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Relevance of Charge-Density Measurements for High-Precision Calculations

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Abstract

High-precision photon diffraction data in beryllium, diamond, silicon, copper and germanium are reanalysed with the aim of assessing the accuracy of experimental X-ray and γ-ray structure factors by comparing derived values for cohesive energy with the thermochemical ones. Special attention is devoted to the diffraction data analysis for a meaningful and accurate comparison between theory and experiment. A good overall agreement of local density approximation calculations is found when the electron density exhibits spherical symmetry around each atomic site. On the contrary, the analysis of experimental data in $3d$ transition metals, namely vanadium, chromium, iron, cobalt and nickel, points out failures of the theory in reproducing the asphericity of the electron distribution.

1. Introduction

It is now well established that one of the most accurate approaches to the calculation of electron properties in crystals is the density functional theory (DFT) originally developed by Hohenberg & Kohn (1964). However, practical application of the DFT to real systems (Moruzzi *et al.*, 1978) is subjected to approximation schemes, frequently containing *ad hoc* assumptions, whose validity should be checked. The most popular scheme is the so-called local density approximation (LDA) (Hohenberg & Kohn, 1964; Kohn & Sham, 1965) based on the local approximation of the real exchange-correlation potential with that of the homogeneous interacting electron gas at the appropriate density. Since the ultimate test of the theoretical approximations relies on a very close comparison between calculated and measured quantities, recognition of those quantities that are treated on an equal footing from both theory and experiment is essential for the comparison to be meaningful and accurate. Moreover, a fruitful test of the approximations should point to possible ways of improving the theory. In principle, by means of DFT–LDA, all the ground-state observables can be calculated, although some care should be taken when observables other than total energy and particle density are considered (Bauer, 1983). This specific point is rather crucial since the calculation of other observables is not straightforward and in general additional assumptions can be necessary (Bauer, 1983). Consequently, the most meaningful comparison between theory and experiment should be confined to only ground-state total energy and directly related quantities, *e.g.* lattice parameter, cohesive energy, crystal structure and particle density.

As to total energy, a reliable check can be carried out for light elements only: even though the cohesive energy of crystals can be accurately measured, knowledge of the experimental free-atom total energy is necessary to obtain the crystal total energy. Of course, theoretical and experimental cohesive energies could be directly compared but this requires the calculation of the free-atom total energy, which, in turn, introduces different and additional approximations in the theory. Despite these difficulties, it is apparent that cohesive energy and related quantities are reasonably well reproduced by the calculations (Moruzzi *et al.*, 1978): the agreement is ~20% for the cohesive energy in most cases and ~1–2% for the lattice parameter and the crystal structure is fairly well reproduced. The open question when testing with this kind of observable is the finding of systematic disagreements whose origin is not easily traced back to some specific aspect of the theoretical approximations or even to numerical accuracy.

The other quantity exactly provided by the theory is the particle density, which allows the theory–experiment comparison to be extended over a set of numbers instead of just a single one. Specifically, the expansion of the electron density in the Fourier lattice series can be exploited, the series coefficients being the observables measured in charge-density experiments. Moreover, as the different Fourier components sample different regions of the real space, information on the dependence of the calculated electron density can be obtained from the theory–experiment comparison. Indeed, the shape of the electron density is strongly related to the characteristics of the system under study and some specific failures of the theoretical approach can be enhanced (Di Fabrizio *et al.*, 1989). Therefore, a systematic investigation of the charge density in crystals, through high-precision measurements and high-accuracy calculations, now appears to be mandatory.

It has been observed that the accuracy required to get reliable experimental data on the crystal charge density must be of the order of 0.1% in most cases, thus making the straightforward application of ordinary X-ray diffraction techniques of little help (Mazzone, 1981). Furthermore, in the X-ray region ($E \leq 20$ keV), the anomalous-scattering contribution causes real problems in getting accurate charge-density data, apart from the case of light elements ($Z \leq 10$). To deal with the above problems, the use of γ-ray diffraction was proposed (Schneider *et al.*, 1981), which makes the extinction corrections negligible and almost eliminates anomalous-scattering contributions. Limitations of this technique are the very small scattering angle attainable in the measurements and the increased possibility of multiple scattering. Alternatively, very accurate data are made available by perfect-crystal diffraction techniques (Aldred & Hart, 1973; Matsushita & Kohra, 1974), although anomalous scattering still contributes. Application of the latter method in the X-ray region is confined to light elements, in practice the only results of real utility are those obtained in silicon (Aldred & Hart, 1973; Teworte & Bonse, 1984) and diamond (Takama *et al.*, 1990) but extension to the γ-ray region was proved to be possible (Graf & Schneider, 1986). This experimental approach is, in fact, limited by the production of almost perfect crystals and the most extended set of available data concerns silicon for which also a very accurate measurement of the forward-scattering amplitude is reported (Deutsch & Hart, 1988).

Even though working in the γ-ray region has the advantage of reducing extinction and anomalous-scattering effects, experiments carried out at relativistic photon energies cannot be interpreted by straightforward application of the non-relativistic scattering theory (Dewey *et al.*, 1994; Smith, 1987; Sacchetti, 1987; Rocchi & Sacchetti, 1993). Extension of the theory to relativistic energies is not simple owing to the difficulties in treating the complex many-body interactions among the electrons and the interactions of the electrons with the external electromagnetic field. Moreover, as the photon–electron interaction is governed by the not vanishingly small fine-structure constant α ($\alpha \simeq 1/137$), such an interaction must be treated at orders higher than the leading one (Rocchi & Sacchetti, 1993) when the accuracy of the experiment is pushed towards 0.1%.

Finally, the effect of nuclear thermal vibrations should be treated carefully. In fact, the nuclear motion produces a disturbance of the electron distribution that is not accounted for by the simple Debye–Waller factor but additional terms are required for a correct treatment of this effect (Sacchetti, 1984; Petrillo & Sacchetti, 1994).

Recently, Zunger and co-workers (Lu *et al.*, 1993, 1995) have carried out an extended theoretical investigation of the electronic charge distribution in C, Si and Ge in view of a comparison with high-precision experimental data. In this study, some of the corrections mentioned above were neglected and it was concluded that the experimental electron density of these crystals was well reproduced by the LDA calculation. In the present paper, the high-accuracy structure-factor data for Be (Larsen & Hansen, 1984; Hansen *et al.*, 1984), C (Takama *et al.*, 1990), Si (Aldred & Hart, 1973; Teworte & Bonse, 1984; Deutsch & Hart, 1985), Cu (Schneider *et al.*, 1981) and Ge (Matsushita & Kohra, 1974; Dewey *et al.*, 1994; Deutsch *et al.*, 1990), as obtained by photon diffraction experiments, are reanalysed taking into account all the possible systematic contributions. Moreover, the corrected sets of data are used as input to deduce the cohesive energy of the crystal to be compared with the thermochemical values. The estimate of the cohesive energy from structure-factor data is a useful test of the overall reliability of the data themselves. One can anticipate that, were wrong values of cohesive energy obtained by this procedure, the set of structure factors is either incomplete or affected by some systematic error, although correct values of cohesive energy do not ensure the reliability of the data set. Comparison of the structure factors with very accurate first-principle calculations available from the literature is also presented and discussed. Finally, an analysis of the reduced sets of data of medium accuracy collected for transition metals (Weiss & De Marco, 1965; De Marco & Weiss, 1965; Diana & Mazzone, 1972, 1974, 1975, 1978; Ohba *et al.*, 1981, 1982; Ohba & Saito, 1982; Kretschmer & Schneider, 1984; Rocchi & Sacchetti, 1995) is briefly discussed.

