sibles pour un vecteur de propagation donné (fourni par l'expérience de diffraction neutronique).

On peut ainsi réexaminer toutes les structures magnétiques connues: ou bien une structure magnétique est compatible avec la structure cristallographique, ou bien elle est à éliminer.

Notons enfin qu'indépendamment de cet aspect géométrique, la méthode de Bertaut permet d'étudier les couplages physiques responsables de l'établissement des structures magnétiques non colinéaires, de préciser les couplages possibles entre sous-réseaux magnétiques. Elle souligne le lien entre les structures magnétiques et cristallographiques; elle est particulièrement intéressante dans les cas de transitions magnétiques successives (mais contrairement à la théorie de Landau, elle ne fournit aucun renseignement sur la nature des transitions magnétiques).

Considérons par exemple les fluorures $KFeF_3$, $KCoF_3$, $KNiF_3$ (Scatturin, Corliss, Elliott & Hastings, 1961) de structure pérovskite idéale; dans la phase antiferromagnétique (mode G, $\mathbf{k}=[\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}]$) ils restent cubiques, il ne peut exister de faible ferromagnétisme f. Au contraire $KMnF_3$ (Heeger, Beckman & Portis, 1961), de même structure à haute température, est orthorhombique (*Pbnm*) dans la phase ordonnée, il peut donc exister un faible ferromagnétisme (on observe successivement les modes G_y et G_zf_x). $RbFeF_3$ (Testardi, Levinstein & Guggenheim, 1967) est cubique dans la phase paramagnétique; à 102°K, il devient quadratique et strictement antiferromagnétique (la structure est vraisemblablement G_z); à 87°K, il devient faiblement ferromagnétique, et on observe effectivement une déformation orthorhombique; enfin à 45°K, l'aimantation change de direction, et la symétrie devient monoclinique.

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References

ALIKHANOV, R. A. (1959). *J. Phys.* **36**, 1690.
BERTAUT, E. F., MERCIER, M. & PAUTHENET, R. (1964). *Proc. Int. Conf. Magnetism*, Nottingham. p. 275.
BERTAUT, E. F., MERCIER, M. & PAUTHENET, R. (1965). *Phys. Letters*, **19**, 13.
BERTAUT, E. F. (1968). *Acta Cryst.* A**24**, 217.
BERTAUT, E. F. (1969). *C. R. Acad. Sci. Paris, série* B, **268**, 625.
CORLISS, L. M. & HASTINGS, J. M. (1964). *J. Phys. Radium*, **25**, 557.
COX, D. E., TAKEI, W. J. & SHIRANE, G. (1963). *J. Phys. Chem. Soc.* **24**, 405.
DACHS, H., STOLL, E. & WEITZEL, H. (1967). *Z. Kristallogr.* **125**, 120.
DZIALOSHINSKY, I. E. (1968). *J. Phys. Chem. Soc.* **4**, 241.
GONZALO, J. A., COX, D. E. & SHIRANE, C. (1966). *Phys. Rev.* **147**, 415.
HEEGER, A. J., BECKMAN, O. & PORTIS, A. M. (1961). *Phys. Rev.* **123**, 1652.
KOEHLER, W. C., YAKEL, H. L., WOLLAN, E. O. & CABLE, J. W. (1964). *Phys. Letters*, **9**, 93.
NEDLIN, G. M. (1965). *Sov. Phys. Solid State*, **7**, 592.
OLBRYCHSKI, K. (1963). *Phys. Stat. Sol.* **3**, 1868.
PEYRARD, J. & SIVARDIÈRE, J. (1969). *Solid State Comm.*, **7**, 605.
PRZYSTAWA, J. (1967). *Phys. Stat. Sol.* **20**, 451.
PRZYSTAWA, J. (1968). *Phys. Stat. Sol.* **30** K, 115.
SCATTURIN, V., CORLISS, L., ELLIOTT, N. & HASTINGS, J. (1961). *Acta Cryst.* **14**, 19.
SIVARDIÈRE, J. (1969). *Acta Cryst.* A**25**, 658.
TESTARDI, L. R., LEVINSTEIN, H. J. & GUGGENHEIM, H. J. (1967). *Phys. Rev. Letters*, **19**, 503.
VARRET, F., IMBERT, P., GERARD, A. & HARTMANN-BOUTRON, F. (1968). *Solid State Comm.* **6**, 889.
VEYRET, C. (1965). Thèse 3*e* Cycle, Grenoble.
WOLLAN, E. O., CHILD, H. R., KOEHLER, W. C. & WILKINSON, M. K. (1958). *Phys. Rev.* **112**, 1132.
WOLLAN, E. O., KOEHLER, W. C. & WILKINSON, M. K. (1959). *Phys. Rev.* **113**, 497.

