Acta Cryst. (1979). A**35**, 821–824

On the Phase Factor due to Antisymmetric Components of Density Distributions

By Makoto Sakata* and Jimpei Harada

Department of Applied Physics, Nagoya University, Nagoya, Japan

(*Received* 1 *February* 1979; *accepted* 23 *April* 1979)

Abstract

In the Fourier and the difference Fourier syntheses, the contribution of antisymmetric components of the density distribution to the phases of structure factors are usually ignored. From an analysis of the asymmetric thermal vibration of the Cu atom in a CuCl crystal by neutron diffraction, the effects of phase error are shown to appear in the following two forms on the difference Fourier map: (i) the peak heights due to antisymmetric density distribution are reduced considerably, and (ii) parasitic peaks appear on the map and modulate the difference density distribution.

Introduction

In an accurate structure analysis by X-ray diffraction, the antisymmetric density distributions of bonding or lone-pair electrons of atoms in a crystal are usually found on the difference Fourier maps. In the synthesis of the maps, the contributions of such low density electrons to the phase of the structure factor are ignored. The validity of this neglect, however, had not been considered until recently Coppens (1974) pointed out that the phase error due to low density electrons affects considerably the density distributions obtained by *X–N* difference Fourier synthesis. In principle, the scattering density map based on neutron diffraction data shows directly the thermal vibrations of atoms in the crystal, provided that the termination effect in Fourier synthesis is not serious. A similar phase error problem also must arise in this case if a centrosymmetric temperature factor is employed in the calculation of the phase factor for an atom whose thermal motion is not purely centrosymmetric.

In an analysis of accurate charge density distributions by diffraction methods, it is, therefore, important to investigate how far the effects of the phase errors which arise from the neglect of the antisymmetric component of density distribution extend on Fourier and difference Fourier maps. There are, however, some difficulties in examining this in detail with X-ray diffraction data, because the existence of these electrons can be found only by synthesizing a difference Fourier map in which the phase errors arising from the neglect of these low density electrons are certainly included. We examined this problem by the Fourier analysis of the antisymmetric thermal vibrations of CuCl in zinc blende type structure with neutron diffraction data obtained previously (Sakata, Hoshino & Harada, 1974). The ambiguity in estimating the phase factor, which arises from the antisymmetric component of thermal vibration, is not involved in this case because the antisymmetric thermal vibrations of atoms are well known to come from the third-order anharmonicities in their atomic potentials (Dawson, 1967). From this examination we found two kinds of effects due to errors of phase estimation on the difference Fourier maps. On the basis of the results obtained, the influence of phase error on accurate Fourier analysis is discussed.

Scattering density maps of CuCl

In the previous least-squares refinement of CuCl (Sakata, Hoshino & Harada, 1974) it was shown that antisymmetric anharmonic thermal vibrations exist for Cu atoms but not for Cl atoms. The centrosymmetric and antisymmetric components of the temperature factor for Cu are given as

$$T_{c,\mathrm{Cu}}(Q)=\exp\left[-\frac{k_BT}{2\alpha_{\mathrm{Cu}}}Q^2\right], \qquad (1)$$

and

$$T_{a,\mathrm{Cu}}(Q)=T_{c,\mathrm{Cu}}(Q)(k_BT)^2\frac{\beta_{\mathrm{Cu}}}{\alpha^3_{\mathrm{Cu}}}Q_XQ_YQ_Z, \qquad (2)$$

where α_{Cu} and β_{Cu} are the 'effective'† harmonic and third-order anharmonic coefficients of potential, and

---

* Present address: Materials Physics Division, AERE, Harwell, OX11 0RA, England.

† When we applied a difference Fourier method to CuCl, we found that a better difference Fourier map could be obtained if the harmonic potential parameter $\alpha_{\mathrm{Cl}} = 1{\cdot}35 \times 10^{-19}$ J Å^{-2} was used instead of the value $\alpha_{\mathrm{Cl}} = 1{\cdot}38 \times 10^{-19}$ J Å^{-2} previously obtained by a least-squares method. We, therefore, employed the new refined value in this paper.

0567-7394/79/050821-04$01.00

Q_X, Q_Y and Q_Z are the three components of scattering vector $\mathbf{Q}$. When we express the structure factor $F(\mathbf{G})$ as

$$F(\mathbf{G}) = A(\mathbf{G}) + iB(\mathbf{G}), \quad (3)$$

the following simple relations hold between the structure factors for the harmonic and anharmonic approximations:

$$A^a(\mathbf{G}) = A^h(\mathbf{G}) \quad (4)$$

$$B^a(\mathbf{G}) = B^h(\mathbf{G}) + \Delta B(\mathbf{G}), \quad (5)$$

where suffixes h and a stand for the harmonic and anharmonic approximations, respectively. $\Delta B(\mathbf{G})$ is the additional term coming from the existence of anharmonicity and is given by

$$\Delta B(\mathbf{G}) = 4b_{\rm Cu}T_{a,\rm Cu}(\mathbf{G}). \quad (6)$$

The effect of antisymmetric thermal vibrations of the Cu atom thus appears only in the imaginary part of the structure factors in this particular case.

