

comparison with our results. Figure 4 of Ref. 2 shows that  $\tau$  scales as predicted in our Eq. (4). A distribution of energetic ions is seen (but there is no measurement of their absolute number) and the observed time scale ( $\sim 2 \mu\text{sec}$ ) for their randomization agrees reasonably with our low- $\beta$  runs.

<sup>1</sup>K. R. Chu and M. Lampe, *Bull. Amer. Phys. Soc.* **19**, 510 (1974).

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<sup>4</sup>C. A. Kapetanacos, W. M. Black, and K. R. Chu, *Phys. Rev. Lett.* **34**, 1156 (1975).

<sup>5</sup>We assume end losses can be neglected on the time scale of interest. No axial inhomogeneities of any kind are considered in this paper.

<sup>6</sup>R. C. Davidson, D. A. Hammer, I. Haber, and C. E. Wagner, *Phys. Fluids* **15**, 317 (1972).

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Vlasov-ion fluid-electron codes have also been used by R. Mason [*Phys. Fluids* **14**, 1943 (1971), and **15**, 1082 (1972)], and by D. W. Forslund and J. P. Freidberg [*Phys. Rev. Lett.* **27**, 1189 (1971)] to study shocks; and by R. Chodura and B. Röhlein [*Proceedings of the Sixth European Conference on Controlled Fusion and Plasma Physics, Moscow, U. S. S. R., 1973* (U.S.S.R. Academy of Sciences, Moscow, 1973), p. 311], and by A. G. Sgro and C. W. Nielson [presented at the Annual Meeting on Theoretical Aspects of Controlled Thermonuclear Research, Naval Research Laboratory, 1975 (unpublished)], to study theta pinches.

<sup>10</sup>The initial expansion is into near vacuum ( $n_0^< = 100n_0^>$ ), so  $v_m^>$  is large and counterstreaming is not expected initially. Mason, Ref. 9, showed that counterstreaming can occur during expansion into a dense background.

<sup>11</sup>T. E. Stringer, *J. Nucl. Energy, Part C* **6**, 267 (1964); K. Papadopoulos, R. C. Davidson, J. M. Dawson, I. Haber, D. A. Hammer, N. A. Krall, and R. Shanny, *Phys. Fluids* **14**, 849 (1971).

<sup>12</sup>W. M. Manheimer and I. Haber, *Phys. Fluids* **17**, 706 (1974); W. M. Manheimer, P. C. Liewer, M. Lampe, R. W. Clark, and K. R. Chu, to be published.

<sup>13</sup>J. Guillory and V. Bailey, Physics International Co. Report No. PIIR-11-73 (unpublished), have also considered the interpretation of these diamagnetic signals.

## Direct Evaluation of the Charge Transfer in the Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ) Complex at 100°K by Numerical Integration of X-Ray Diffraction Amplitudes\*

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(Received 17 April 1975)

A numerical charge integration procedure has been applied to diffraction data of TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) measured at 100°K. The results indicate an average charge transfer of  $(0.48-0.60) \pm 0.15$  electrons from a TTF to a TCNQ molecule.

The amount of intermolecular charge transfer in the TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) radical-ion salt is of considerable interest in the interpretation of the electrical properties of this solid. The coexistence of neutral and charged TCNQ molecules in one solid was inferred by comparison of the intramolecular interatomic distances in the salt  $\text{Cs}_2(\text{TCNQ})_3$  with those in  $\text{K}(\text{TCNQ})$  and neutral TCNQ.<sup>1</sup> On the same basis Kistenmacher, Phillips, and Cowan<sup>2</sup> conclude that in TTF-TCNQ and assignment of a -1 charge to the TCNQ residue is consistent

with the observed molecular dimensions. However, their choice between a -1 charge and a -0.5 charge is not convincing when the standard deviations in the experimental bond lengths are considered. A later low-temperature study<sup>3</sup> of the complex shows that at least at 100°K the bond lengths are in better agreement with those listed for TCNQ with a -0.5 charge. It has been emphasized that structural studies do not provide information on whether this charge is localized on part of the TCNQ molecules or is equally distributed.<sup>4</sup> In the former case the observed bond

lengths are averages over two species and a contribution of disorder to the apparent thermal vibration amplitudes may be expected. However the differences between the bond lengths in neutral TCNQ and TCNQ with a  $-1$  charge are at most  $0.03 \text{ \AA}$ ,<sup>5</sup> and the expected contribution of  $0.001 \text{ \AA}^2$  to the mean square amplitudes is therefore small compared with the observed values (even at  $100^\circ\text{K}$ ), which are typically  $0.01-0.02 \text{ \AA}^2$ .<sup>3</sup> Recent measurements by uv-photoemission spectroscopy<sup>6</sup> which provide no evidence for fractional ionization are therefore not in contradiction with the x-ray diffraction results.

The exact interpretation of the x-ray-photoemission data is still being questioned.<sup>7,8</sup> Grobman *et al.* have interpreted their measurements as indicating a partial charge transfer of  $\approx \frac{2}{3}$  of an electron per molecule.<sup>7</sup> This result has been criticized by Epstein *et al.* whose analysis of the same data leads to the conclusion that one can only say that the extent of charge transfer is probably greater than 50%.<sup>8</sup>

Inference of the charge transfer from a comparison of bond lengths suffers from the disadvantage that it is based on the assumption of transfer of a full electron in salts such as NaTCNQ in which the real charge separation may be less than indicated by the formal charges. A direct measurement of the average charge transfer may be obtained, however, if reasonably accurate diffraction data are available. Those employed here from the study by Blessing and Coppens<sup>3</sup> were collected at  $100^\circ\text{K}$  with a step-scan followed by profile-analysis technique.<sup>9</sup> The total electron population can be evaluated (in the centrosymmetric case) according to

$$P = \int \sum (F_{\text{obs}}/k) \cos 2\pi \vec{H} \cdot \vec{r} d\tau + \int F_{000} d\tau, \quad (1)$$

where the integrals are over the molecular volume,  $k$  is the scale factor defined by  $F_{\text{obs}} = kF_{\text{calc}}$ , and  $F$  and  $H$  are the structure factor and reciprocal-lattice vector, respectively.

