

Neutron Diffraction Study of Asymmetric Anharmonic Vibration of the Copper Atom in Cuprous Chloride

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Neutron diffraction measurements of CuCl with the zincblende structure were carried out at room temperature and the results examined on the basis of three possible structure models: (1) harmonic thermal vibration of atoms, (2) asymmetric anharmonic vibrations and (3) statistical disorder arrangement of the copper atom. It was found that the anharmonic model was the most plausible for the structure of CuCl. The final R value in the least-squares analysis was 0.037. The parameters in the effective one-atomic-potential fields for the zincblende structure

$$V_j(\mathbf{r}) = V_{0j} + \frac{1}{2}\alpha_j(u_1^2 + u_2^2 + u_3^2) + \beta_j u_1 u_2 u_3 + \dots$$

were obtained as $\alpha_{\text{Cu}} = 0.74 \pm 0.01$, $\alpha_{\text{Cl}} = 1.35 \pm 0.02 \times 10^{-12} \text{erg } \text{Å}^{-2}$, and $\beta_{\text{Cu}} = 1.15 \pm 0.66$, $\beta_{\text{Cl}} = 0.0 \pm 1.6 \times 10^{-12} \text{erg } \text{Å}^{-3}$. It is also shown that the temperature dependence of the Bragg reflexion observed from room temperature to 523°K can be explained very well with the use of the above parameters.

1. Introduction

It is well known that cuprous halides, CuCl, CuBr and CuI, undergo first-order phase transitions from the zincblende-type to the wurtzite-type structure. It is also known that these crystals show anomalously large ionic conductivities at high temperature.

In connexion with the interesting ionic properties, the structural investigations of the phase transition in these crystals have been carried out using powder samples of CuI and CuBr (Miyake, Hoshino & Takehana, 1952; Hoshino, 1952; Miyake & Hoshino, 1958). In these studies, an anomalous increase of a mean-square displacement $\langle u^2 \rangle$ for copper atoms with increasing temperature was found from the analysis of measurements of the temperature dependence of X-ray Bragg intensities. The value of $\langle u^2 \rangle^{1/2}$ for the copper

atom in cuprous iodide, for example, was reported to be as large as 0.9 Å at 415°C. Such anomalous thermal behaviour of these substances was discussed on the basis of the following three possible models;

Harmonic model: Vigorous isotropic thermal vibrations of copper atoms.

Anharmonic model: Asymmetric anharmonic thermal vibrations of copper atoms along the tetrahedral diagonals.†

Disordered model: Statistical disorder of the copper atom with moderate thermal vibration among four metastable positions which are displaced from the normal position along the tetrahedral diagonals.‡

The schematic illustration of these models is given in Fig. 1.

It was pointed out that the above three models give almost the same intensity effect, because they are alike in assuming extended distributions of metal atoms around the normal positions. But it was suggested that the anharmonic model might be the most plausible one, although further studies using single-crystal specimens would be necessary to determine the structure.

A similar intensity anomaly in the Bragg reflexions with temperature has been noticed by Willis (1963*a*, *b*) for the actinide oxides (UO₂ and ThO₂). These oxides were found to possess the fluorite structure, in which the positions of the oxygen atoms have the same tetrahedral surroundings as seen in the cuprous halides having the zincblende structure. It was shown that if a temperature-dependent oxygen shift was in-

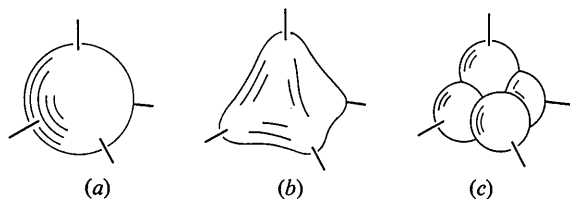


Fig. 1. The schematic models for thermal vibrations of copper atoms in cuprous halides, (a) harmonic thermal vibration, (b) asymmetric anharmonic vibration and (c) atoms located statistically at four displaced positions with moderate thermal vibration.

† This model was originally proposed by Matsubara (1952) to explain specific heat data for α -CuI.