2. Analysis of experimental data

The high-precision charge-density data available in the literature on elemental systems were analysed with the same procedure in order to obtain a common protocol for reliable internal comparison. Measurements providing a nominal uncertainty on the scattering amplitude per atom of the order of or better than $0.1r_0$, $r_0 = e^2/mc^2$ being the classical electron radius, were accepted as accurate enough. Such a requirement implies a relative accuracy increasing as the atomic number increases. To our best knowledge, extended experimental data sets on pure elements fulfilling the above accuracy requirement are those on Be (Larsen & Hansen, 1984; Hansen *et al.*, 1984), C (Takama *et al.*, 1990), Si (Aldred & Hart, 1973; Teworte & Bonse, 1984; Deutsch & Hart, 1985), Cu (Schneider *et al.*, 1981) and Ge (Matsushita & Kohra, 1974; Dewey *et al.*, 1994; Deutsch *et al.*, 1990). This selection may appear arbitrary to some extent; however, it was brought about by the need to have *accurate* and, at the same time, *extended* structure-factor data sets that were as internally consistent as possible. Some of the experiments were performed using low-energy photons (Aldred & Hart, 1973; Matsushita & Kohra, 1974; Teworte & Bonse, 1984; Takama *et al.*, 1990; Larsen & Hansen, 1984) and part of these data was affected to some extent by anomalous scattering. The other cited measurements (Schneider *et al.*, 1981; Dewey *et al.*, 1994; Hansen *et al.*, 1984) were carried out at relativistic energies where the amount of anomalous scattering is expected to be negligible but some departure from the Thomson scattering could be observed. In all the measurements, apart from Ge (Matsushita & Kohra, 1974), photons with energy much greater than the electron binding energy were employed.

When the incoming photon energy is relatively high in comparison with the electron binding energy, the electron–photon scattering can be treated in the framework of the relativistic theory under the plane-wave approximation for the intermediate states and, at least at small momentum transfer, a simple correction to the Thomson cross section (Sacchetti, 1987) can be derived. As discussed by Smith (1987) and Sacchetti (1987), the measured structure factor can be written as

$$\mathcal{F}_{\mathbf{G}} = \sum_s [f_m(\mathbf{G}, s) + f'_{LE} + f_{\text{rad}}(\mathbf{G}, s) + f_N(s)] \exp(i\mathbf{G} \cdot \mathbf{r}_s) \qquad (1)$$

where $\mathbf{G}$ is a reciprocal-lattice vector and $\mathbf{r}_s$ is the position of the sth atom in the unit cell. $f_m(\mathbf{G}, s)$ is the modified scattering factor, which, as discussed by Sacchetti (1987), is given by:

$$f_m(\mathbf{G}, s) = \int_{\Omega_{WS(s)}} d\mathbf{r} [\exp(i\mathbf{G} \cdot \mathbf{r})\rho(\mathbf{r})]/[1 - V(\mathbf{r}) + E_0], \qquad (2)$$

where $\rho(\mathbf{r})$ is the electron number density, $V(\mathbf{r})$ and E_0 are the one-electron potential and the ground-state energy in units of the electron rest energy mc^2. The integral in (2) is over the volume of the Wigner–Seitz cell $\Omega_{WS(s)}$ centred around the sth atom. f'_{LE} is the anomalous-scattering contribution as deduced from the dispersion-relation approach (Gell-Mann *et al.*, 1954) and assumed to be independent of the site. $f_{\text{rad}}(\mathbf{G}, s)$ is the contribution due to the so-called radiative corrections (Sacchetti, 1987; Rocchi & Sacchetti, 1993; Jauch & Rohrlich, 1980), which turns out to be proportional to $f_m(\mathbf{G}, s)$ (Rocchi & Sacchetti, 1993). Actually, additional contributions are expected when the photon energy increases, namely Delbruck scattering and nuclear giant resonance, however, they are almost completely negligible in the energy range of the experiments performed to date (Sacchetti, 1987; Jauch & Rohrlich, 1980). Finally, $f_N(s)$ accounts for nuclear Thomson scattering from a charge Ze and mass M, that is $f_N(s) = (Ze)^2/Mc^2$. The modified scattering factor can be written in the more suitable form:

$$\begin{aligned} f_m(\mathbf{G}, s) &= \int_{\Omega_{WS(s)}} d\mathbf{r}\rho(\mathbf{r}) \exp(i\mathbf{G} \cdot \mathbf{r}) \\ &\quad + \int_{\Omega_{WS(s)}} d\mathbf{r}\rho(\mathbf{r})\{[V(\mathbf{r}) - E_0]/[1 - V(\mathbf{r}) + E_0]\} \\ &\quad \times \exp(i\mathbf{G} \cdot \mathbf{r}) \\ &= f_0(\mathbf{G}, s) + \Delta(\mathbf{G}, s), \end{aligned} \qquad (3)$$

which points out how $f_m(\mathbf{G}, s)$ is obtainable from the ordinary scattering factor $f_0(\mathbf{G}, s)$ by adding the correction term $\Delta(\mathbf{G}, s)$. Such a term, which is very small, can be safely calculated employing a suitable approximation for $\rho(\mathbf{r})$ and $V(\mathbf{r})$. It is important to remark that in solid-state physics the key quantity is the ordinary scattering factor $f_0(\mathbf{G}, s)$, so it is this part of the total scattering amplitude that must be deduced from the experimental data. It is also worthwhile to note that the correction $\Delta(\mathbf{G}, s)$ at $\mathbf{G} = 0$ is equal to the high-energy correction discussed by Smith (1987) with reference to the forward-scattering amplitude. Such a correction is purely kinematic in its origin and can be interpreted as a relativistic change of the electron mass.

The effect of the nuclear thermal motion on the scattering amplitude is quite complex and it reduces to the ordinary multiplicative Debye–Waller factor only when the charge densities of different atoms are assumed to be tightly bound to the corresponding nuclei (Sacchetti, 1984). Such an approximation is generally acceptable but it has to be checked when accurate results are desirable. In general, the effect of the thermal motion can be accounted for by assuming that the electron-density fluctuations are linear in the nuclear displacements (Sacchetti, 1984). The effective structure factor $\mathcal{F}^{\text{eff}}_{\mathbf{G}}$ resulting from this assumption is given by

$$\mathcal{F}^{\text{eff}}_{\mathbf{G}} = \mathcal{F}_{\mathbf{G}} \exp[-W(\mathbf{G})] + \sum_{\mathbf{G}'} \mathcal{R}(\mathbf{G}, \mathbf{G}') \exp[-W(\mathbf{G}')], \qquad (4)$$

where $\mathcal{R}(\mathbf{G}, \mathbf{G}')$ is the appropriate response function describing the electron-density fluctuations induced by the nuclear displacement field. The Debye–Waller factor $\exp[-W(\mathbf{G})]$ is given by:

$$\exp[-W(\mathbf{G})] = \langle \exp(i\mathbf{G} \cdot \mathbf{u}) \rangle, \qquad (5)$$

where $\mathbf{u}$ is the displacement operator of a nucleus and the average is taken over the phonon ensemble. $W(\mathbf{G})$ depends on the nuclear coordinates only and it can be obtained by neutron diffraction measurements. However, as equation (4) shows, the knowledge of the Debye–Waller factor is not sufficient to derive the structure factor $\mathcal{F}_{\mathbf{G}}$. It is quite difficult to get a reliable theoretical model of the response function $\mathcal{R}(\mathbf{G}, \mathbf{G}')$, which is related to the dielectric matrix of the system (Sacchetti, 1984). Only in the case of simple metals can a reasonable estimate of $\mathcal{R}(\mathbf{G}, \mathbf{G}')$ be obtained rather straightforwardly without resorting to complex solid-state calculations (Sacchetti, 1984). As to structure-factor measurements, need of going beyond the Debye–Waller factor occurred in a neutron diffraction experiment in the intermetallic FeCo compound and only at temperatures rather high compared with the Debye temperature (Petrillo & Sacchetti, 1994). In this particular case, the observed change of the magnetic structure factor of the 110 reflection was about $0.18r_0$ at 1000 K and reduced down to $0.06r_0$ at room temperature against a hypothetical static lattice. Since this effect is expected to be generally small at temperatures that are not too high, the problem of thermal motion beyond the Debye–Waller correction is neglected in the present analysis of experimental data. Moreover, whenever an accurate measurement of the Debye–Waller factor by neutron diffraction was available, it was used to analyse the experimental data, as the most meaningful estimate of this term is that provided by a neutron measurement. When the Debye–Waller-factor data were not available or not accurate enough, we preferred to deduce it from the experimental phonon-dispersion relations or density of states, measured by neutron scattering, under the quasi-harmonic approximation (Maradudin, 1974).