The neutron scattering density maps of CuCl on the (110) plane were constructed for the two cases of the imaginary part in (5), that is $B^h(\mathbf{G})$ and $B^a(\mathbf{G})$. The area investigated corresponds to half of the (110) plane of one unit cell as shown in Fig. 1. The density maps obtained for harmonic approximation $\rho^h_{\rm obs}(\mathbf{r})$ and anharmonic approximation $\rho^a_{\rm obs}(\mathbf{r})$ are shown in Fig. 2(*a*) and (*b*), respectively, where 49 independent intensity data, up to the *hkl* reflection with $h^2 + k^2 + l^2 = 100$, were used.

It is noticed that the contours of the Cu atom are reproduced as anisotropic and elongated along the antibonding [111] directions from the equilibrium position in Fig. 2(*b*) where correct phase terms were used in the synthesis. This is what we can expect from the characteristics of antisymmetric thermal vibration of this atom due to third-order anharmonicity. Such anisotropy of the contours, however, is not clearly seen in Fig. 2(*a*) where harmonic approximations are used to estimate the phase terms. On the other hand, contours for Cl atoms are represented by full circles in Fig. 2(*a*) and (*b*). It indicates that isotropic harmonic approximation for the thermal vibration is good for this atom. The difference between the contours of the Cu atom in Fig. 2(*a*) and those in Fig. 2(*b*) can, thus, be understood as arising from the difference of the phase factors used. We may say from these facts that it would be fairly difficult to detect such anisotropic density distribution due to noncentrosymmetric thermal vibration,

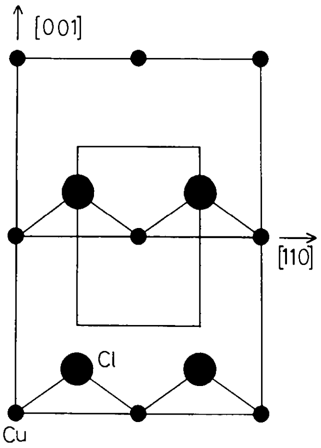


Fig. 1. The area of the (110) plane of CuCl on which Fourier and difference Fourier maps are synthesized.

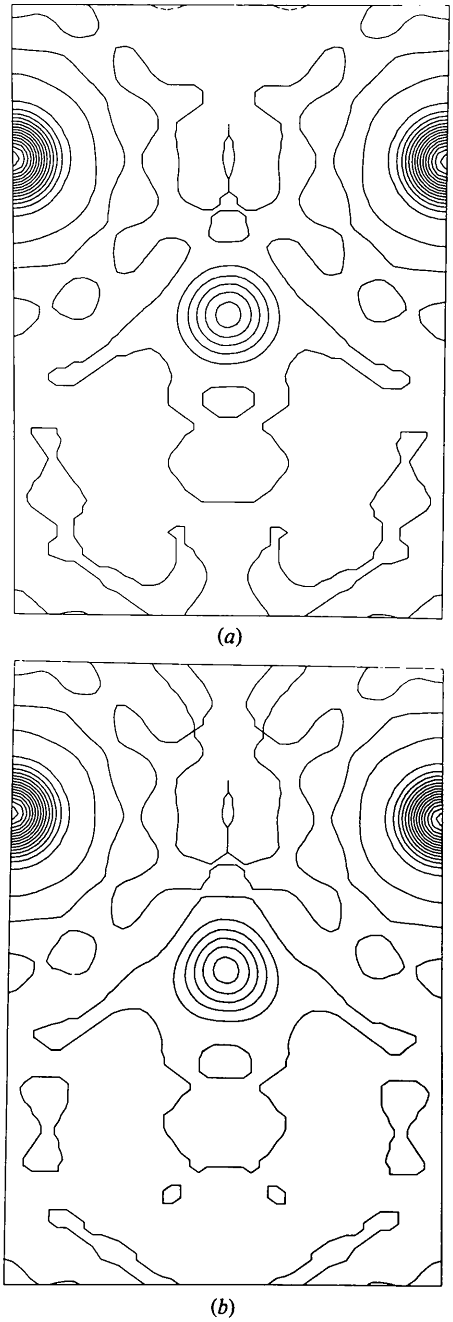


Fig. 2. The neutron scattering density distributions of CuCl in the (110) plane, (*a*) for $\rho^h_{\rm obs}(\mathbf{r})$ and (*b*) for $\rho^a_{\rm obs}(\mathbf{r})$.

if the phase factors are not correctly assigned. In other words, the use of proper phase factors in Fourier summation is essential in reproducing accurate density distribution.