‡ This is the model put forward first by Helmholtz (1935).

roduced, the disordered arrangements of the oxygen atoms fitted the observed data very well for a wide temperature range from room temperature to 1100°C. The model based on the assumption of asymmetric anharmonic vibrations of the oxygen atoms was also suggested by Willis (1963*b*) as another possible interpretation of the data.

Recently, Dawson, Hurley & Maslen (1967) have shown that these characteristic features in the diffraction data for UO₂ and also for CaF₂ could be interpreted in terms of the generalized formulation of the structure factor (Dawson, 1967) in which the effect of the asymmetric anharmonic vibration on the temperature factor was included on the basis of the effective one-atom-potential field approximation. This approach is extremely useful for estimating the anharmonicity in the thermal vibration without the complexity of rigorous treatments such as those of Maradudin & Flinn (1963) and Kashiwase (1965).

Further development of this treatment to the more general cases has been made by Willis (1969). With the general approach, the studies to investigate anharmonicity in the thermal vibration have been carried out by neutron diffraction for the several compounds of the fluorite-type structure, such as BaF₂ (Cooper, Rouse & Willis, 1968), SrF₂ and CaF₂ (Cooper & Rouse, 1971), and also for some with the diamond structure [Si and Ge by Keating, Nunes, Batterman & Hastings (1971), Niimura & Kimura (1972) and Trucano & Batterman (1972)] and zincblende type structure [ZnS and ZnTe by Cooper, Rouse & Fuess (1973)].

As a problem relating to the asymmetric anharmonicity in the thermal vibration in crystals it is interesting to re-examine the dynamical behaviour of the cuprous halides by neutron diffraction. Since a good large single crystal of CuCl was available, we collected three-dimensional neutron diffraction data from CuCl at room temperature and also investigated the variations of several Bragg intensities with the increase in temperature. The three models proposed previously were then examined in the light of the present data.

The purpose of this paper is to show that the anharmonic model obtained by least-squares analysis of the data at room temperature can explain the data for temperature dependence very well. By this analysis a fairly large component of asymmetric anharmonicity in the thermal vibration was found to exist for the Cu atom but not for the Cl atom.

2. Representations of the three models

In the kinematical approximation in diffraction theory, integrated Bragg intensity is proportional to the square of the structure factor $F(\mathbf{Q})$ which is represented as

$$F(\mathbf{Q}) = \sum_j b_j T_j(\mathbf{Q}) \exp(i\mathbf{Qr}_j), \quad (1)$$

where b_j is the scattering length, $T_j(\mathbf{Q})$ the temperature factor depending on the scattering vector \mathbf{Q} ($|\mathbf{Q}| =$

$4\pi \sin \theta/\lambda$) and \mathbf{r}_j the position vector from the origin of the unit cell to the equilibrium position of the j th atom. In general $T_j(\mathbf{Q})$ is given by ensemble average

$$T_j(\mathbf{Q}) = \langle \exp \{i(\mathbf{Q}\mathbf{u}_j)\} \rangle, \quad (2)$$

where \mathbf{u}_j is the displacement of the j th atom from its equilibrium position due to the lattice vibration. If the approximation of an effective one-particle potential is applied, the average of equation (2) can be replaced by

$$\langle \exp \{i(\mathbf{Q}\mathbf{u}_j)\} \rangle = \frac{\int \int \int \exp \{i(\mathbf{Q}\mathbf{u}_j)\} \exp \{-V_j/k_B T\} d\mathbf{u}_j}{\int \int \int \exp \{-V_j/k_B T\} d\mathbf{u}_j}, \quad (3)$$

where V_j is the effective one-particle-potential field seen by atom j and has a different form depending on the site symmetry of the position in the crystal, k_B is Boltzmann's constant and T the temperature.