In general, there is not an *a priori* criterion to judge the real accuracy of a given set of experimental structure factors. Moreover, when the accuracy demand is so high, the effect of possible systematic errors, other than those discussed, in nominally high-precision data becomes extremely critical. A check of the validity of a given data set, which was suggested by Mazzone & Sacchetti (1984), is to calculate the cohesive energy from the diffraction data and to compare it with that deduced from thermochemical measurements. To carry out this calculation using the available diffraction data, we adopted the procedure described in the following. The total energy of an elemental many-electron system is given by (Mazzone & Sacchetti, 1984):

$$E_0 = E_{eN} + E_{ee}^{H} + E_{ee}^{xc} + E_M, \tag{6}$$

where E_{eN}, E_{ee}^{H}, E_{ee}^{xc} and E_M are, respectively, the electron–nucleus interaction energy, the electron–electron Hartree energy, the electron–electron exchange-correlation energy and the Madelung energy. In particular,

$$E_{eN} = -N_c\pi(Ze^2/\Omega_0)\sum_{\mathbf{G}}{}'[F_{\mathbf{G}}(F_{\mathbf{G}}^{g})^* + \mathrm{c.c.}]/G^2 \tag{7}$$

$$E_{ee}^{H} = N_c\pi(e^2/\Omega_0)\sum_{\mathbf{G}}{}'|F_{\mathbf{G}}|^2/G^2 \tag{8}$$

$$E_{ee}^{xc} = (Ne^2/8\pi^2)\int \mathrm{d}\mathbf{q}\,[S(\mathbf{q}) - Z]/q^2 \tag{9}$$

$$E_M = -\tfrac{1}{2}N(Ze)^2(\alpha/2R_0), \tag{10}$$

where N is the number of atoms, N_c the number of unit cells, Ω_0 the unit-cell volume, Z the atomic number, α the Madelung constant and R_0 given by $\Omega_0 N_c/N = 4\pi R_0^3/3$. $F_{\mathbf{G}} = \sum_s f_0(\mathbf{G}, s)\exp(i\mathbf{G}\cdot\mathbf{r}_s)$ is the ordinary structure factor, $F_{\mathbf{G}}^{g} = \sum_s \exp(i\mathbf{G}\cdot\mathbf{r}_s)$ is the geometrical structure factor and $S(\mathbf{q})$ is the incoherent scattering factor. In equations (7) and (8), $\sum_{\mathbf{G}}'$ means that the (000) reciprocal-lattice vector is omitted from the sum. The cohesive energy can be deduced by subtracting the energy of one atom in the crystal, *i.e.* E_0/N, to the free-atom energy which is given by

$$E^{\mathrm{at}} = (e^2/2\pi)\int_0^\infty \mathrm{d}q\,\{S^{\mathrm{at}}(q) + [f_0^{\mathrm{at}}(q)]^2 - Z\} - (Ze^2/\pi)\int_0^\infty \mathrm{d}q\, f_0^{\mathrm{at}}(q). \tag{11}$$

Therefore, apart from the exchange-correlation term, which depends on the incoherent scattering factor $S(\mathbf{q})$, appropriate to the atom or the crystal, the cohesive energy is directly obtainable from the structure factors $F_{\mathbf{G}}$ measured in real diffraction experiments. Since only a reduced set of structure factors is available from the diffraction experiment and the sums over $\mathbf{G}$ in equations (7) and (8) are slowly converging, E_0 can be calculated by assuming that the scattering factor of the crystal approaches that of the atom for high $\mathbf{G}$ vectors. This assumption is well founded since in a typical experiment appreciable differences between the two scattering factors are observed for just the first four–five reflections. Moreover, through a simple manipulation of equations (7)–(11) and according to the discussion reported in Mazzone & Sacchetti (1984), it can be shown that the crystal scattering factor *must* approach the free-atom scattering factor when $\mathbf{G}$ increases otherwise the cohesive energy diverges. As many reciprocal-lattice vectors as necessary to obtain a convergence of the energy sums better than 0.01 eV atom^{-1} were included. The atomic scattering factors in the high $\sin(\theta)/\lambda$ region were interpolated from the extended tabulation of Hubbell & Øverbø (1979) by means of a power law.

In the following, the experimental structure factors are analysed according to the described procedure and the cohesive energy check is applied to all the corrected sets of data. Throughout the following sections, a simplified notation for the scattering factors is adopted, namely the $\mathbf{G}$ and s dependences are not explicitly written out.

2.1. *Beryllium*

The experiment reported by Hansen *et al.* (1984) was performed at 412 keV incoming photon energy and this, according to the estimate of Rocchi & Sacchetti (1993), makes the f_{rad} and f_{LE}' contributions safely negligible. The kinematic correction Δ was calculated using charge density and one-electron potential data from Moruzzi *et al.* (1978) and it was found to be less than $0.0014r_0$ for all the reflections. The contribution of the nuclear Thomson term f_N amounted to less than $0.001r_0$ and it was neglected. Therefore in a light element like Be, the experimental scattering factor turned out to be coincident with f_0 times the Debye–Waller factor within less than $0.003r_0$, which is a figure smaller than the experimental errors. Hence, the experimental scattering amplitudes, as reported by Hansen *et al.* (1984), were corrected for just the Debye–Waller factor. An accurate neutron measurement of this term is reported by Larsen *et al.* (1980), further discussed by Larsen & Hansen (1984), and it was used to correct the data.

A second set of data in Be is that reported by Larsen & Hansen (1984) where the measurements were carried out by a more conventional X-ray diffraction technique. Again, direct use of these data for the present analysis can be performed since no anomalous correction is needed in the case of this very light element even at this lower photon energy (Mo $K\alpha$ and Ag $K\alpha$). However, the original data were not put on an absolute scale but they were properly normalized (Larsen & Hansen, 1984) by comparison with both the data of Hansen *et al.* (1984) and the free-atom scattering factor (*International Tables for X-ray Crystallography*, 1989). In Fig. 1, a comparison is shown between the data as provided by Larsen & Hansen (1984) and the atomic scattering factor over the $\sin(\theta)/\lambda$ region from 0.8 to 1.21 Å^{-1}. It is apparent that the experimental data are systematically lower than the free-atom curve, that is convergence between the crystal and the free-atom scattering factors is not achieved over this *high* $\sin(\theta)/\lambda$ region. This trend has already been observed and discussed by Larsen & Hansen (1984). The explanation proposed by the authors invoked the core expansion of the crystal charge density against that of the free atom. However, this interpretation, which implies maintaining the difference with the same sign for higher values of $\sin(\theta)/\lambda$, may lead to wrong values of the cohesive energy and should be carefully considered. This point was discussed in Mazzone & Sacchetti (1984) where the effect of a possible difference between the two scattering factors in the region of high $\sin(\theta)/\lambda$ was shown to result in the crystal energy series not converging. Therefore, the estimate of the cohesive energy obtainable from the experimental data of Larsen & Hansen (1984) was a relevant test of the scattering-factor data themselves. Following the procedure described in the previous section, the sums over **G** [equations (7) and (8)] were calculated using the available experimental data and convergence of the series was provided by addition of the calculated free-atom data to the experimental set. The same set of atomic data, namely the free-atom scattering factor up to $\sin(\theta)/\lambda = 70$ Å^{-1}, was used to calculate $E^{\rm at}$ in equation (11). The Coulomb contribution to the cohesive energy $E^C_{\rm coh}$, defined as the sum of the electron–electron Hartree term and the electron–nucleus interaction term, was found to be −0.92 (37) eV atom^{-1}. In Table 1, the thermochemical value of the cohesive energy and the exchange-correlation contribution to it, $E^{xc}_{\rm coh}$, are quoted. The latter term was calculated through equation (9) using the incoherent scattering factor measured by Mazzone *et al.* (1983). From the reported values, $E^C_{\rm coh}$ is expected to be 0.5 (3). Moreover, repeating the calculation for a smaller set of experimental data, quite different values of $E^C_{\rm coh}$ were found. This incorrect finding is well represented in Fig. 2 where the Coulomb cohesive energy is plotted *versus* the maximum value of $\sin(\theta)/\lambda$ corresponding to the last reflection included in the series, the atomic data set being fixed. A non-converging trend is apparent from Fig. 2, which invalidates every possible estimate of the cohesive energy