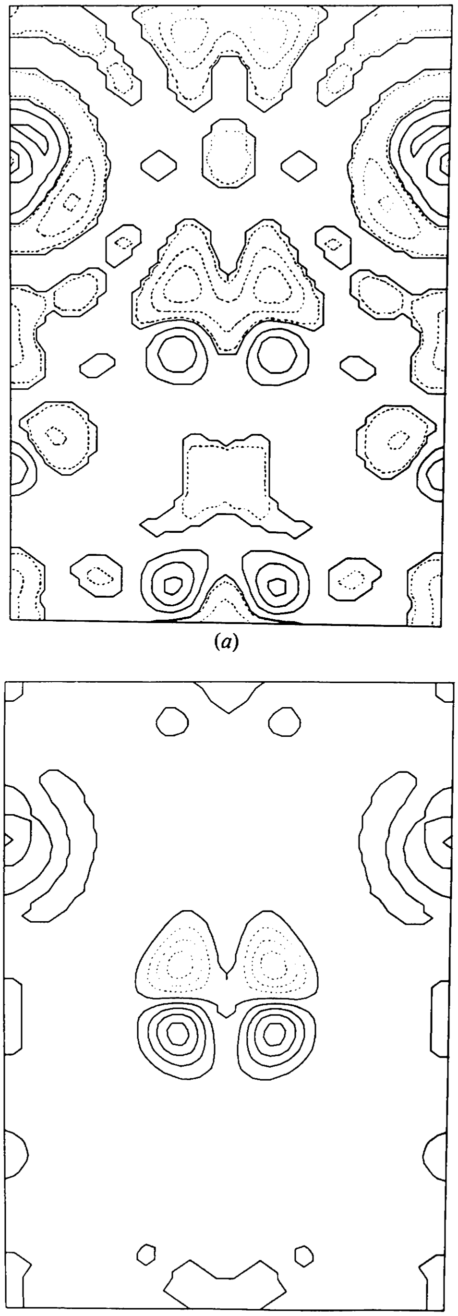
Difference Fourier maps of CuCl

In order to see the antisymmetric anharmonic thermal vibrations only, the contour maps of difference density $\Delta\rho(\mathbf{r})$ are constructed in which the contributions of centrosymmetric thermal vibrations are subtracted. They are shown in Fig. 3(*a*) and (*b*) for harmonic and anharmonic approximations, respectively. As expected, the peaks arising from the anharmonicity of the Cu atom are recognized in the central part of the figures; that is the two positive peaks at positions slightly off and along the two antibonding directions from the Cu atom position and the two negative peaks along the two bonding directions. The heights of these peaks are the same as the depths of the negative peaks in both Fig. 3(*a*) and (*b*). It is noticed that the heights of the positive peaks and the depths of the negative peaks in Fig. 3(*b*) for $\Delta\rho^a(\mathbf{r})$ are just twice as much as those in Fig. 3(*a*) for $\Delta\rho^h(\mathbf{r})$. In addition to such a quantitative difference between $\Delta\rho^a$ and $\Delta\rho^h$, the appearance of extra peaks is noticed in Fig. 3(*a*): two positive and two negative peaks are seen at the top and the bottom parts of the map of $\Delta\rho^h$, respectively, while such peaks are not observed in the map of $\Delta\rho^a$. It is easily shown that the extra peaks appear at positions as if Cu atoms were located also at ($\frac{1}{2}$,0,0) + f.c. Since such extra peaks disappear completely in Fig. 3(*b*), it is very clear that these extra peaks are parasitic ones arising from wrong estimates in the phase factors.

Estimation of error in phase factors

In the particular case of CuCl, the structure factors, $\mathbf{F}^a$, calculated on the basis of the antisymmetric anharmonic thermal vibrations can be regarded as representing very well the true structure factors. The $\mathbf{F}^h$ and the $\mathbf{F}^a$ were, then, compared in the complex space diagram for the two reflections with the largest differences, as shown in Fig. 4. The corrections to the structure factors $\mathbf{F}^h$ are noticed to be small and the errors in the phases of $\mathbf{F}^h$ from those of $\mathbf{F}^a$ are estimated to be about 5°. It should be emphasized that the contours representing antisymmetric thermal vibration are not well reproduced in the Fourier map, unless such small differences of the phase factors are taken into account.

