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DISCUSSION

Herbstein: I notice that of the two different temperature factors which you deduce from the two sets of experimental data for MgO, one leads to a Debye temperature which is considerably closer to that obtained by other methods. I would regard this agreement as a better assessment of the experimental data than the *R* factors.

Hosoya: I had not taken notice of this feature. However, according to our experience, for instance, on MnO (Hosoya & Yamagishi, 1966, p. 2641) a Debye temperature value is apt to be heavily affected by the difficulty in taking a suitable range of background to be subtracted, when a sample is subject to heavy strain. The agreement in a Debye temperature value, therefore, may not always be a good criterion.

Dr B. Dawson then discussed a comparison of the available experimental evidence on MgO with a variety of models, using the same temperature factors for both atoms. This discussion appears in the written version of his paper in the present proceedings.

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Charge Density and Momentum Density - A Comparison Between Theory and Experiment

By R. J. Weiss

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X-ray structure factors and Compton line shape measurements provide complementary information on charge and momentum density, the latter measurement evidencing very much greater sensitivity to the valence electrons. Theoretical calculations of structure factors and Compton line shapes for solids have been sparse and have probable errors in excess of 3%. When these errors are compounded with experimental errors of several per cent the cases for which comparison between theory and experiment is meaningful are presently limited to diamond, silicon, germanium, MgO, LiH, Li, Be, Mg, Al and perhaps a few others. In diamond the 111 and 222 structure factors are in agreement with theory as are the 111 structure factors of LiH and MgO. The experimental momentum densities in Li, Be, Mg, and Al do not agree with conventional band calculations since these are unable at present to account for a significant electron–electron correlation effect.

This paper is concerned with a comparison between X-ray measurements and theoretical calculations of electron charge and momentum density. Some of this material has already been considered in a previous publication (Weiss, 1966) and therefore emphasis will be placed on recent developments.

Introduction

For the past 35 years, and especially since World War II, experimental efforts in X-ray diffraction have shown little success in providing reliable details of valence electron distributions in solids, in sharp contrast to the enormous success in crystal structure determinations. The reason, of course, is that the valence electron contribution to structure factors is overwhelmed by the inner electron contribution so that, at the very least, measurements of absolute structure factors must be in error by no more than 1% to provide even the barest of information. In a few cases (like the 'forbidden' 222 reflection in diamond) such restraints on the errors are considerably relaxed but the information gained is limited and is only useful in comparing various theoretical calculations of the charge density. One might have thus guessed from the Heisenberg uncertainty principle that a large indeterminacy in valence electron positions would be compensated by a well-defined determination of their momenta. This, indeed, is the case and X-ray Compton line profile measurements have revealed significant details of momenta distributions. Furthermore, the problems inherent in structure factor measurements like extinction, absolute scale, termination errors, and Debye–Waller factor are absent from Compton line profile measurements.

The errors in the theory

It is pointless to discuss various theoretical approaches employed in calculating charge and momentum density without having some idea of the magnitude of the errors in such calculations. Only in the case of Hartree–Fock free atom calculations have theoreticians specifically investigated these errors and they conclude that Hartree–Fock scattering factors are in error by ~1%. (Hall, 1964; Goodisman & Klemperer, 1963). These scattering factors are tabulated in *International Tables for X-ray Crystallography* (1962), but the only accurate X-ray measurements of free atom scattering factors are those of Chipman & Jennings (1963) on Ne, Ar, Kr and Xe. Their quoted error was about 1% and comparison between theory and experiment shows agreement within these errors.

The next more complex theoretical problem is the charge density of simple diatomic molecules and theoreticians so engaged believe that at best one can only approach the accuracy of Hartree–Fock atomic calculations. It is reasonable to assign an error of $1\frac{1}{2}$ to 2% to scattering factors evaluated from these charge densities. However, accurate X-ray measurements are unavailable for comparison.

There is a prodigious jump in theoretical complexity when one treats crystalline charge density, so much so that we do not have a good idea of the errors in the calculated scattering factors. In addition, there are only a handful of theoretical crystalline scattering factors (diamond: Goroff & Kleinman, 1968; MgO: Tokonami, 1965; LiH: Hurst, 1959; Fe: De Cecco & Kitz, 1967; Cu: Arlinghaus, 1967; Al: Weiss, Phillips & Harvey, 1968) and we can only say that the errors must be significantly greater than the Hartree–Fock scattering factors. We suggest an error of ~3% based on calculated differences of this magnitude between Hartree–Fock and simple Hartree scattering factors. A few typical cases are given in Table 1.

Since band calculations do not employ the determinantal form of the wave function (as is done in Hartree-Fock calculations but not in simple Hartree calculations), such band calculations are in error at least as much as Hartree calculations.

Because of the sparsity of theoretical scattering factors for crystals, experimentalists compare their measurement with a superposition of Hartree–Fock free atom scattering factors. If the errors in both the theory and experiment can be limited to ~1%, any difference significantly greater than this (>3%) might be attributed to solid state effects, *i.e.* changes in the charge density accompanying the formation of the crystalline bond.