In an earlier study of the TCNE (tetracyanoethylene)-pyrene charge-transfer complex,<sup>10</sup> the integration was performed analytically using a technique developed previously.<sup>11</sup> However the molecular volumes of neither the TTF nor the TCNQ molecule are easily described by a regular volume required for the analytical-integration method. The molecular volume was therefore divided into a large number of small cubes of equal size centered on an isometric grid. The analytically integrated<sup>11</sup> density of the cubes was summed over all cubes associated with the mole-

cule under consideration. To improve the accuracy of the numerical technique the integration is performed over the more slowly varying valence density rather than over the total electron density. To this purpose the  $F_{\text{obs}}$  in (1) were replaced by the valence structure factors which were obtained from

$$F_{\text{valence}} = F_{\text{obs}} - kF_{\text{core}}, \quad (2)$$

where  $F_{\text{core}}$  is calculated with core-scattering factors listed by Fukamachi<sup>12</sup> and x-ray structural parameters.<sup>3</sup>

Though the regions between the molecules contain little density, they should nevertheless be subdivided among the adjacent molecules. For this purpose the distance  $r$  of the center of a cube to adjacent atoms was considered. The cube was assigned to the molecule containing atom  $i$  for which the ratio  $r_i/R_i$  is smallest,  $R_i$  being the Van der Waals radius of atom  $i$ . The use of a parameter such as  $R$  is a necessary consequence of the differences in size of the atoms in molecular crystals such as TTF-TCNQ. We should emphasize that it is the ratio of the Van der Waals radii of contacting atoms and not their absolute value that influences the resulting populations. Results which converged on reduction of the elementary cube edge to  $0.25 \text{ \AA}$  are summarized in Table I. Two sets of Van der Waals radii were tested. For the present purpose they differ mainly in the radii of the hydrogen atoms, which have a strong influence on the molecular size as the hydrogens are located on the periphery of the molecules. Nevertheless the integrated charges are not very dependent on the radii employed. This is as expected as the electron density is concentrated between bonded atoms and not in the intermolecular regions. As the differences are smaller than the estimated standard deviations in the electron populations  $P$  (see below), the choice of Van der Waals radii is not of decisive importance.

There are three main contributions to the error in  $P$ . They are (1) errors in the extinction

TABLE I. Results of charge integration.

Van der Waals radii used ( $\text{\AA}$ )				Electron population (electrons)	
S	N	C	H	$P_{\text{TCNQ}}$	$P_{\text{TTF}}$
1.85	1.50	1.75	1.1	72.45	51.56
1.85	1.55	1.65	1.2	72.50	51.51

correction of the intensity measurements, (2) errors in the scale factor  $k$ , and (3) experimental errors in the observed intensities. Extinction is relatively small in the present data set and in a range in which existing formalisms are quite adequate.<sup>13</sup> The scale-factor error affects the first term in expression (1), which shifts about 6 electrons from TTF to TCNQ compared with the uniform density represented by the second term. Thus a 1% error in  $k$  causes a 0.06-electron error in  $P$ . Experimental measurements of  $k$  for a series of crystals<sup>14</sup> show that scale factors obtained in a conventional spherical-atom least-squares refinement are systematically overestimated. For the present low-temperature data set, however, this bias should not be larger than 2%. It follows that the contribution of the first term in Eq. (1) of 6 electrons may have been underestimated by at most 0.12 electrons, i.e., that  $P_{\text{TCNQ}}$  may be larger and  $P_{\text{TTF}}$  smaller by this amount. The effect of the measurement errors was evaluated from  $\sigma(F_{\text{obs}})$  based on statistical counting errors plus a factor proportional to the measured intensity. A 2% proportionality factor was selected on the basis of the agreement between symmetry equivalent reflections in the data set. An analytical expression given by Coppens and Hamilton was used [Ref. 11, expression (1)] with an approximate shape for the molecular volume. Such a procedure is quite adequate, as the electron density error is not very position dependent.<sup>11</sup> An error estimate of 0.15 electrons was obtained. Thus, as the neutral TCNQ and TTF molecules contain 72 and 52 electrons, respectively, one finds, on averaging the entries in the table and taking into account error contributions of types (2) and (3), a best estimate for the charge transfer of  $(0.48-0.60) \pm 0.15$  electrons.

The result is in agreement with conclusions derived from examination of the bond lengths summarized above which suggests transfer of close to a full electron in salts of the type NaTCNQ. It is also compatible within the estimated error with conclusions based on the x-ray-photoemission data.<sup>7,8</sup> The relatively large standard deviation is somewhat disappointing. Nevertheless,

charge transfer *averaging* a fraction of an electron from TTF to TCNQ is a definite implication of the results. It should finally be noted that the error bar can be reduced with improved accuracy in the measurements. The present data set, though of better than routine quality, is not quite as good as some other low-temperature sets recently measured in our laboratory (at Buffalo), in which a less than 2% proportionality factor was obtained on examination of the data sets.

The author would like to thank Dr. P. Becker for helpful discussions on the calculation aspects of the numerical integration procedure.

\*Research supported in part by the National Science Foundation.

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