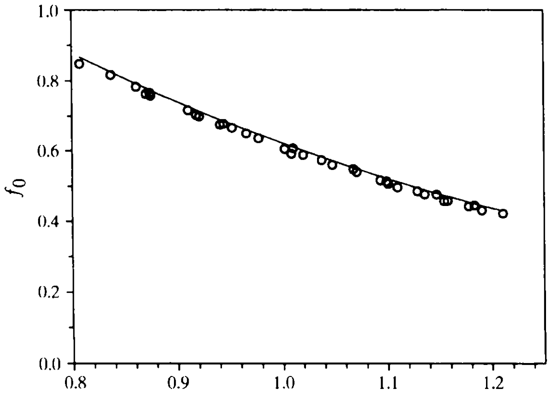

Fig. 1. Beryllium. Comparison between the scattering factors (circles) measured by Larsen & Hansen (1984) and the free-atom curve over the high $\sin(\theta)/\lambda$ region.

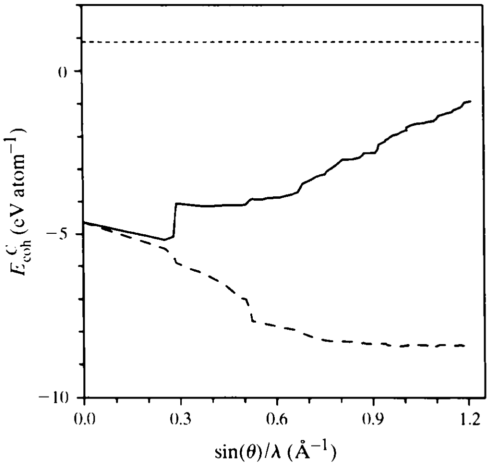

Fig. 2. Convergence of the energy series in beryllium: Coulomb contribution to the cohesive energy, $E^C_{\rm coh}$, *versus* $\sin(\theta)/\lambda$ corresponding to the maximum term included into the series. Full line: data from Larsen & Hansen (1984). Dashed line: data from Larsen & Hansen (1984) normalized to the free atom. Short-dashed line: expected sum value.

Table 1. *Cohesive energy data from X-ray measurements, E^{RX}_{coh}, compared with the experimental thermochemical values E^{TC}_{coh}*

The X-ray term $E^{RX}_{\rm coh}$ is given by the sum of $E^{C}_{\rm coh}$, arising from structure-factor measurements, and $E^{xc}_{\rm coh}$, obtained from incoherent scattering-factor measurements (see text). The Coulomb contribution to the total energy of the atom, $E^{C}_{\rm at}$ [see equation (11)], is also quoted. The number of independent reflections used to calculate the cohesive energy is listed in the last column.

(*a*) Structure-factor data for Be from Hansen *et al.* (1984). (*b*) Structure-factor data for Be from Larsen & Hansen (1984). (*c*) Structure-factor data for Be from Larsen & Hansen (1984), normalized to the free atom.

	$E^{C}_{\rm coh}$ (eV atom^{-1})	$E^{xc}_{\rm coh}$ (eV atom^{-1})	$E^{RX}_{\rm coh}$ (eV atom^{-1})	$-E^{TC}_{\rm coh}$ (eV atom^{-1})	$E^{C}_{\rm at}$ (eV atom^{-1})	$N_{\rm ref}$
Be$^{(a)}$	−4.15 (50)	−3.8 (2)	−8.0 (5)			
Be$^{(b)}$	−0.92 (37)	−3.8 (2)	−4.7 (4)			
Be$^{(c)}$	−8.41 (37)	−3.8 (2)	−12.2 (4)	−3.34	362.4	14513138
C	−1.6 (2)	−4.4 (2)	−6.0 (3)	−7.06	951.3	1008247
Si	−1.4 (3)	−3.9 (2)	−5.3 (3)	−4.66	7601.2	28087859
Cu	12.5 (47)	–	–	−3.51	44445.3	66218089
Ge	0.5 (62)	–	–	−3.38	56947.9	253465234

Table 2. *Beryllium: scattering factors per atom of the first 15 reflections*

(*a*) Experimental data from Larsen & Hansen (1984). (*b*) Experimental data from Larsen & Hansen (1984), normalized to the free atom. (*c*) Theoretical data from Chou *et al.* (1983). (*d*) Theoretical data from Dovesi *et al.* (1982). (*e*) Free-atom data from *International Tables for X-ray Crystallography* (1989). Average ratios and fluctuations of the experimental data over the theoretical ones are reported.

hkl	$\sin(\theta)/\lambda$ (Å^{-1})	$f^{\rm exp}_0$ (*a*)	$f^{\rm exp}_0$ (*b*)	$f^{\rm th}_0$ (*c*)	$f^{\rm th}_0$ (*d*)	$f^{\rm at}_0$ (*e*)
100	0.2526	1.895	1.936	1.885	1.949	1.818
002	0.2791	1.731	1.768	1.721	1.755	1.742
101	0.2886	1.689	1.725	1.689	1.677	1.718
102	0.3764	1.570	1.604	1.536	1.526	1.559
110	0.4375	1.460	1.491	1.434	1.437	1.462
103	0.4889	1.379	1.409	1.349	1.363	1.379
200	0.5052	1.341	1.370	1.317	1.330	1.352
112	0.5189	1.321	1.349	1.302	1.314	1.329
201	0.5241	1.318	1.346	1.296	1.308	1.320
004	0.5582	1.265	1.292	1.240	1.253	1.264
202	0.5772	1.218	1.244	1.207	1.219	1.232
104	0.6127	1.172	1.197	1.149	1.160	1.173
203	0.6561	1.088	1.111	1.075	1.087	1.101
210	0.6683	1.065	1.088	1.053	1.066	1.081
211	0.6827	1.042	1.064	1.029	1.043	1.058
		±0.01	±0.01			
		$R\pm\sigma$		$R\pm\sigma$		
(*a*)/(*c*)		1.014±0.007				
(*b*)/(*c*)		1.036±0.007				
(*a*)/(*d*)				1.004±0.012		
(*b*)/(*d*)				1.026±0.013		

from the measured data. This finding could be due to either a scale-factor error in the original data or to a very slow convergence of the crystal scattering factor towards that of the free atom. The latter case would support the hypothesis of the core expansion in Be (Larsen & Hansen, 1984). Expected values of $E^{C}_{\rm coh}$ might be recovered by a slow convergence trend of the experimental data towards the free-atom curve, taking place, however, in the unexplored region of $\sin(\theta)/\lambda > 1.21$ Å^{-1}. Of course, the possibility that the free-atom scattering factors were incorrect cannot be excluded *a priori*. The reference scattering factor used in Be and shown in Fig. 1 is that obtained by the relativistic Hartree–Fock approach (RHF) (*International Tables for X-ray Crystallography*, 1989), which is known to be a well founded calculation. One can question that the RHF calculation misses completely any correlation effects. However, it is known (Brown, 1970; Benesch & Smith, 1970) that the use of accurate many-body wavefunctions does not appreciably change the free-atom scattering factor of light elements.