Momentum density calculations are more sparse than charge density calculations, although at the time charge density calculations are made it is not difficult to add a program to determine momentum density. But with the renewed interest in the Compton line shape the demand is now recognized and such calculations should become more plentiful. It is difficult to assign inherent errors to such calculations of momentum density but the differences expected in the Compton line shape between free atom and crystal are so large (10-40%) that we are not so concerned with theoretical errors of a few per cent for comparison between Hartree–Fock free-atom momentum density and experimental momentum density in the solid. We can say, though, that momentum density is a more sensitive test of a wave function than charge density since the momentum depends on the slope of the wave function while the charge depends on its magnitude. My own guess is that the H.F. free atom momentum densities are in error by something like 2-3%.

The errors in the experiment

The problems in obtaining absolute structure factors to an error of 1% are formidable although it appears that most of the difficulties are at least identifiable. The most consistent group of measurements are on silicon (Göttlicher & Wölfel, 1959; DeMarco & Weiss, 1965; Hattori, Kuriyama & Kato, 1965; Jennings, 1968*a*) and even here the differences amongst experimentalists employing different techniques (powders, perfect crystals, Pendellösung fringes) are greater than 1%. Since the experimentalists have not yet demonstrated their ability to concur within 1%, we believe that the minimum errors are 1% and the probable ones greater.

Table 1. *Hartree and Hartree-Fock scattering factors for* Al, Ca^{2+}, Cu *and* Rb^{+}

	$\sin\theta/\lambda$	0	0·2	0·3	0·4	0·5	1·1
Al	Hartree	13	9·02	7·77	6·63	5·53	2·01
	H.F.	13	9·16	7·88	6·77	5·69	2·05
	%diff.	—	1·6	1·4	2·1	2·9	2·0
Ca^{2+}	Hartree	18	14·11	11·38	9·39	8·14	4·61
	H.F.	18	14·4	11·7	9·61	8·25	4·68
	%diff.	—	2·0	2·8	2·3	1·4	1·5
Cu	Hartree	29	22·87	19·16	15·91	13·24	6·63
	H.F.	29	23·63	19·9	15·60	13·10	6·45
	%diff.	—	1·1	3·9	2·0	1·07	2·7
Rb^{+}	Hartree	36	28·83	24·66	21·57	19·06	8·88
	H.F.	36	29·3	25·08	21·87	19·34	9·05
	%diff.	—	1·6	1·7	1·4	1·5	1·9

Compton line shape measurements are possibly accurate to a few per cent primarily due to the absence of the difficult problems encountered in structure factor measurements. Extinction is absent since we have an incoherent process, and there are no significant corrections for thermal motion since the momentum added to the electron due to the thermal motion of the atom is less than 10^{-3} of its own momentum. Absolute measurements are not required since measurements are made at $\sin/\lambda > 1{\cdot}0$ Å^{-1} where the Compton cross section of the valence electrons in electron units is just equal to the number of valence electrons. Furthermore, the Compton line shift is only a few per cent, requiring only minor wavelength dependent corrections. Lastly, the Compton line makes a complete scan of electron momentum space and this eliminates termination errors which are always present in charge density determinations. Since the Compton cross sections are small the only real problem is intensity and the error is primarily one of statistical counting.

Comparison of theory and experiment

I shall limit my discussion to those cases for which the errors in theory and experiment are considered small enough to make the comparison significant.

I. Valence electrons

1. *Carbon, silicon, and germanium*

For diamond only the 111 and 222 Bragg reflections have significant valence electron contributions. The latter reflection is missing for spherically symmetric charge densities and its presence is a direct measure of the asphericity. Although quite weak, it is probably in error by only 10%. Table 2 summarizes the experimental and theoretical valence electron scattering factors for diamond, silicon, and germanium. The core electron contributions which were subtracted were assumed to be a superposition of free atom Hartree–Fock cores. The errors are my own assessments.

Table 2. *Experimental and theoretical valence electron scattering factors per atom for diamond,* Si *and* Ge

	Experiment	H.F. free atom	Band theory
References	Göttlicher & Wölfel (1959) DeMarco & Weiss (1965) Hattori, Kuriyama & Kato (1965) Jennings (1968*b*)	*International Tables* (1962)	Goroff & Kleinman (1968) Clark (1964)
111			
Diamond	1·35 ± 0·05	1·09 ± 0·04	1·24 – 1·42 ± 0·1
Silicon	1·43 – 1·65 ± 0·015	1·20 ± 0·1	
Germanium	1·1 ± 0·4	1·10 ± 0·1	
222			
Diamond	0·14 ± 0·15	0	0·064 – 0·015 ± 0·05
Silicon	0·18 ± 0·01	0	
Germanium	0·14 ± 0·02	0	