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Some Molecular Compton Profiles

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Several calculations of atomic Compton profiles have shown that this physical property is very sensitive to the choice of the wave functions used to characterize the scattering system when calculating its kinetic energy as well as the mean values of its momentum and radius of charge distribution. The same method related to Dumond theory was applied to the case of molecules isoelectronic with neon and argon atoms. The results obtained give useful information about the charge distribution in the scattering system.

Introduction

Many authors (Bonham, 1965, 1967; Tavard & Roux, 1965; Kilby, 1965; Cornille, 1967; Bartell & Gavin, 1964; Bonham & Cox, 1967) have shown how useful the scattering effects are for studying physical properties such as total and kinetic energies of scattering systems which are special cases of $\langle r^n \rangle$ and $\langle p^n \rangle$

defined by:

$$\langle r^n \rangle = \int \psi(\mathbf{r}) r^n \psi^*(\mathbf{r}) d\mathbf{r}$$

$$\langle p^n \rangle = \int \chi(\mathbf{p}) p^n \chi^*(\mathbf{p}) d\mathbf{p}$$

where $\psi(\mathbf{r})$ and $\chi(\mathbf{p})$ are wave functions in coordinate and momentum space respectively for the system. The aim of this article is to give some new results obtained using the method applied by Roux, Cornille, Tsapline, Rouault & Tavard (1967), and to suggest new measurements. The importance of these subjects was clearly explained in *Intensities and Structure Factors Conference Report* (1969). The $\langle r^n \rangle$ and $\langle p^n \rangle$ values, as well as the scattered intensities and shapes of the momentum distributions, are related to the expansion of the charge distribution in the scatterer.

The method has been used for simple molecules for which core wave functions are available. The following quantities were calculated:

$\langle p^{-1} \rangle$	related to the maximum of the Compton profile;
$\langle p \rangle$	the mean value of the momentum;
$\langle p^2/2m \rangle$	the kinetic energy;
$\langle r \rangle$	the electronic contribution to dipole moments;
$\langle \Delta q \rangle$	the width of the Compton profile directly related to the momentum distribution.

From these results, calculated for HF, H_2O, NH_3, CH_4, HCl, H_2S, PH_3, SiH_4, it appears that the wave functions used have over-extended electronic densities.

Method of calculation

The method of Dumond (1933), which corresponds to simple collisions between an incident photon of high energy and one electron of the scattering system, gave good results for the study of Compton profiles of atoms (Cornille, 1967). This method was justified at the Sagamore Conference II (Cornille, 1967*b*) as far as high-energy incident beams are concerned and was applied to some light molecules. If the scatterer in its ground state has the wave function $\psi(\mathbf{r})$, the momentum wave-function is obtained by the Dirac transform which is a special type of the Fourier transform, and if

$$\chi(\mathbf{p}) = (2\pi)^{-3/2} \int \psi(\mathbf{r}) \exp(-i\mathbf{p}\,.\,\mathbf{r}) d\mathbf{r} \qquad (1)$$

it is possible to express the radial momentum density by:

$$I(p) = \int \chi(\mathbf{p}) \chi^*(\mathbf{p}) p^2 d\Omega_p \,, \qquad (2)$$

and the various $\langle p^n \rangle$ values by:

$$\langle p^n \rangle = \int \chi(\mathbf{p}) \chi^*(\mathbf{p}) p^n d\mathbf{p} \qquad (3)$$

Table 1. *Results for* Ne, HF, H_2O, NH_3 *and* CH_4

All quantities are in atomic units.