Were the observed effect due to a scale-factor error, it could be checked by introducing a scale factor properly chosen to produce matching of the two scattering factors over a rather extended region at high $\sin(\theta)/\lambda$. Therefore, scaling over the last measured 20 reflections was carried out. The resulting scattering factors of just the first 15 reflections are listed in Table 2 together with the original data from Larsen & Hansen (1984). The Coulomb cohesive energy calculated using

Table 3. *Diamond: best estimate of the experimental scattering factors per atom,* f_0^{be}

Theoretical data are from Lu *et al.* (1993) and the RHF calculation of the free-atom scattering factor is from *International Tables for X-ray Crystallography* (1989). The average ratio and fluctuation of the experimental data over the theoretical ones is also reported.

hkl	$\sin(\theta)/\lambda$ (Å^{-1})	f_0^{be}	f_0^{th}	f_0^{at}
111	0.2428	3.276 (11)	3.282	3.028
220	0.3965	1.966 (5)	1.976	1.961
311	0.4649	1.703 (4)	1.700	1.758
222	0.4856	0.148 (10)	0.111	–
400	0.5607	1.564 (6)	1.564	1.589
331	0.6110	1.570 (7)	1.558	1.524
422	0.6867	1.464 (10)	1.434	1.439
511	0.7284	1.420 (2)	1.384	1.395
333	0.7284	1.395 (6)	1.364	1.395
440	0.7929	1.318 (3)	1.316	1.328
			$R \pm \sigma$	
			1.008±0.011	

the scaled scattering factors turned out to be -8.41 eV atom^{-1}, which is definitely too negative a value. In Fig. 2, the curve of the Coulomb cohesive energy obtained using the scaled scattering factors is also shown. The convergence of the series, which is recovered in this case, coupled to the wrong value found for $E^C_{\rm coh}$, can be kept as evidence that *correction of the experimental scattering factors by just a scale factor is not adequate*. Finally, the accurate scattering-factor calculations in crystalline Be, reported by Chou *et al.* (1983) and Dovesi *et al.* (1982) and based respectively on LDA and Hartree–Fock approximation, are quoted in Table 2. A quantitative estimate of the overall agreement between experimental and theoretical data is given by the average ratios and corresponding r.m.s. fluctuations. These quantities, also reported in Table 2, point out that neither the LDA nor the Hartree–Fock calculations reproduce the experimental data.

The conclusion we can draw is that there is not a straightforward way to reconcile measured and theoretical scattering factors and expected values of the cohesive energy without introducing arbitrary distortions of the data since a correction for simply a scale factor is not sufficient. Therefore, two alternatives are left: either the set of experimental data is affected by some systematic error or the measurements have to be extended to higher values of $\sin(\theta)/\lambda$ since the convergence of the crystal scattering factor to that of the free atom is very slow (see Fig. 1). To get some hint about the latter possibility, the original experimental data were extrapolated to $\sin(\theta)/\lambda \simeq 2$ Å^{-1}, maintaining the same difference between crystal and free-atom scattering factors and the free-atom scattering factor was used for $\sin(\theta)/\lambda > 2$ Å^{-1}. The cohesive energy calculated using this set of data as input was found to be in close agreement with the thermochemical value. This finding, although resulting from a simulation of the scattering factor outside the measured range [$\sin(\theta)/\lambda < 1.2$ Å^{-1}], suggests that additional data should be measured in Be. This would help in understanding whether the difference observed in Fig. 1 is a real core expansion as this effect could play an important role in defining constraints for the theory.

2.2. *Diamond*

The high-accuracy investigation in diamond reported by Takama *et al.* (1990) was carried out using white radiation in the energy range from 12 to 40 keV and a recent review of these data can be found in Spackman (1991). In the present analysis, the anomalous-scattering contribution and the kinematic correction Δ were neglected, being much smaller than the experimental errors. The $f_{\rm rad}$ term did not contribute because of the low energy of the measurement. As in the case of Be, the nuclear Thomson term f_N, amounting to $\sim 0.001 r_0$, was neglected. Contrary to Takama *et al.* (1990), the Debye–Waller factor was deduced from the experimental phonon-dispersion relations (Warren *et al.*, 1967; Patel *et al.*, 1984). It turned out to be:

$$\exp[-W(\mathbf{G})] = \exp\{-0.152[\sin(\theta)/\lambda]^2\} \qquad (12)$$

with $\sin(\theta)/\lambda$ in Å^{-1}. The so-corrected data are reported in Table 3, where the LDA values from Lu *et al.* (1993) are also presented. The 222 forbidden reflection, as quoted by Spackman (1991), is also reported in Table 3. The agreement between calculated and experimental values is quite satisfactory, as is also apparent from the value of the average ratio. The cohesive energy terms, calculated by means of the corrected set of diffraction data and making use of the incoherent scattering factor measured by Petrillo & Sacchetti (1995), are reported in Table 1. Convergence was achieved including the free-atom scattering factor data up to $\sin(\theta)/\lambda = 50$ Å^{-1}. The cohesive energy obtained from the diffraction data compares well with the value obtained from thermochemical measurements. The contribution of the 222 reflection to the cohesive energy amounts to 2 meV atom^{-1} as compared with the total Coulomb contribution of -1.6 eV atom^{-1}. Contrary to the case of Be, the convergence of the

Table 4. *Silicon: best estimate of the experimental scattering factors per atom, f_0^{be}*

Theoretical results are also reported: (*a*) data from Lu *et al.* (1993); (*b*) data from Wang & Klein (1981). Free-atom values are from the RHF calculation in *International Tables for X-ray Crystallography* (1989). In the last column, values of the kinematic correction Δ are listed. Average ratios and fluctuations of the experimental data over the theoretical ones are reported for the whole $\sin(\theta)/\lambda$ region; in the case of the free atom, these quantities are calculated for $\sin(\theta)/\lambda \geq 0.52$ Å^{-1}.

hkl	$\sin(\theta)/\lambda$ (Å^{-1})	f_0^{be}	f_0^{th} (*a*)	f_0^{th} (*b*)	f_0^{th}	Δ
111	0.1595	10.737	10.726	10.68	10.549	−0.013
220	0.2604	8.667	8.665	8.63	8.752	−0.015
311	0.3053	8.030	8.033	8.04	8.173	−0.015
222	0.3189	0.191	0.168	0.13	–	–
400	0.3683	7.454	7.452	7.46	7.521	−0.015
331	0.4013	7.256	7.225	7.19	7.189	−0.016
422	0.4510	6.725	6.696	6.69	6.707	−0.016
333	0.4784	6.436	6.404	6.41	6.445	−0.016
511	0.4784	6.449	6.428	6.42	6.445	−0.016
440	0.5208	6.056	6.030	6.02	6.041	−0.016
444	0.6378	4.993	4.968		4.981	−0.016
551	0.6575	4.815	4.802		4.815	−0.016
642	0.6889	4.560	4.546		4.559	−0.016
800	0.7365	4.183	4.182		4.193	−0.016
660	0.7812	3.883	3.870		3.876	−0.017
555	0.7973	3.770	3.761		3.768	−0.017
844	0.9020	3.151	3.155		3.151	−0.017
880	1.0416	2.548	2.551		2.541	−0.017
			$R\pm\sigma$	$R\pm\sigma$	$R\pm\sigma$	
			1.0022±0.0021	1.0040±0.0031	1.0009±0.0016	

energy sums was found to be satisfactory even with this reduced experimental set of data. The contribution to the cohesive energy brought about by the structure factors is rather small, as expected in light elements where cohesion is dominated by the exchange-correlation contribution.