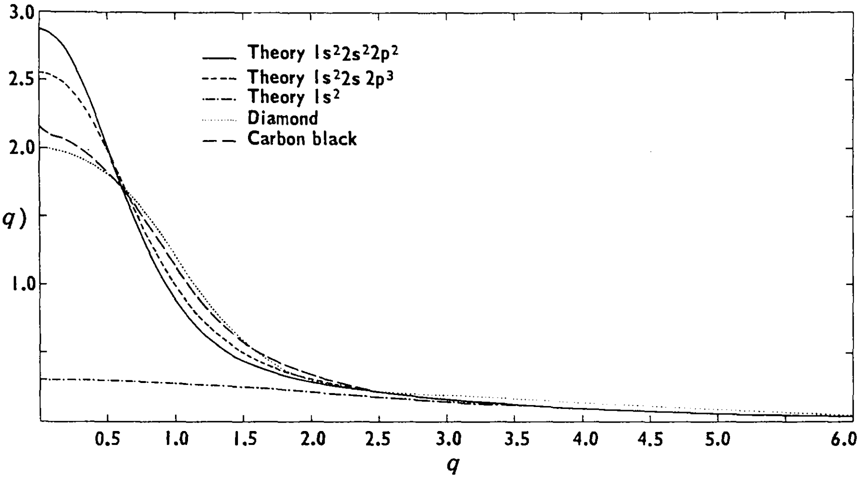

Fig. 1. The measured Compton line shapes for polycrystalline diamond and graphite. Theoretical Hartree–Fock free atom line shapes for the configurations $1s^22s^22p^2$ (ground state) and $1s^22s\,2p^3$ are included as well as the $1s^2$ (core) contribution.

Band theory and experiment appear satisfactory for diamond. For silicon there appears to be some evidence for an electronic structure change when comparing Hartree–Fock free atom theory to the range of experimental values 1·43–1·65 for the 111 reflection. Of course, the 222 in silicon is a direct measure of an electronic structure change. For germanium we cannot say anything about the 111 since the valence electron contribution is so small (4%), but we can be reasonably certain of the electron asphericity from the 222. Of course, the information gleaned from the 111 and 222 reflections, no matter how accurately determined, only provides limited idea of the valence electron distribution.

Momentum density has been measured in diamond, in pyrolytic graphite, and in carbon black (Weiss & Phillips, 1969) In Fig. 1 are shown the Compton line shapes for diamond and graphite together with the calculated Hartree–Fock free atom line shapes for the configurations $1s^22s^22p^2$ (free atom ground state) and for the frequently discussed $1s^22s2p^3$ configuration. Not only do we see a sizeable difference between these free atom configurations and the solid, but we also see an experimental difference between diamond and graphite (carbon black is similar to graphite). There are noticeable anisotropies in diamond and graphite but these are reported elsewhere (Weiss & Phillips, 1969). The difference in the line shape between a superposition of free atoms of carbon in their ground state and the measured diamond line shape is ~40% at $J(0)$, significantly outside the few-per-cent errors in both theory and experiment. This provides striking evidence of the effect of bonding on the valence electrons. In spite of the many published band calculations of the charge density in diamond, no momentum density calculation is available for comparison.

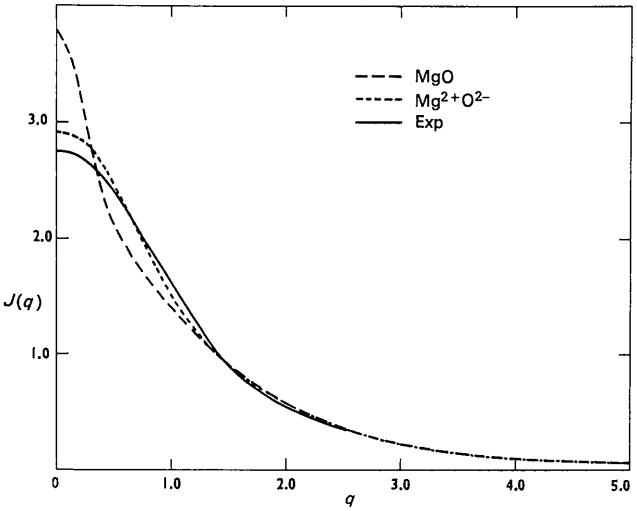

Fig. 2. The measured Compton line shape for polycrystalline MgO together with the theoretical line shapes for a superposition of Hartree–Fock free atom momentum densities Mg^0+O^0 and $Mg^{2+}+O^{2-}$.

2. MgO *and* LiH

Only the 111 structure factors for these rocksalt type crystals have significant valence electron contributions and in both cases the differences between the measured structure factors and those calculated from a superposition of Hartree–Fock *neutral* free atoms is ~10%. In Table 3 we summarize the experimental and theoretical results for these cases.

The Compton line shape measurement of MgO is shown in Fig. 2 and we note the large change between a superposition of Hartree–Fock neutral free atoms (Weiss, Phillips & Harvey, 1968) and experiment. (Weiss, 1968). The agreement with a superposition of ionized free atoms is better.

