment of  $\text{HF}_2^-$  were taken as the starting point of the calculations. Using standard (Slater-type) atomic wave functions, the total electron density in the ion was calculated, and from this a 'difference density' was derived by subtracting non-bonded atomic distributions from the F positions, allowance being made for the excess charge of  $\frac{1}{2}e$  on each of the F atoms. The difference density so calculated was found to have roughly spherical symmetry within a radius of  $0.5 \text{ \AA}$  from the centre of the H atom. A line section of the radially averaged three-dimensional distribution is shown in Fig. 1 [curve (a)]. The departure from

These methods are now being applied on a large number of acicular KCl crystals. The results will be published soon.

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spherical symmetry did not amount to more than  $\pm 0.03 e.\text{\AA}^{-3}$  within the stated range, which is considerably less than the probable error of the experimental measurements (standard deviation  $0.1 e.\text{\AA}^{-3}$ ). The distribution of curve (a) is probably a true representation of the electron density near the H atom, but no physical significance can be attached to it further out. The difference density goes negative near the F atoms, and its value is sensitive to the choice of basic wave functions. The density near the H atom, on the other hand, is largely independent of the precise method of derivation.

Curve (a) has two interesting features. Firstly, the peak density is only  $1.27 e.\text{\AA}^{-3}$  compared with a value of  $2.16 e.\text{\AA}^{-3}$  for an unbonded H atom at rest. The H atom appears to have lost about half an electron, in agreement with Hamano's estimate of the charge distribution. This effect is undoubtedly due to the large polarity of the F-H bond. Secondly, the shape of the charge cloud is found to be precisely the same as that in a free atom, again within the limits of accuracy to which we are working. We can make use of this fact to simplify the subsequent analysis.

The effects of thermal vibrations in the crystal lattice may be allowed for by convoluting the difference density with an appropriate function of a temperature parameter  $\beta$ , which is related to the mean square displacement of an atom from its equilibrium position by the expression  $\beta = 2\pi^2\langle u^2 \rangle$ , and is numerically equal to

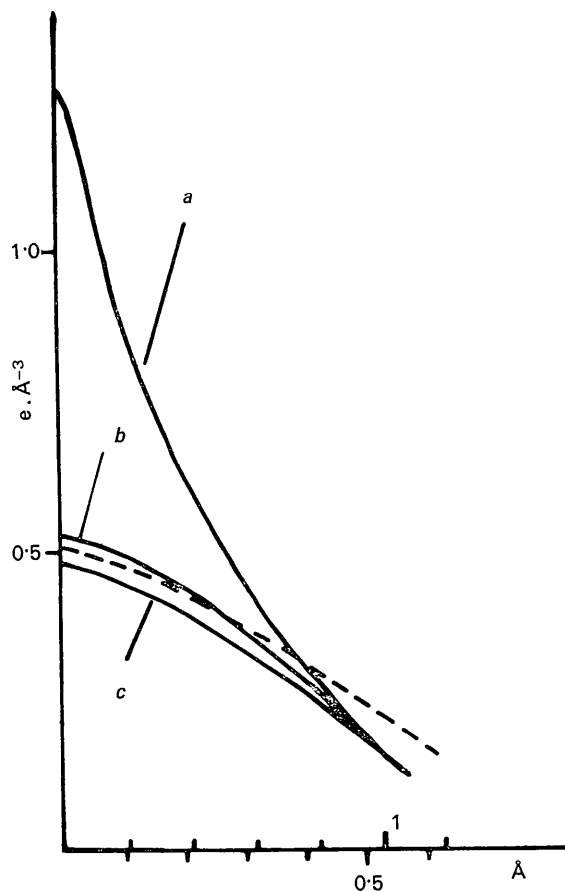


Fig. 1. The electron density in the H atom of the bifluoride ion for different values of the temperature parameter. (a)  $\beta=0$ , (b)  $\beta=0.50$ , (c)  $\beta=0.60$ . The broken line represents the experimentally determined density.

one quarter of the usual parameter  $B$  used in crystallographic work. If we assume that the difference function is spherically symmetrical and has the same shape as a free atom, then the problem is greatly simplified, because the mathematical analysis for this case has already been worked out (McDonald, 1956). Table 1 of this reference may be used directly to plot the modified difference density for different values of  $\beta$ . This is a considerable approximation, of course, but it can easily be shown that the negative regions near the F atoms in the difference function will have a negligible effect upon the convoluted density. Line sections of the modified density obtained in this way are plotted in Fig. 1 for two values of  $\beta$ . The experimentally determined difference density is plotted as a broken line. This

again is an averaged density, derived as described in the first reference (McDonald, 1960).

The experimental curve is fitted near the peak by taking  $\beta=0.55 \text{ \AA}^2$ , the deviation further out being well within the experimental error. It is of course not possible to obtain an independent measure of  $\beta$  for the H atom from the X-ray work on  $\text{NH}_4\text{HF}_2$ , but the results of other physical measurements on similar systems are available. McGaw & Ibers (1963) and Ibers (1964) give vibrational amplitudes for the H atoms in crystals of  $\text{KHF}_2$  and  $\text{NaHF}_2$ , as measured by neutron diffraction, which may reasonably be compared with the present results. In  $\text{KHF}_2$  and  $\text{NaHF}_2$  the mean values of  $\langle u^2 \rangle$  averaged over different directions are 0.032 and 0.028  $\text{\AA}^2$  respectively; these correspond to values of 0.63 and 0.55  $\text{\AA}^2$  for  $\beta$ , in good agreement with the above. The question of the true symmetry of the ion is not relevant to the present discussion.

There is thus no real conflict between theory and experiment. The earlier conclusions were, in effect, based upon a comparison of the experimental and theoretical electron densities at distances greater than 0.5  $\text{\AA}$  from the centre. It is now clear that such a comparison has no validity; the experimental difference density, like the theoretical one, has little physical significance except in the immediate neighborhood of the H atoms.

A redetermination of the electron density in this system seems desirable. Nothing is to be gained, however, by simply repeating the X-ray work on  $\text{NH}_4\text{HF}_2$ . In this compound, and in  $\text{KHF}_2$  also, the H atoms of the bifluoride ions are located at special positions of the unit cell (centres of symmetry), where the s.d. of the error in electron density is a maximum. What is needed is some salt in which the bifluoride ions are located in general positions of the unit cell. If such could be found, then there is no reason why the electron density in the H atoms should not be measured to  $\pm 0.05 \text{ e. \AA}^{-3}$  or better. A more detailed comparison with theory might then be possible.

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