		Ne(1)	HF(2)	H_2O(2)	NH_3(2)	CH_4(3)
1	$\langle p^{-1} \rangle$	0·545	0·646	0·721	0·923	1·080
2	$\langle p \rangle$	3·52	3·036	2·5935	2·2160	1·8225
3	$\langle p^2 \rangle$	128·547	100·0096	75·909	55·9256	39·264
4	Total energy calculation	−128·547	−100·0053	−75·9224	−55·9742	−39·866
5	Experimental energy	−129·056	−100·48	−76·46	−56·578	−40·522
6	Calculated dipole moment	0	0·825	0·820	0·5949	0
7	Experimental dipole moment	0	0·716	0·728	0·583	0
8	Δq calc.	2·77	2·366	2·04	1·72	1·44
9	R_e		1·728	1·814	1·925	2·067

Values in lines 5, 6, 7 and 9 are taken from: (1) Sachs (1961); (2) Moccia (1964); (3) Allavena (1965).

Table 2. *Results for* HCl, H_2S, PH_3 *and* SiH_4

All quantities are in atomic units.

		HCl(2)	H_2S(2)	PH_3(2)	SiH_4(2)
1	$\langle p^{-1} \rangle$	0·610	0·672	0·821	0·852
2	$\langle p \rangle$	4·499	4·135	3·852	3·5232
3	$\langle p^2 \rangle$	450·7963	389·105	338·105	292·209
4	Total energy calculation	−458·8378	−397·5891	−341·3960	−290·1024
5	Experimental energy	−462·81	−400·81	−343·42	−292·141
6	Calculated dipole moment	0·8524	0·6789	0·461	0
7	Experimental dipole moment	0·413	0·362	0·217	0
8	Δq calc.	1·96	1·74	1·50	1·34
9	R_e	2·41	2·52	2·68	2·76

Values in line 2 are taken from Moccia (1964).

or

$$\langle p^n \rangle = \int_q^\infty I(p) p^n \mathrm{d}p \,. \qquad (4)$$

The Compton profile is given by:

$$J(q) = \frac{1}{2} \int \frac{I(p)}{p} \mathrm{d}p \qquad (5)$$

with

$$q = \frac{cl}{2\lambda_i \sin\theta/2} \text{ in atomic units.} \qquad (6)$$

Here c is the velocity of the light, λ_i the wave length of the incident beam, l is measured from the centre of the Compton profile and θ is the scattering angle.

Equations (1) to (6) have been used to calculate $\langle p^{-1} \rangle$, $\langle p \rangle$, $\langle p^2 \rangle$ and Δq for Ne, HF, H_2O, NH_3 and CH_4 and also for HCl, H_2S, PH_3 and SiH_4.

Results and discussion

Tables 1 and 2 give the results obtained for the two sets of molecules. Comparison of calculated and experimental energies, dipole moments, and equilibrium distances shows that the $\langle p^n \rangle$ and Δq values are sensitive to the change of molecular length from one molecule to another. It would be desirable to make accurate measurements on gases, in order to test the theory of Dumond and the accuracy of the Hartree Fock calculations of momentum densities, and to get experimental values of $\langle p^{-1} \rangle$ and Δq. This was achieved recently for the water molecule in the liquid state by Cooper, Roux, Cornille & Tsapline (1968) and the results are given in Table 3.