3. *Lithium*

The valence electron contribution to the structure factors is extremely small in Li but it does provide a good example of the advantage and sensitivity of the Compton line profile to these valence electrons. Fig. 3 shows the experimental profile together with the theoretical profiles. There is a marked difference between a superposition of Hartree–Fock free atom momentum densities and that actually observed. It is common to treat valence electrons in metals like Li as so-called 'free electrons' for which the momentum density is a constant from zero momentum to its maximum value at the Fermi momentum. This gives an inverted parabola for the Compton line shape. But Fig. 3 shows that while the free electron theory provides a better fit than a superposition of Hartree–Fock free atom momentum densities, it fails to account for the observed high momentum 'tail' above the Fermi momentum at 0·59 (atomic units). Neither do conventional band calculations like OPW (orthogonalized plane waves) yield the observed line shape. (Such band calculations on Li (Melngailis & De Benedetti, 1966) give a Compton

Table 3. *Experimental and theoretical* 111 *structure factors for* MgO *and* LiH

	Observed	H.F. neutral free atom	Solid state calculation
MgO	4(2·69) to (2·85 ± 0·10) (Togawa, 1965; Burley, 1965; Raccah & Arnoff, 1967; Jennings, 1968*b*)	4(3·15 ± 0·15)	4(2·64 ± 0·12) (Tokonami, 1965)
LiH	4(1·086 ± 0·03) (Calder, Cocran, Griffiths & Lowde, 1962)	4(0·99 ± 0·02)	4(1·062 ± 0·03) (Hurst, 1959)

line shape which differs only slightly from that obtained from free-electron theory.) The reason for this discrepancy is that electron–electron correlations must be neglected owing to their mathematical complexity. Such electron–electron correlations can be included though, in the so-called interacting electron gas problem (Daniel & Vosko, 1960). Fig. 4 shows the momentum density deduced from the measurement and that calculated from the interacting electron gas whose electron density and Fermi momentum are appropriate to Li. This provides the best fit between theory and experiment. Similar work on Be, Mg, and Al is reported elsewhere (Phillips & Weiss, 1968).

II. Core electrons

1. Al *and* Mg.

The contribution of the valence electrons to the Al structure factors is almost neglible and it is indeed perplexing that several independent absolute measurements (Batterman, Chipman & De Marco, 1961; Bensch, Witte & Wölfel, 1955; De Marco, 1967) of the 111 and 200 reflections are lower by 3-4 % than a superposition of Hartree–Fock free-atom scattering factors. It had been generally accepted that the core electrons are essentially unaffected in the metallic bonding. In recent Compton line shape measurements of Al for which the valence electron and core electron contributions can be separated, one also finds the core electron contribution to be in disagreement with a superposition of Hartree–Fock free atom momentum densities. Furthermore, the disparities in both types of measurement are consistent since the scattering factors indicate an expansion of the core charge density while the Compton line profile measurements indicate a contraction of the momentum density. (This is just what one expects). Some light has been shed on this dilemma by Ransil (1967) who has shown that in accurate diatomic molecular calculations (such as Li_2) there is a noticeable change in the 'core electron' charge distribution when compared with a superposition of Hartree–Fock free atom charge densities. We await further theoretical investigations of this point. Interestingly enough, absolute structure factor measurements (Weiss, 1967) and Compton line shape measurements (Phillips & Weiss, 1968) on Mg both agree with a superposition of Hartree–Fock core electrons.

It appears that one cannot make the assumption that the core densities are unaffected in bonding (at least to within one per cent or so). While this assumption has been made in deducing the valence electron contribu-

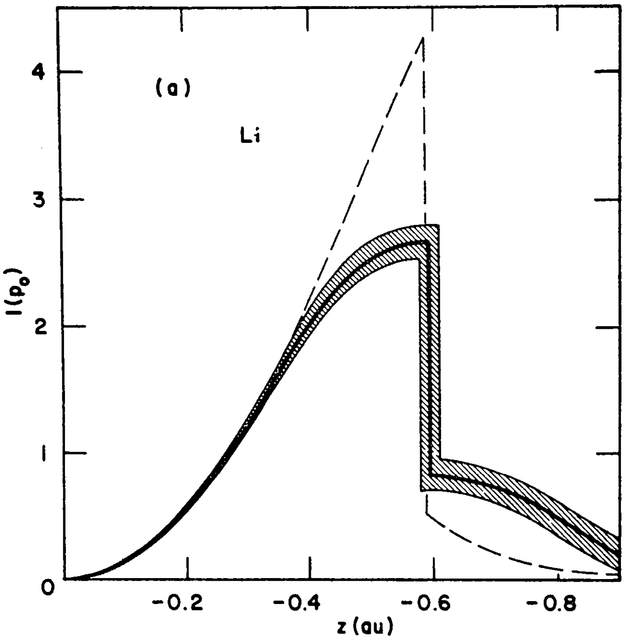

Fig. 4. The radial momentum density $I(p_0)$ deduced from experiment for Li (shaded region) and that calculated for the interacting electron gas.