The atoms in the unit cell of CuCl (zincblende structure of space group $F\bar{4}3m$) have coordinates

$$\begin{array}{ll} \text{Cu;} & 0, 0, 0; \text{ f.c.} \\ \text{Cl;} & \frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \text{ f.c.} \end{array} \quad (4)$$

Both the atoms are situated at positions with the non-centrosymmetric site symmetry $\bar{4}3m$ so that the effective potential fields for these atoms can be expressed as

$$V_j = V_{0j} + \frac{1}{2}\alpha_j(u_1^2 + u_2^2 + u_3^2) + \beta_j u_1 u_2 u_3 + (\text{higher-order terms}), \quad (5)$$

where u_1, u_2, u_3 are the components of \mathbf{u}_j . For this type of crystals, the Bragg reflexions which follow the extinction rule for the face-centred lattice are classified into three types;

$$(i) \quad h+k+l=4n \\ F(\mathbf{Q})F^*(\mathbf{Q}) = [b_{\text{Cu}}T_{\text{Cu}}(\mathbf{Q}) + b_{\text{Cl}}T_{\text{Cl}}(\mathbf{Q})]^2 \quad (6)$$

$$(ii) \quad h+k+l=4n+2 \\ F(\mathbf{Q})F^*(\mathbf{Q}) = [b_{\text{Cu}}T_{\text{Cu}}(\mathbf{Q}) - b_{\text{Cl}}T_{\text{Cl}}(\mathbf{Q})]^2 \quad (7)$$

$$(iii) \quad h+k+l=4n \pm 1 \\ F(\mathbf{Q})F^*(\mathbf{Q}) = [b_{\text{Cu}}T_{\text{Cu}}(\mathbf{Q})]^2 + [b_{\text{Cl}}T_{\text{Cl}}(\mathbf{Q})]^2. \quad (8)$$

2.1. Harmonic model

In this model, we assume that the potential is quadratic and isotropic with respect to \mathbf{u}_j . Thus, the integral (3) can be easily carried out and $T_j(\mathbf{Q})$ in equations (6), (7) and (8) is given by

$$T_j(\mathbf{Q}) = \exp \{ -B_j(\sin \theta/\lambda)^2 \}, \quad (9)$$

where B_j are the so-called temperature parameters and

related to the mean-square displacement $\langle u_j^2 \rangle$ by

$$B_j = 8\pi^2 \langle u_j^2 \rangle \quad (10)$$

or to the parameter α_j in equation (5) by

$$B_j = 8\pi^2 k_B T / \alpha_j. \quad (11)$$

If equation (9) is substituted into equations (6), (7) and (8) and the B_j left as unknown parameters, the number of parameters to be determined in this model is two apart from a scale factor, *i.e.* the two temperature parameters for the Cu and Cl atoms.

2.2. Anharmonic model

In this model, the third-order term $\beta_j u_1 u_2 u_3$ is taken into account in addition to the harmonic quadratic term. The integration of equation (3) was given by Willis (1969) in the case of cubic symmetry and the temperature factor $T_j(\mathbf{Q})$ was shown to become complex in the form

$$T_j(\mathbf{Q}) = T_{cj}(\mathbf{Q}) + iT_{aj}(\mathbf{Q}). \quad (12)$$

$T_{cj}(\mathbf{Q})$ and $T_{aj}(\mathbf{Q})$ represent centrosymmetric and antisymmetric components with respect to \mathbf{Q} and they are due to the centrosymmetric and antisymmetric terms of the potential fields in equation (5) respectively,

$$T_{cj}(\mathbf{Q}) = \exp \{ -(k_B T / 2\alpha_j) \mathbf{Q}^2 \} \quad (13)$$

$$T_{aj}(\mathbf{Q}) = T_{cj}(\mathbf{Q}) (k_B T)^2 (2\pi/a_0)^3 (\beta_j/\alpha_j^3) hkl. \quad (14)$$

By comparing equation (9) with equation (13), one can find that the centrosymmetric component $T_{cj}(\mathbf{Q})$ is identical to the harmonic temperature factor. Substitution of equation (12) into equations (6), (7) and (8) leads to additional contributions from $T_{aj}(\mathbf{Q})$ which represents the antisymmetric phenomena in diffraction data (Dawson, Hurley & Maslen, 1967). Thus, we have:

$$(i) \quad h+k+l=4n$$

$$F(\mathbf{Q})F^*(\mathbf{Q}) = [b_{Cu}T_{cCu}(\mathbf{Q}) + b_{Cl}T_{cCl}(\mathbf{Q})]^2 + [b_{Cu}T_{aCu}(\mathbf{Q}) + b_{Cl}T_{aCl}(\mathbf{Q})]^2 \quad (15)$$