2.3. *Silicon*

The data analysed in the following are those from the high-precision measurements of Aldred & Hart (1973), Teworte & Bonse (1984) and Deutsch & Hart (1985). All the data were corrected for the nuclear Thomson contribution, $f_N = 0.004r_0$, the kinematic term Δ and the Debye–Waller factor. The kinematic correction Δ was calculated employing the free-atom electron density as tabulated by Herman & Skillman (1963). Since the Δ values thus obtained range from $-0.013r_0$ to $-0.017r_0$ (see Table 4), use of the electron density of the free atom instead of the crystal did not introduce a large error. As, to our best knowledge, a not accurate enough measurement of the Debye–Waller factor from neutron diffraction is available, it was deduced from the experimental phonon density of states (Weber, 1977). At room temperature (293 K),

$$\exp[-W(\mathbf{G})] = \exp\{-0.460[\sin(\theta)/\lambda]^2\}, \qquad (13)$$

where $\sin(\theta)/\lambda$ is in Å^{-1}. The data of Aldred & Hart (1973) and Teworte & Bonse (1984) were collected using Mo $K\alpha_1$ and Ag $K\alpha_1$ radiations, so that a non-negligible contribution from anomalous scattering affected the experimental structure factors. The anomalous scattering contribution f'_{LE}, assumed to be wave-vector independent, was deduced from the experimental forward-scattering amplitude, reported by Deutsch & Hart (1988), properly corrected by Δ at $\mathbf{G} = \mathbf{0}$, *i.e.* $\Delta = -0.010r_0$. Indeed, neglecting $f_{\rm rad}$ and at $\mathbf{G} = 0$, the experimental structure factor is given by

$$\begin{aligned}\mathcal{F}_0 &= 2[f_m(0) + f'_{LE}(0) + f_N] \\ &= 2[Z + \Delta(0) + f'_{LE}(0) + f_N], \qquad (14)\end{aligned}$$

from which $f'_{LE}(0)$ can be obtained.

The corrected values of f_0, separately produced from the experimental data of Aldred & Hart (1973), Teworte & Bonse (1984) and Deutsch & Hart (1985), were also averaged because of the very small difference found between the various sets, the average fluctuation of f_0 being of the order of $0.005r_0$. The best estimate data for f_0 are reported in Table 4 together with the theoretical data from Lu *et al.* (1993) and Wang & Klein (1981). A good agreement is found between the calculated values and the best estimate of the experimental data. The calculated average ratios and fluctuations (see Table 4) indicate a better agreement for the LDA calculation of Lu *et al.* (1993). In any case, the discrepancies observed between calculated and measured values are of the same order as the probable experimental errors. Finally, the cohesive energy, deduced from the present scattering factors employing the free-atom data up to $\sin(\theta)/\lambda = 100$ Å^{-1} and the measured data of the incoherent scattering factor (Paakkari & Suortti, 1974), is reported in Table 1. The good agreement with the thermochemical value indi-

Table 5. *Silicon: experimental scattering factors per atom*

Free-atom values are from the RHF calculation of *International Tables for X-ray Crystallography* (1989). In the last column, values of the kinematic correction Δ are listed.

hkl	$\sin(\theta)/\lambda$ (Å^{-1})	$f_0^{\rm exp}$	$f_0^{\rm at}$	Δ
777	1.1162	2.273 (3)	2.302	−0.016
888	1.2757	1.834 (3)	1.922	−0.016
10,10,0	1.3020	1.730 (2)	1.869	−0.016
999	1.4351	1.529 (8)	1.675	−0.015
12,12,0	1.5624	1.356 (3)	1.540	−0.015

cates that the present data are very accurate. Moreover, the overall agreement between theory and experiment suggests that LDA is a fairly accurate theory for this system.

For completeness, the 222 forbidden reflection, as measured by Alkire *et al.* (1982) and without any applied correction, is reported in Table 4. Actually, the structure factors of forbidden reflections are quite sensitive to either the detailed shape of the electron density around each atom or the asymmetry effects of the Debye–Waller factor. In the case of Si, a large body of data on forbidden reflections is available. However, a proper analysis of these reflections would be quite complex and beyond the present purpose. The measured value of the 222 scattering factor was used to calculate the cohesive energy and its contribution turned out to be 21 meV atom^{-1} only, as compared with the total contribution of −1.4 eV atom^{-1}.

Actually, some more reflections, namely 777, 888, 10,10,0, 999 and 12,12,0, were measured in Si (Deutsch & Hart, 1985). These experimental data were treated in the same way as those reported in Table 4 but they are separately listed in Table 5 because of their rather puzzling behaviour. An inspection of Table 5 shows that the difference between these data and the free-atom scattering factor increases rapidly with increasing $\sin(\theta)/\lambda$. In Deutsch & Hart (1985), this finding was used as experimental evidence of the difference between the Debye–Waller factor appropriate to core or valence electrons. By fitting the whole of the experimental data over two separate regions of $\sin(\theta)/\lambda$, the authors deduced two different values of the Debye–Waller coefficient, *i.e.*

$$\exp[-W(\mathbf{G})] = \exp\{-0.4632 \pm 0.0041[\sin(\theta)/\lambda]^2\} \qquad 0.5 \le \sin(\theta)/\lambda \le 1.05\,\text{Å}^{-1} \tag{15}$$

$$\exp[-W(\mathbf{G})] = \exp\{-0.5085 \pm 0.0035[\sin(\theta)/\lambda]^2\} \qquad 1.3 \le \sin(\theta)/\lambda \le 1.57\,\text{Å}^{-1}. \tag{16}$$

Since, as already observed in Deutsch & Hart (1985), core electrons are more tightly bound to the nucleus, the Debye–Waller factor appropriate to them should be substantially equal to that measured by neutron diffraction. Actually, even though not accurate enough for the previous data analysis, neutron determinations of the Debye–Waller factor in Si do exist. The neutron result reported by Zhang *et al.* (1990), namely,

$$\exp[-W(\mathbf{G})] = \exp\{-0.45[\sin(\theta)/\lambda]^2\}, \tag{17}$$

where the probable error on the coefficient 0.45 is in the range 0.01–0.02, rules out the possibility that the interpretation of Deutsch & Hart (1985) was correct. At present, a reliable interpretation of the behaviour exhibited by the data of Table 5 is lacking.

A final remark concerns the free-atom scattering factors, also reported in Table 4. It is apparent that the RHF calculation (*International Tables for X-ray Crystallography*, 1989) is, in the case of Si, extremely accurate providing a convergence to the crystal scattering factor better than 0.1% in the high $\sin(\theta)/\lambda$ region.