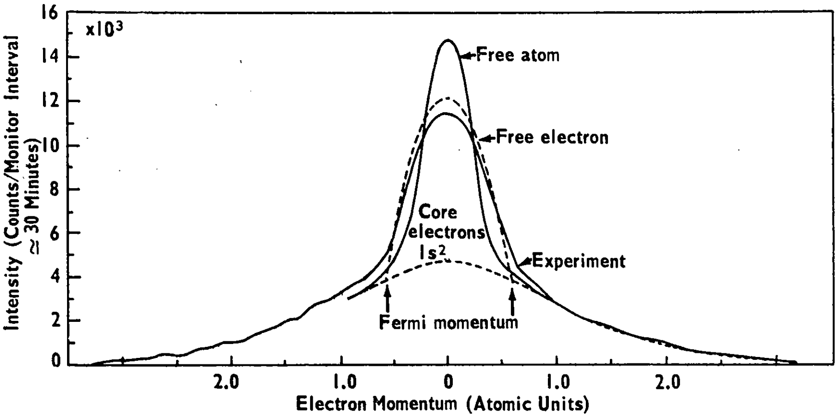

Fig. 3. The measured Compton line shape for Li metal together with two theoretical line shapes: (1) free-electron theory and (2) a superposition of free atom H.F. momentum densities. The Fermi momentum is seen at 0·59 a.u. as a discontinuous change in slope.

tion to the 111 structure factors in silicon and germanium, Table 2, it is believed to be a good approximation in these cases since the measured 220 reflections agree to within 1% with a superposition of Hartree–Fock free atom core densities.

Summary

In general, reliable information obtained from structure factor measurements about valence electron wave functions is limited to only a few cases. However, Compton line shape measurements appear capable of filling the gap. This does not imply abandonment of careful structure factor measurements but rather a realistic consideration of the errors involved in both theory and experiment. (This is discussed further in Appendix II). Compton line shape and structure factor measurements should be considered complementary (as indeed are position and momentum in quantum systems). When reliable information on a substance is available from both types of measurements the theoretician is put to the severest test. It is likely that where structure factor measurements are sensitive to the valence electrons the information so obtained could not be readily deduced from Compton profile measurements even if the latter were known to high precision.

APPENDIX I

The Sagamore conference

Two summer conferences have been held at the Sagamore reservation in upper New York State (1964 and 1967) and a third is planned for Grenoble in 1970 (Chairman: E. Bertaut). They have been small conferences (less than 80) devoted to determination of charge, spin and momentum density. A summary of the more recent conference follows:

The second conference was held September 5–8, 1967, three years after the first conference.* Approximately eighty scientists from U.S.A., U.K., France, W. Germany, U.S.S.R., Japan, Italy, Finland and the Netherlands attended. The conference site is administered by Syracuse University and support for this conference came from the U.S. Army Research Office (Durham), Lico Inc. (Burlington, Mass.) and Materials Research Corp. (Orangeburg, N.Y.). The conference chairman was Professor C.G. Shull.

Since the first conference, the subject of momentum density has seen considerable improvement both in the positron annihilation and the Compton line shape measurements. In a typical latter measurement a monochromatic X-ray beam of ~17 keV (~0·7 Å) scattered 120° ejects single electrons from the atoms imparting ~800 eV kinetic energy to each electron. For a valence electron bound by approximately 10 eV or less the time of interaction is so short that the Coulomb potential of the system can be considered constant. The interaction can then be treated as a simple billiard ball collision between photon and electron, the electron having an initial linear momentum $\mathbf{p}_0$ and initial kinetic energy $p_0^2/2m$. By measuring the change in X-ray energy and momentum with a crystal analyzer (LiF 400 or 600 Bragg reflection), one can deduce the initial momentum of the electrons. In a typical metal like Li, Mg, Na, or Al the linear momentum distributions of the valence electrons are found to have a sharp discontinuity associated with the Fermi momentum and a higher momentum 'tail' associated with electron–electron correlations. Positron annihilation experiments on the other hand provide the momentum distribution of the annihilating electron—positron pairs. A detailed comparison with the X-ray results gives information on the perturbation of the positron. Qualitatively, the presence of the positron shields out the electron–electron correlations so that these experiments evidence only a very small high momentum 'tail'. One can expect the two measurements to complement each other, especially in the case of magnetic materials for which polarized positron measurements yield details of the impaired momenta distributions.