Table 3. *Compton profile for the water molecule*

	Theoretical, from Table 1	Experimental, Cooper's work
$\Delta q_{a.u}$	2·04	2·0 ± 0·1
$\langle p^{-1} \rangle_{a.u}$	0·72	0·80 ± 0·1

These results are in very good agreement, but an increase of resolution would be useful to test the accuracy of momentum densities.

In recent work on atoms (Cornille, 1967), it was possible with the use of $\langle p^n \rangle$ and Δq values together with scattered intensities and $\langle r^n \rangle$ values to classify the wave functions into two types: the Slater type wave functions with over-contracted electronic densities and the Hartree–Fock type with over-extended electronic densities. Some relationships were established between $\langle p^n \rangle$ and Δq values and some $\langle r^n \rangle$. It seemed interesting to see what happens in molecular cases, and HF and HCl molecules were investigated. Table 4 gives the results obtained for HF using $\langle p^2 \rangle$ and $\langle p^n \rangle$ and the dipole moment μ which contains a nuclear term which is quite constant in the whole set, and does not change the classification of the results. We can see that the results, which are quite similar to the atomic ones for the expansion of the charge distributions, agree with the Cade & Huo (1966) work on dipole moments for the AH molecules and the work of Tavard (1966) on scattered intensities.

The results are the same for the HCl molecule, given in Table 5.

Conclusion

In this work some $\langle p^n \rangle$ values and the width of the Compton profile Δq were calculated and compared with total energies and $\langle r^n \rangle$ values, allowing a classification of the wave functions used in the calculations for two sets of hydride molecules. All these physical properties are mean values of integrated quantities. For the details of electron distributions the shape of Compton profiles remains essential. Accurate shapes given by $\chi(\mathbf{p})$ are very useful not only for the study of the scattering system, but also to study the position wave function in position annihilation experiments, as was discussed at the Sagamore Conference (1967), but also for some properties of the Faltung theorem which establishes a relation between the Fourier transform of the electron density and a sum of overlap integrals in momentum space, as was suggested by Bonham (1967).

Table 4. *Results for* HF *using* $\langle p^2 \rangle$, $\langle p^n \rangle$ *and* μ

All quantities are in atomic units.

	Moccia (1964)	Cade & Huo (1966)	Experiment	Ransil (1957)	Ransil (1957)	Ransil (1957)
Total energy	−100·0053	−100·0703	−100·527	−99·536	−99·491	−99·478
$\langle p^2 \rangle$	100·0096	100·02718	100·527	99·536	99·4910	99·478
Dipole moment	0·825	0·764	0·715	0·566	0·441	0·345

Table 5. *Results for* HCl *using* $\langle p^2 \rangle$, $\langle p^n \rangle$ *and* μ

All quantities are in atomic units.

	Moccia (1964)	Moccia (1967)	Cade & Huo (1966)	Experiment
Total energy	−458·8388	−460·05810	−460·1103	−462·81
$\langle p^2 \rangle$	458·838	460·05810	460·1103	462·81
Dipole moment	0·852	0·533	0·461	0·413

References

ALLAVENA, M. (1965). *Cahiers Phys.* **19**, 401.

BARTELL, L. S. & GAVIN, R. M.(1964). *J. Amer. Chem. Soc.* **86**, 349.

BONHAM, R. A. (1965). *J. Chem. Phys.* **43**, 1103, 1460, 1933, 1434.

BONHAM, R. A. (1967). Private communication.

BONHAM, R. A. & COX, H. L. JR (1967). *J. Chem. Phys.* **47**, 3504.

CADE, P. E. & HUO, W. M. (1966*a*). *Techn. Report. Chicago University.*

CADE, P. E. & HUO, W. M. (1966*b*). *J. Chem. Phys.* **45**, 1063.

COOPER, M. J., ROUX, M., CORNILLE, M. & TSAPLINE, B. (1968). *Phil. Mag.* **18**, 309.

CORNILLE, M. (1967*a*). Thèse de Doctorat, Paris.