2.4. *Copper*

The set of data selected as the best available for the present analysis are those from Schneider *et al.* (1981). Since high-energy photons were used for the measurements, the advantage of neglecting the f'_{LE} contribution could be exploited. The $f_{\rm rad}$ contribution was found to be $\sim 0.001 f_0$ (Rocchi & Sacchetti, 1993), *i.e.* smaller than the experimental errors and the nuclear Thomson contribution, $f_N = 0.008 r_0$, was neglected as well. Furthermore, the experiment was performed at two different temperatures, thus allowing for a reasonable check of the Debye–Waller factor. In the case of copper, a quite reliable experimental phonon density of states (Svensson *et al.*, 1967) is available that yields a specific heat Debye temperature in close agreement with that derived from calorimetric experiments. Use of the measured density of states, under the quasi-harmonic approximation (Maradudin, 1974), yielded

$$\exp[-W(\mathbf{G})] = \exp\{-0.163[\sin(\theta)/\lambda]^2\} \tag{18}$$

at 50 K. This result compares favourably with the estimate deduced by Schneider *et al.* (1981) by means of a direct comparison of the experimental scattering factors with those of the free atom. At room temperature, the factor in the exponent of equation (18) takes the value 0.532 Å^2, still in close agreement with the estimate of Schneider *et al.* (1981). Therefore, the original data were corrected using equation (18). The kinematic correction Δ, as derived from the electron density and one-particle potential of Moruzzi *et al.* (1978), was applied to the data, being of the same order as the experimental errors. Since in Schneider *et al.* (1981) the experimental data were compared to the free atom neglecting the Δ contribution, in the present analysis the original data were scaled in order to fit the RHF free-atom scattering factor (*International Tables for X-ray Crystallography*, 1989) at $\sin(\theta)/\lambda$ values greater than 0.5 Å^{-1}. A scaling factor very close to 1 was found, namely 1.0042 (62). The f_0 data thus obtained are

Table 6. *Copper: experimental scattering factors per atom*

Theoretical results are from Bagayoko *et al.* (1980) and the free-atom RHF calculation is from *International Tables for X-ray Crystallography* (1989). In the last column, values of the kinematic correction Δ are listed. The average ratio and fluctuation of the experimental data over the theoretical ones is reported.

hkl	$\sin(\theta)/\lambda$ (Å^{-1})	$f_0^{\rm exp}$	$f_0^{\rm th}$	$f_0^{\rm at}$	Δ
111	0.240	21.68 (14)	21.68	22.08	−0.06
200	0.277	20.38 (13)	20.35	20.72	−0.07
220	0.391	16.60 (12)	16.62	16.78	−0.08
311	0.459	14.68 (11)	14.70	14.78	−0.08
222	0.479	14.22 (11)	14.17	14.23	−0.08
400	0.553	12.42 (10)	12.42	12.46	−0.08
331	0.603	11.42 (9)	11.41	11.46	−0.09
420	0.619	11.14 (10)	11.13	11.17	−0.09
422	0.678	10.18 (10)	10.16	10.20	−0.09
333	0.719	9.58 (9)	9.58	9.61	−0.09
511	0.719	9.62 (9)	9.58	9.61	−0.09
440	0.782	8.92 (11)		8.85	−0.09
600	0.830	8.37 (11)		8.37	−0.09
444	0.958	7.38 (12)		7.40	−0.09
800	1.107	6.77 (16)		6.66	−0.09
660	1.174	6.42 (15)		6.39	−0.09
555	1.198	6.30 (15)		6.30	−0.09
10,0,0	1.383	5.57 (17)		5.68	−0.09
666	1.437	5.48 (19)		5.49	−0.09
880	1.565	5.08 (20)		5.09	−0.09
			$R\pm\sigma$		
			1.0009±0.0017		

reported in Table 6, together with the theoretical values from Bagayoko *et al.* (1980). It is apparent that the experimental data, after subtraction of Δ and scaling to the atomic scattering factor, are in very good agreement with the theoretical ones. In the past, several theoretical and experimental investigations of the scattering factors in Cu have been carried out (see, for instance, Mackenzie & Mathieson, 1992). However, in all cases the correction Δ was not applied since its importance was recognized only recently (Dewey *et al.*, 1994). The most important difference between the present data reduction and the previous ones is the use of the Δ correction to define the scale factor more appropriately. This results in the good agreement observed between theory and experiment, without any further adjustment.

The Coulomb contribution to the cohesive energy, calculated using the data of Table 6 and including free-atom data up to $\sin(\theta)/\lambda = 200$ Å^{-1}, is quoted in Table 1. The exchange-correlation contribution could not be deduced in this case since an incoherent scattering-factor measurement is not available. However, the magnitude of this term is expected to be of the order of a few eV atom^{-1} (Mazzone & Sacchetti, 1984). The cohesive energy value derived from the experimental structure factors can be considered rather satisfactory. Indeed, although different from the thermochemical value, it amounts to $\sim 3\times 10^{-4}$ of the total ground-state energy E_0 of the system. Therefore, the experimental data reported in Table 6 can be reliably assumed as representative of the actual crystal values within about $0.1r_0$.

2.5. *Germanium*

The analysis of Ge data from Matsushita & Kohra (1974), Cu $K\alpha$ radiation, and Deutsch *et al.* (1990), W $K\alpha_1$ radiation, together with the high-accuracy data collected at 342 and 1381 keV incoming photon energy (Dewey *et al.*, 1994), is reported in Dewey *et al.* (1994), where the same data-reduction procedure as in §2 was applied. For a meaningful internal comparison of these sets of data, correction of the low-energy data for the anomalous contribution f'_{LE} was necessary. The determination of f'_{LE} took advantage of the experimental data measured at 1381 keV and it was described in Dewey *et al.* (1994). However, at this high energy, the $f_{\rm rad}$ contribution could not be neglected and it was found to amount to $0.0028f_0$, whereas it did not affect the data at 8, 59 and 342 keV. This term was accounted for in deducing f'_{LE} (Dewey *et al.*, 1994). The kinematic correction Δ was calculated from the free-atom electron density (Herman & Skillman, 1963) and applied to all the experimental data. No high-accuracy neutron diffraction data on the Debye–Waller factor in Ge are available. So it was deduced from the measured phonon dispersion relations (Neliu & Nilsson, 1972). As reported in Dewey *et al.* (1994), it was found to be

$$\exp[-W(\mathbf{G})] = \exp\{-0.560[\sin(\theta)/\lambda]^2\}. \qquad (19)$$

The best estimate of the scattering factors deduced in Dewey *et al.* (1994) as well as the theoretical results from Lu *et al.* (1995) and Wang & Klein (1982) are presented in Table 7. As in the case of Si, the overall

Table 7. *Germanium: best estimate of the experimental scattering factors per atom, f_0^{be}*

Theoretical results are also reported: (*a*) data from Lu *et al.* (1995); (*b*) data from Wang & Klein (1982). Free-atom values are from the RHF calculation of *International Tables for X-ray Crystallography* (1989). In the last column, values of the kinematic correction Δ are listed. Average ratios and fluctuations of the experimental data over the theoretical ones are reported.

hkl	$\sin(\theta)/\lambda$ (Å^{-1})	$f_0^{\rm be}$	$f_0^{\rm th}$ (*a*)	$f_0^{\rm th}$ (*b*)	$f_0^{\rm at}$	Δ
111	0.1531	27.450 (22)	27.519	27.46	27.381	−0.083
220	0.2500	23.581 (35)	23.683	23.62	23.792	−0.092
311	0.2931	22.181 (75)	22.172	22.13	22.360	−0.096
400	0.3535	20.257 (70)	20.318	20.28	20.452	−0.101
331	0.3852	19.606 (87)	19.432	19.37	19.488	−0.103
422	0.4329	18.059 (71)	18.016	17.96	18.085	−0.106
333	0.4592	17.345 (32)	17.275	17.22	17.338	−0.107
440	0.5000	16.173 (32)	16.187	16.12	16.227	−0.110
444	0.6123	13.528 (20)	13.493		13.509	−0.115
660	0.7499	11.006 (55)	10.924		10.949	−0.119
555	0.7653	10.669 (31)	10.684		10.704	−0.120
777	1.0715	7.531 (35)	7.543		7.542	−0.121
			$R\pm\sigma$	$R\pm\sigma$		
			1.0010±0.0040	1.0034±0.0044		

agreement between calculated and experimental scattering factors is very satisfactory. Use of these data to calculate the cohesive energy, using the atomic data up to $\sin(\theta)/\lambda = 200\,\text{Å}^{-1}$, yielded the value reported in Table 1. The agreement with the thermochemical value of the cohesive energy can be considered fairly satisfactory since for Ge, as in the case of Cu, the total ground-state energy E_0 is very high. Therefore, it is quite reasonable to state that the data of Table 7 are representative of the Ge crystal scattering factors at least within $0.05r_0$. Finally, comparison with the free-atom scattering factors (*International Tables for X-ray Crystallography*, 1989) in Table 7 shows that the relativistic treatment of the Ge atom is important in order to describe the distribution of the more tightly bound electrons.