Large observable differences in the outer electron momenta distributions are expected between free atom and solid. This is in contrast to the X-ray measurements of electron charge density in crystalline matter. The valence electrons in solids are generally extended so far radially that they contribute only a negligible amount to the scattered intensity at the Bragg reflections. A superposition of free atom charge densities provides a good first approximation to account for the absolute intensities at the Bragg peaks. Only when absolute X-ray scattering factors can be measured with an error no greater than 1% can one expect to observe the effects of bonding on the charge density. Such accuracies cannot be routinely realized and discussion at the conference concerned efforts being made to solve the experimental difficulties. In one such effort, identical powder samples of nickel were measured at various laboratories with variations as great as 8%! The sources of error are not understood and experimentalists engaged in accurate measurements on powders must apply themselves to this problem. A parallel approach to accurate absolute intensity measurements utilizes single crystals but knowledge of the state of perfection of the crystal is necessary in order to relate the X-ray intensities to the atomic scattering factors. Only in the case of so-called 'perfect' crystals, do we have high confidence in the accuracy of the results but only a limited number of such crystals are available (Si, Ge, GaAs, and Cu). In some cases, such as Al and Mg, very thin single crystals (~0·2 mm) can be produced that appear to be sufficiently 'imperfect' so that one can probably achieve the accuracies required. In Al there is some evidence that the core electrons ($2s^22p^6$) are affected by bonding since the X-ray scattering factors (which are insensitive to the three valence electrons) differ by several per cent from Hartree–Fock free-atom

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* R.J. Weiss, *Physics Today*, April 1965, p. 43.

scattering factors. In addition, Compton line shape measurements of Al show departures in the core momentum density ($2s^22p^6$) from that calculated by a superposition of Hartree–Fock free atom momenta distributions. In accurate diatomic molecular calculations there is also evidence of significant changes in charge densities in regions of the atoms near the nucleus normally dominated by the core electrons. Thus the question of the effect of bonding on 'core' charge and momentum densities must be taken seriously, and one should not rely on calculated free atom scattering factors to better than a few per cent in order to evaluate scattering factors in solids.

An interesting demonstration of the deviation of charge density from spherical symmetry occurs in the rare earth metals with helical arrangements of spin directions in the lattice. Because of spin-orbit coupling, the $4f$ orbitals follow the spin direction so that the $4f$ contribution to the scattering factor varies from atom to atom along the helix. This produces a periodic modulation on the structure factor which has been observed in X-ray diffraction. In addition to the X-ray diffraction determination of charge density, recent developments in absolute electron diffraction measurements should provide complementary measurements for dilute systems such as molecular and metallic vapors. Since the electron scattering factor is $\sim 10^4$ greater than equivalent X-ray scattering factors, only a low density gas ($\sim 10^{-5}$ mm) is required for the former. Electron diffraction measurements on N_2 and O_2 suggest significant departures in the atomic charge density due to molecular bonding.

It is unfortunate that the number of scientists engaged in accurate measurements of charge or momentum density is quite limited since such measurements provide the most fundamental information required to place the theoretical approaches on a sound basis. This is in contrast with the field of spin density which, for understandable reasons, has many more devotees. For one thing, neutron diffraction measurements of spin density are not plagued by many of the problems in X-ray diffraction (particularly the primary extinction problem). In addition, polarized neutrons are capable of achieving very high accuracy. Minute three-dimensional details of spin density are known for many substances. Deviations of spin density from spherical symmetry are now almost routinely measured and in some cases such as Fe, Co, and Ni, small regions of negative spin density have been observed. While such accurate measurements of spin density provide a considerable challenge to the theoretician, his problem is considerably more difficult than for those calculating charge density. The energies involved in spin densities of solids are $\sim 0{\cdot}1$ eV, an order of magnitude less than bonding energies in solids. Such calculations as the deviation from spherical symmetry in the spin density of nickel and iron have been attempted but they are really only tractable with considerable simplification. Another subtle effect explored both experimentally and theoretically is the weak ferromagnetic component in antiferromagnetic $MnCO_3$. This weak ferromagnetic component is associated with the superexchange between the manganese atoms *via* the oxygen atoms.

One of the principal purposes of the conference was to encourage interchange of ideas between theoreticians and experimentalists. In this regard there are three points to be underscored:

1. Theoreticians are encouraged to evaluate scattering factors and momentum line shapes whenever they calculate wave functions.
2. Experimentalists are urged to determine charge and momentum density of simple molecules since these represent the first step toward understanding bonding in solids.
3. The possibility of changes in core charge and momentum densities in solids should be investigated.

An international register is maintained of several hundred scientists actively engaged in the fields of charge, spin, and momentum density. Those who wish to be included in the register are asked to write the author and briefly outline their activities in these fields.

I should like to acknowledge the help and advice of Drs G. Mazzone, W. Kleiner, T. Kaplan, and E. Bertaut. The next conference will be held at Grenoble in 1970 under the Chairmanship of Dr E. Bertaut.

APPENDIX II

Further discussion on errors in structure factors

No mention has been made of a series of experiments aimed at obtaining information on $3d$ valence electrons. These include measurements on Fe (Weiss, 1963), Cr (Cooper, 1962, 1964) Cu (Weiss, 1963; Jennings, Chipman & De Marco, 1964), Fe_4N (Elliott, 1963), VN (Hosoya, Yamagishi & Tokonami, 1968), *etc.* In general, these measurements fail to show agreement amongst various experiments or else have not been measured by more than one laboratory. One also finds that some additional consideration of errors would be desirable in many papers, and as an example I should like to consider the paper of Hosoya *et al.* (1968) since it appears to be of the most recent vintage.