CORNILLE, M. (1967*b*). 12*th Sagamore Conference AMRA*. Syracuse Univ. Press.

DUMOND, J. W. M. (1933). *Rev. mod. Phys.* **5**, 1.

Intensities and Structure Factors Conference Report, (1969). *Acta Cryst.* A**25**, Part 1.

KILBY, G. E. (1965). *Proc. Phys. Soc.* **86**, 1037.

MOCCIA, R. (1964). *J. Chem. Phys.* **40**, 2164.

MOCCIA, R. (1967). *Theor. Chim. Acta (Berlin)*, **8**, 8.

RANSIL, B. J. (1957). *Techn. Rep. Chicago Univ.* **9**.

ROUX, M., CORNILLE, M., TSAPLINE, B., ROUAULT, M. & TAVARD, C. (1967). *Acta Cryst.* **22**, 634.

SACHS, L. M. (1961). *Phys. Rev.* **24**, 1283.

TAVARD, C. (1966). *Cahiers Phys.* **195**, 397.

TAVARD, C. & ROUX, M. (1965). *C. R. Acad. Sci. Paris*, **260**, 4460, 4933.

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The Temperature Dependence of Lattice Vibrations in Gold from X-ray Diffraction Measurements[*]

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The measurements of the Debye characteristic temperatures Θ and mean-square vibrational amplitudes $\overline{u^2}$ of gold in the temperature range from 300 to 1150°K are presented. All data were determined from the X-ray integrated intensities of a gold single crystal. The room temperature value $\Theta = 188 \pm 4$°K was found to be larger than Θ-values reported in the literature from X-ray data. The new value of Θ can be compared, however, with $\Theta = 186 \pm 8$°K calculated from the specific heat value of $\Theta_D = 178 \pm 8$°K and Poisson's ratio for gold. The temperature dependence of Θ is in satisfactory agreement with the volume dependence given by Grüneisen's law.

The Debye characteristic temperature was determined because of an apparent anomaly in the curve of thermal vibrational amplitudes *versus* concentration resulting from the X-ray diffraction measurements. If the room temperature value of $\Theta = 177 \pm 5$°K for gold reported by Alexopoulos, Boskovits, Mourikis & Roilos [*Acta Cryst.* (1965) **19**, 349] were employed a sharp drop of the $\overline{u^2}$ *versus* concentration curve would result for silver–gold alloys of high gold content. However, if the value of $\Theta = 188 \pm 4$°K reported in this investigation together with the value of $\Theta = 190 \pm 4$°K for an Ag–94·9 atom per cent Au are plotted on the above curve a smooth curve of $\overline{u^2}$ *versus* gold composition is obtained.

Introduction

This X-ray diffraction study of lattice vibrations in gold resulted as a consequence of a detailed investigation of thermal vibrations in silver–gold alloys (Simerska, Synecek & Chessin, 1969). The mean-square vibrational amplitudes, $\overline{u^2}$, of atoms in these alloys have been found by us to be lower as compared with their values in pure metallic components. The deviations of the $\overline{u^2}$ values from the mean of silver and gold data were much larger than the negative excess thermodynamic properties of silver–gold alloys (White, Orr & Hultgren, 1957) would indicate for vibrational contributions. The data for silver-rich solid solutions were consistent with previous X-ray diffraction measurements on pure silver (Herbstein, 1961; Simerska, 1961; Alexopoulos, Boskovits, Mourikis & Roilos, 1965). On the other hand, the mean-square vibrational amplitudes of gold extrapolated from the $\overline{u^2}$-curve for gold-rich solid solutions was not consistent with previous measurements of Θ reported by Owen & Williams (1947) and Alexopoulos *et al.* (1965). Their low value of Θ would lead to an abrupt break of the concentration dependence of $\overline{u^2}$ at high gold contents as well as to unusually high vibrational entropy changes, much higher in comparison with the excess entropies reported by White *et al.* (1957) for silver–gold alloys.

This paper presents the measurements of X-ray

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