$$(ii) \quad h+k+l=4n+2$$

$$F(\mathbf{Q})F^*(\mathbf{Q}) = [b_{Cu}T_{cCu}(\mathbf{Q}) - b_{Cl}T_{cCl}(\mathbf{Q})]^2 + [b_{Cu}T_{aCu}(\mathbf{Q}) - b_{Cl}T_{aCl}(\mathbf{Q})]^2 \quad (16)$$

$$(iii) \quad h+k+l=4n \pm 1$$

$$F(\mathbf{Q})F^*(\mathbf{Q}) = [b_{Cu}T_{cCu}(\mathbf{Q})]^2 + [b_{Cl}T_{cCl}(\mathbf{Q})]^2 \pm 2b_{Cu}b_{Cl}[T_{aCu}(\mathbf{Q})T_{cCl}(\mathbf{Q}) - T_{cCu}(\mathbf{Q})T_{aCl}(\mathbf{Q})] + [b_{Cu}T_{aCu}(\mathbf{Q})]^2 + [b_{Cl}T_{aCl}(\mathbf{Q})]^2. \quad (17)$$

In view of the fact that $T_{aj} \ll T_{cj}$, the effect of the anharmonicity on the Bragg intensity is particularly

enhanced for the reflexions of type (iii) to the first approximation, in which T_{aj}^2 terms are neglected. Miyake & Hoshino (1958) have suggested from their X-ray studies that the anisotropic anharmonic thermal vibration would be considerable only for the metal atoms. In the present anharmonic model, however, the anharmonicity in the Cl atom was also taken into account. Thus, the parameters to be determined in the analysis are two harmonic parameters α_{Cu}, α_{Cl} and two anharmonic ones β_{Cu}, β_{Cl} .

2.3. Disordered model

In this model, each copper atom is assumed to be statistically located with the same probability at four equivalent positions which are displaced in the tetrahedral directions from the normal position in the zincblende-type structure. That is, the coordinates of these four equivalent positions for the Cu atom, which is located at 0,0,0 in the normal zincblende structure, are as follows,

$$\text{Cu}; \bar{\delta}, \bar{\delta}, \bar{\delta}; \bar{\delta}, \delta, \delta; \delta, \bar{\delta}, \delta; \delta, \delta, \bar{\delta}$$

where δ is the coordinate representing the positions. Atomic coordinates of Cl atoms, however, are the same as those in (4). As for $T_j(\mathbf{Q})$, the isotropic harmonic temperature factors are assumed. The squares of structure factors are also classified into three types in this model:

$$(i) \quad h+k+l=4n$$

$$F(\mathbf{Q})F^*(\mathbf{Q}) = [b_{Cu}T_{cCu}(\mathbf{Q})C_h C_k C_l + b_{Cl}T_{cCl}(\mathbf{Q})]^2 + [b_{Cu}T_{cCu}(\mathbf{Q})S_h S_k S_l]^2 \quad (18)$$

$$(ii) \quad h+k+l=4n+2$$

$$F(\mathbf{Q})F^*(\mathbf{Q}) = [b_{Cu}T_{cCu}(\mathbf{Q})C_h C_k C_l - b_{Cl}T_{cCl}(\mathbf{Q})]^2 + [b_{Cu}T_{cCu}(\mathbf{Q})S_h S_k S_l]^2 \quad (19)$$

$$(iii) \quad h+k+l=4n \pm 1$$

$$F(\mathbf{Q})F^*(\mathbf{Q}) = [b_{Cu}T_{cCu}(\mathbf{Q})C_h C_k C_l]^2 + [b_{Cl}T_{cCl}(\mathbf{Q})]^2 \pm 2b_{Cu}b_{Cl}T_{cCu}(\mathbf{Q})T_{cCl}(\mathbf{Q})S_h S_k S_l + [b_{Cu}T_{cCu}(\mathbf{Q})S_h S_k S_l]^2. \quad (20)$$

In these equations

$$S_h = \sin(2\pi h\delta) \quad \text{and} \quad C_h = \cos(2\pi h\delta). \quad (21)$$