Relative measurements on VN (CsCl structure) are reported by Hosoya *et al.* and compared with free atom calculations for different ionic states. The purpose of their paper is to decide the 'state of ionization' in the crystal. Only the 111 reflection is sensitive to the valence electrons and in this measurement Hosoya *et al.* use the 220 reflection as a reference standard. Compared with Hartree–Fock neutral free atoms, the experimental ratio of the two reflections is about 4% low. From the point of view of free atom theory alone, the 220 reflection is in error by say 1% but the 111 reflection (a difference reflection) is in error by almost 2% (only the individual atomic scattering factors can be assumed to be in error by 1%). The theoretical error in the ratio then is something over 2%. In addition, Hosoya *et al.*

employ a theoretical dispersion correction. Unfortunately, the radiation chosen (Cu $K\alpha$) requires a dispersion correction of over 20% to the 111 and 10% to the 220 structure factor and such theoretical corrections are uncertain by something like 10%. Furthermore, the uncertainties in this correction are additive when comparing the 111 and 220 reflections since the former is a difference reflection and the latter a sum reflection. Thus, an additional theoretical error of 3% must be compounded with the 2% or so error in the Hartree–Fock scattering factors yielding an overall theoretical uncertainty of well over 3%. Even assuming *no* experimental uncertainty, the 4% experimental difference is no longer well outside the theoretical uncertainty.

Because of the current difficulty in obtaining reliable valence electron information from structure factor determinations, we suggest that authors devote some space in their papers to a tabular assessment of the errors in the experiment including such factors as theoretical errors, extinction, TDS and Debye–Waller factors, absorption coefficient, preferred orientation, *etc.* Such critical evaluations provide the reader with very useful information. Table 4 is included as a guide to assessing the errors.

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Table 4. *Some sources of uncertainly in structure factor measurements*

	Uncertainty	Reference and comments
1. Hartree–Fock free atom scattering factor (theory)	~1%	Very few measured (Hall, 1964; Goodisman & Klemperer, 1963).
2. Molecular scattering factors (theory)	~2%	Very few calculated.
3. Crystal structure factors (theory)	~3%	Very few calculated.
4. Debye–Waller correction $(1-l^{-M})$	>10%	Especially difficult at high temperatures or when anharmonicity is large (Chipman, 1960; Batterman & Chipman, 1962).
5. Thermal diffuse scattering correction	>10%	Very few measurements (Nilsson, 1957; Schwartz, 1964; Chipman & Paskin, 1959; Cochran, 1969).
6. Dispersion corrections	>10%	Very few direct measurements. Reliance placed on Kramers–Kronig relations (Weiss, 1966).
7. Extinction corrections	>20%	Needs considerable experimental study (Zachariasen, 1969).
8. Absorption coefficients	1–10%	*International Tables* unreliable (Deslattes, 1969).
9. Umweganregung	?	Needs experimental study (Post, 1969).
10. Dead time error corrections	~20%	
11. Porosity correction	~20%	Needs more experimental work (Cooper, 1965; Harrison & Paskin, 1964).
12. Polarization correction $(1-K^2)$	~20%	Depends on the extinction in the monochromator and the sample (Jennings, 1968*c*).
13. Preferred orientation in powders	?	Extreme care required to reduce to less than 1%.
14. Size effect correction in disordered alloys	?	Very little experimental work reported (Borie, 1957).
15. Geometrical factors	?	Beam homogeneity, sample shape, absorption factors *etc.*

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DISCUSSION

POST: Would you care to comment on reports of X-ray Raman spectra in the Compton region?

WEISS: There have been reports but they do not appear to have been substantiated. We have been unable to locate them. In any case, they have nothing to do with momentum density.

EWALD: You say you take a slice in momentum space. Does that mean you integrate over that – which means you select those momenta that have a definite component? Then you proceed from one direction to another?

WEISS: Yes, the curve is only for one component and if the momentum is strongly directional, you would spot this on moving to a different direction.

POST: You would not observe it in carbon black but you would in diamond.

SCHOMAKER: Or rather, in carbon black you could observe it in any direction you please, but in diamond you would be limited.

POST: What about more complicated cases? Has there been much success in obtaining information about valence electrons in atoms heavier than Be or C, using Compton methods?

WEISS: At the present time, the number of examples are very few because of problems of intensity. We are limited to the lower atomic number elements, because the process of photo-electric absorption steals our X-rays and gives nothing in return. This process varies as Z_4. The problems posed by lack of intensity need not be completely restrictive in this technique since we do not require a small focal area. Powers up to 100 kW are perfectly feasible, the focal area being increased to a value which does not exceed normal specific loading.

LANG: Have the curves which you have shown been published and, if so, where?

WEISS: Mainly in *Phys. Rev.*

SANDOR: Do you think that slight fluctuations observed in diamond at low momentum densities are significant and, if so, what interpretation do you give to these fluctuations?