In the case of the difference Fourier synthesis, however, the situation is much more severe than that in the case of the simple Fourier synthesis. Since it is difficult to estimate the phase factors for $\mathbf{F}^a$, approximate vectors $\Delta\mathbf{F}'[=(|\mathbf{F}^a| - |\mathbf{F}^h|) \times (\mathbf{F}^h/|\mathbf{F}^h|)]$ must be synthesized, instead of $\Delta\mathbf{F}(=\mathbf{F}^a - \mathbf{F}^h)$. Both the amplitudes $|\mathbf{F}^a| - |\mathbf{F}^h|$ and the phases $(\mathbf{F}^h/|\mathbf{F}^h|)$ are considerably different from the correct values, *i.e.* $|\mathbf{F}^a - \mathbf{F}^h|$ and $(\mathbf{F}^a - \mathbf{F}^h)/|\mathbf{F}^a - \mathbf{F}^h|$, respectively. In Table 1, $|\mathbf{F}^a - \mathbf{F}^h|$, $|\mathbf{F}^a| - |\mathbf{F}^h|$ and the differences of the phase angles $\Delta\theta$ (the angle between $\Delta\mathbf{F}'$ and $\Delta\mathbf{F}$) are listed for several reflections of CuCl. As expected


(*a*)

(*b*)

Fig. 3. The difference density distributions of CuCl in the (110) plane, (*a*) for $\Delta\rho^h(\mathbf{r})$ and (*b*) for $\Delta\rho^a(\mathbf{r})$.

$|\mathbf{F}^a| - |\mathbf{F}^h|$ are always smaller than the correct values $|\mathbf{F}^a - \mathbf{F}^h|$ but the differences of the phase angles $\Delta\theta$ are particularly large. We can, therefore, interpret the reduction of the peak heights and the appearance of the ghost peaks as due to wrong estimates of amplitudes and phase angles, respectively. This situation is exactly the same as the systematic error pointed out by Coppens (1974) for the case of *X–N* difference density distribution in noncentrosymmetric structures.

Table 1. *The phase errors for some typical reflections of* CuCl

h k l	$\lvert F^a - F^h \rvert$	$\lvert F^a \rvert - \lvert F^h \rvert$	$\Delta\theta$
1 1 1	0·202	−0·164	37°
3 1 1	0·456	0·383	33
3 3 3	2·254	2·039	26
5 5 5	1·743	−1·678	12
2 2 2	1·172	0·064	90
4 2 2	1·494	0·031	90
4 4 2	1·960	0·167	90
4 4 4	2·430	0·149	90
4 0 0	0·000	0·000	0

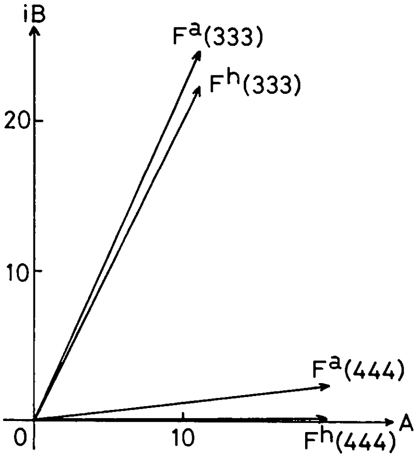


Fig. 4. The phase relation between $\mathbf{F}^a$ and $\mathbf{F}^h$.

Conclusions

From the present investigations of the antisymmetric thermal vibration of the Cu atom in CuCl, the following conclusions are obtained.

In order to reproduce accurately the density distribution for a noncentrosymmetric structure in the Fourier synthesis, the contribution to the phases of the structure factors should not be ignored, although they are estimated generally to be very small. In the difference Fourier map, the two sorts of modulations are received when the phases based on the centrosymmetric density distribution are utilized instead of the phases of the difference of the structure factors; that is (i) the heights of the peaks are reduced considerably and (ii) parasitic peaks may often appear and cause a disturbance on the map.

These conclusions are obtained with the very simple example of the thermal vibration in a CuCl crystal, but they can be extended to more general cases, such as the analysis of bonding and lone-pair electrons by X-ray diffraction. The FDP method proposed recently by Ito & Shibuya (1977) may be one way to estimate phase terms. It should be, however, kept in mind that the situation of X-ray analysis is much more complex than that in the present analysis of antisymmetric anharmonic thermal vibration, because a further difficulty is involved in separating out the effects of antisymmetric thermal vibration and those of bonding or lone-pair electrons when they exist. It is necessary to confirm by neutron diffraction whether the antisymmetric thermal vibration of atoms exist, before analyzing the electron density distribution on the basis of X-ray data alone.

The computation was performed on a FACOM230-60 computer of Nagoya University Computation Centre.

References

Coppens, P. (1974). *Acta Cryst.* B**30**, 255–261.
Dawson, B. (1967). *Proc. R. Soc. London, Ser. A*, **298**, 255–263.
Ito, T. & Shibuya, I. (1977). *Acta Cryst.* A**33**, 71–74.
Sakata, M., Hoshino, S. & Harada, J. (1974). *Acta Cryst.* A**30**, 655–661.