2.6. *Transition metals*

In the case of transition metals, no extended high-precision measurements are available. Nonetheless, medium-accuracy data are reported for some couples of reflections occurring at the same $\sin(\theta)/\lambda$ values. This is the case for V (Weiss & De Marco, 1965; Diana & Mazzone, 1975; Ohba *et al.*, 1981; Kretschmer & Schneider, 1984), Cr (Diana & Mazzone, 1972; Ohba *et al.*, 1982), Fe (De Marco & Weiss, 1965; Diana & Mazzone, 1974; Ohba & Saito, 1982), Co (Diana & Mazzone, 1978) and Ni (Rocchi & Sacchetti, 1995). These data are particularly useful for modelling the aspherical behaviour of the electron density. In fact, in 3*d* transition metals, the ratio between the structure factors of two reflections occurring at the same $\sin(\theta)/\lambda$ value can be well approximated using symmetry arguments (Weiss & Freeman, 1959):

$$\frac{f_0(\mathbf{G}_1)}{f_0(\mathbf{G}_2)} = \frac{1 + Z_a A(\mathbf{G}_1) R(G_1)}{1 + Z_a A(\mathbf{G}_2) R(G_2)}, \tag{20}$$

where G_1 and G_2 are the reciprocal-lattice vectors of the two reflections, $R(G)$ is a ratio between the spherical and aspherical form factors, $A(\mathbf{G})$ is a function of the direction of $\mathbf{G}$ and Z_a is an aspherical charge. $R(G)$ can be obtained from free-atom data (*International Tables for X-ray Crystallography*, 1989) with adequate accuracy. Considering that the ratio in equation (20) is always very close to 1, a very small error is introduced using the free-atom data for $R(G)$. Δ and f'_{LE} have little effect on the structure-factor ratio and can be safely neglected. Values of Z_a were deduced from both the experimental data and the theoretical data (Laurent *et al.*, 1978, 1981; Callaway & Wang, 1977; Wang & Callaway, 1977), applying in the latter case the same analysis procedure. Results are shown in Fig. 3, where a clear trend is apparent. In fact, all b.c.c. metals exhibit a negative almost constant Z_a value, while Ni, which is f.c.c., has a positive value of the aspherical charge and f.c.c. Co shows an intermediate behaviour. This qualitative trend is fairly well reproduced by the LDA calculations (Laurent *et al.*, 1978, 1981; Callaway & Wang, 1977; Wang & Callaway, 1977), although they fail in reproducing the experimental data on a quantitative base: *the absolute value of Z_a is systematically a factor of two smaller.*

3. Conclusions

The analysis described in the previous sections allowed us to derive sets of experimental scattering factors $f_0(\mathbf{G})$, *i.e.* the Fourier components of the electron density, for Be, C, Si, Cu and Ge crystals with an accuracy adequate for a meaningful comparison between experiment and state-of-the-art calculations based on the LDA, apart from the case of Be. A further useful comparison between theory and experiment was carried out on the asphericity of the electron density in 3*d* transition metals.

A first observation concerns the behaviour of the scattering factor of either Si or Ge in the high $\sin(\theta)/\lambda$ region. The experimental data here reported for these two elements can be definitely recognized as the most accurate *absolute* determinations available to date. The present analysis points out that the RHF calculation of the free-atom scattering factor reproduces very well the crystal data (0.1%) at high $\sin(\theta)/\lambda$. This finding makes us confident that use of the RHF scattering factors in the cases of Be, C and Cu was adequate. The present analysis confirms that the relativistic kinematic correction $\Delta(\mathbf{G})$ cannot be neglected in analysing the photon scattering amplitudes as it provides a non-negligible contribution compared with the high accuracy of the experimental data. This statement is much more severe in the case of the heaviest elements we analysed, namely Cu and Ge, where the effect of $\Delta(\mathbf{G})$ even on the cohesive energy is appreciable.

As to comparison with theory, the present analysis shows that the LDA calculations of the electron density reproduce fairly well the experimental data in C, Si, Cu and Ge, whereas failures concerning the size of the aspherical charge Z_a are observed in the case of transition metals. Generally, the LDA provides fairly good values for the cohesive energy. However, in the framework of the LDA, the calculated cohesive energy depends mainly on the spherical average of the electron density over each atomic volume. Therefore, if the exact electron density is well represented by a superposition of nearly spherical electron distributions centred around the atomic sites, good results for both cohesive energy and electron density would be provided by the LDA calculation. This is actually the case for C, Si, Cu and Ge, where the electron-density decomposition is adequate because of the symmetry of p-like electrons in the T_d crystal field (C, Si and Ge) and the full $3d$ band in Cu. This conclusion can also be drawn looking at the small difference in the scattering factors of the reflection pair 511–333, which produces an aspherical charge Z_a 5–10 times smaller than in transition metals. On the other hand, when the electron density exhibits a strong aspherical behaviour around each atomic site, as it does in $3d$ transition metals, one can expect larger disagreements between calculated and experimental electron density. The case of Be is different since a definite answer to the goodness of the theory–experiment comparison cannot be obtained from the available experimental data. Nonetheless, it deserves more experimental attention because an indication of core expansion is reported that could represent a strong test of first-principle calculations. Disagreements are systematically confined to those $3d$ systems, like V, Cr, Fe, Co and Ni, which exhibit an appreciable asphericity of the $3d$ electron distribution. A similar remark, although based on different considerations, was made by Gunnarsson & Jones (1985) and the same arguments were applied by Wang & Klein (1981) although on a reduced set of data.

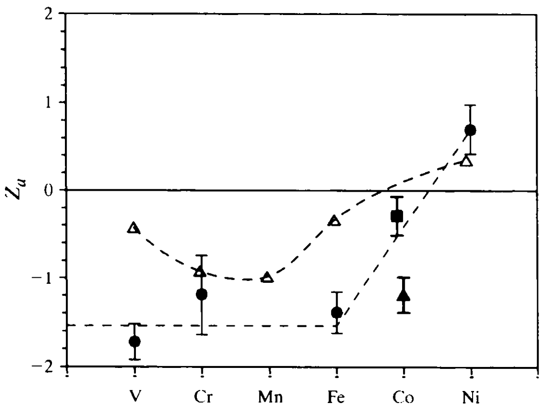

Fig. 3. Aspherical charge values along the $3d$ series. Experimental data from X-ray diffraction measurements (dots) in comparison with theoretical data (empty triangles) obtained by applying the same data analysis to the calculated scattering factors (see text). In the case of Co, the experimental data for f.c.c. Co (square) is from Fe_8Co_{92} alloy and for b.c.c. Co (triangle) from the compound FeCo. Dashed lines are a guide to the eye.

The interpretation arising from the whole comparative analysis could be that LDA failures are unlikely owing to an error in the exchange-correlation potential of the electron gas as employed in the most recent calculations, rather the error should be in the local approximation itself, that is the exchange-correlation potential should depend on the electron density in a region with size of the order of the inverse of the local Fermi momentum. A non-local dependence of the exchange-correlation potential on the electron density would result in a sort of smoothing of the potential itself. Therefore, one can guess that, for a given potential, the electron density generating it should be less smooth than that used in the standard local approximation. The inclusion of some degree of non-locality in the exchange-correlation potential is expected to increase the amount of asphericity of the electron density, thus improving the agreement with the experimental data in the case of transition metals.

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