WEISS: (*a*) The difference between the free atom and the corresponding entity in the solid is due to the difference in binding.

(*b*) The structure of the Compton line is symmetrical irrespective of the symmetry of the structure. What you are referring to is the smoothness of the function with $\sin\theta/\lambda$ of the integrated Compton scattering, *i.e.* the whole integral of the curve which is different from the structure in momentum space. This latter is the energy analysis of the Compton scattering.

HOSOYA: May I remind you that Dr T. Suzuki in Japan reported the existence of X-ray Raman scattering in light elements, including carbon. (*J. Phys. Soc. Japan* (1967) **22**, 1139]. I consider his findings to be reliable because he confirms the expected difference in the dependence of Raman and Compton scattering upon scattering angle and atomic number. We can avoid the overlapping of these two types of scattering to some extent by the choice of experimental conditions.

WEISS: It seems likely that the Raman lines are nowhere near the effects due to valence electrons. In this case, since our own interest is in the valence electrons, there is probably no danger of confusion.

POST: Have you considered multiple-photon as well as single-photon interactions?

WEISS: Yes. We feel sure that these effects are very small. For example, the calculations of the Compton line shift referred to a single electron and this fits closely with the experimental results. Also, calculation of the multiple photon turns out to be very very small.

HIRSHFELD: On the tail end of the curve shown, the difference between the total Hartree–Fock and core contributions is small; that is, one might conclude that the valence electrons are not contributing much – yet there seems to be a significant discrepancy in that region between calculated and experimental values for carbon black. Do you interpret this as due to a significant effect core electrons?

WEISS: Not at the present time. The difference could still be due to valence electrons. The reason is that since this is essentially a measurement of momentum density, it gives the probability of having an electron of a certain momentum and you can determine the kinetic energy. You can integrate what you think is the valence electron contribution, that is, everything above the four-electron contribution and get the total kinetic energy which is some sort of measure of the energy in the bond. We could not, however, rule out the possibility that there was still some valence electron contribution. We have found a few cases where we consider we could rub out this possibility and where the core electrons have indicated an alteration from the free atom state.

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Accuracies of Experimental Structure Factor Values

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A survey of the present status of the error problem concerning the experimental structure factor values (*F*-values) is given, with special reference to the fluctuation, or the reproducibility, of original data obtained by various methods under different experimental conditions. It is pointed out that in most methods the reproducibility of *F*-values approaches the range of 1% ~0·5% in favourable cases; the absolute accuracy is lower than this in all but a few examples.

Introduction

Experimental determination of accurate values of the crystal structure factors, or, in short, the *F*-values, becomes increasingly important not only for traditional crystal structure determinations but also for X-ray crystallography as a whole in relation to problems in solid state physics. This paper gives a survey of the present status of the error problem concerning experimental *F*-values. However, too detailed considerations of this sort of problem are not only difficult but will not be fruitful in view of the involved nature of the errors in general. Therefore, discussions in what follows are concerned only with restricted aspects of the subject.

Table 1. *Methods for determination of F-values*

A. X-ray methods:
  (1) Intensity measurements
    (*a*) Single crystals.
      (i) Kinematical formula, with correction for extinctions.
      (ii) Dynamical formula, for perfect crystals.
    (*b*) Powders. Kinematical formula.
  (2) Reflexion-profile method. Dynamical formula, for perfect crystals.
  (3) Pendellösung-fringe method. Dynamical formula, for perfect crystals.

B. Electron diffraction methods:
  (1) Intensity measurement
  (2) Dynamical-interaction method (Kikuchi-line method).

Table 1 lists the experimental methods available for obtaining accurate *F*-values and the principle of each method.

Before discussing individual problems, the so-called error in *F*-values must be distinguished as being of two kinds. The first is the fluctuation in the original data due to differences in specimens, series of measurements, methods, researchers, laboratories, *etc.* They may be of either statistical or systematic nature. The second one is the error which is introduced by the processing of the original data. For instance, in the powder method we have to take account of various quantities and effects, such as Debye–Waller factors, dispersion terms, the correction of thermal diffuse scattering, and of extinctions, the effect of porosity and surface roughness, *etc.* These two kinds of error cannot always be separated from each other; in particular, those due to Debye–Waller factors influence the data presented in Tables 5–7 and in Figs. 5 and 6. However, the absolute accuracy of the final data will receive little discussion and in the following sections we shall be concerned mainly with the first kind of error, namely with the fluctuation, or in other words, with the reproducibility of the original data. Where the experimental errors have a Gaussian distribution the 'fluctuation' or 'reproducibility' is measured by the standard deviation. However, in general, the error distribution is not strictly Gaussian.

Pendellösung-fringe method

The Pendellösung method (Kato & Lang, 1959) has high merit because of its firm theoretical basis in the dynamical theory, and its experimental method is essentially simple. Therefore, if this method is applied under ideal conditions, a high accuracy, better than 0·5%, may readily be expected. However, this is not always