If an approximation,

$$\cos(2\pi h\delta) = 1 \quad \text{and} \quad \sin(2\pi h\delta) = 2\pi h\delta, \quad (22)$$

is justified by regarding δ as small quantity and δ^3 is replaced by $(k_B T)^2 \beta_j / (a_0 \alpha_j)^3$ in equation (14), the structure factor of this model becomes the same as that described for the anharmonic model except for the anharmonicity for Cl atom. Therefore, it should be noticed that the anharmonic model and the disordered model are not distinguishable if δ is small. The parameters involved in this model are B_{Cu} , B_{Cl} and δ .

3. Experimental

3.1. Measurement of the Bragg intensities

The single-crystal specimen of CuCl used in this study has a spherical shape with diameter of 7 mm. In the high-temperature measurement, the crystal was sealed into a fused quartz capsule to avoid oxidation. Integrated intensities of 46 independent Bragg reflexions at room temperature (25°C) were measured on the four-circle single-crystal neutron diffractometer of the Institute for Solid State Physics, the University of Tokyo, installed at JRR-3 reactor of Japan Atomic Energy Research Institute, using Cu(422) as the monochromator. The wavelength of the incident neutrons was 1.04 Å. The maximum available scattering angle of this diffractometer is 150°. In the measurements a step-by-step ω -scanning method was employed.

At least two equivalent reflexions (hkl and $\bar{h}\bar{k}\bar{l}$) were measured in order to estimate the accuracy of the present measurement. The errors among the equivalent reflexions were less than those due to counting statistics, which were less than about 5%, except for three very weak reflexions 842, 680 and 10,0,0. No anomalies were observed in the background scattering and background measurements were, therefore, made on both sides of the Bragg peaks.

3.2. Corrections

Absorption corrections for the observed intensities were made utilizing the analytical expression for the transmission factor for a spherical crystal given by Rouse & Cooper (1970).

The extinction effect was not particularly evident in the present crystal; this was deduced by comparing the observed intensities with those obtained from powder diffraction measurement.

Recently it has been emphasized that the observed data should be corrected for the contribution of thermal diffuse scattering (TDS) when the accurate determination of the temperature factor is the purpose of the study. TDS is known to produce sharp maxima under the Bragg reflexions and to contribute to the observed integrated intensities if the background is subtracted in the normal way. In the present study, TDS correction was made using a newly developed method by Harada & Sakata (1974) and Sakata & Harada (1974).

4. Experimental results

Fig. 2 (a), (b) and (c) shows plots of the observed structure factor, $|F(\text{obs})|$, against $\sin \theta/\lambda$ for the three types of reflexion. The structure factors for $h+k+l=4n$ and $4n \pm 1$ decrease monotonically with an increase of $\sin \theta/\lambda$, whereas for $h+k+l=4n+2$ they do not show such a monotonic decrease. With reference to equation (7) this anomalous behavior can be understood as a result of the very rapid decrease of $b_{\text{Cu}}T_{\text{Cu}}(\mathbf{Q})$ in comparison with $b_{\text{Cl}}T_{\text{Cl}}(\mathbf{Q})$. Since b_{Cl} is larger than b_{Cu} , the temperature parameter B_{Cu} should be larger than B_{Cl} .

Another point to be noticed in Fig. 2(c) is a difference of structure factors between the pairs of Bragg reflexions such as 333 and 511, 711 and 155 and so on, while this kind of difference is not evident in Fig. 2(a) and (b). They are depicted by arrows in the figure. This is what was expected from the intensity formula for the anharmonic model as well as for the disordered model described in §§2.2 and 2.3. It is clear that such a phenomenon cannot be explained by the harmonic model.

5. Least-squares refinement

The least-squares analysis of these three models was carried out on the FACOM 230-60 computer of Nagoya University Computation Centre using the non-linear least-squares *POWLS* program (Hamilton, 1964) which was modified so as to be available for the present single-crystal analysis. Using this program, parameters in the models were refined by minimizing a quantity

$$\sum_i w_i [F_i^2(\text{obs}) - F_i^2(\text{calc})], \quad (23)$$

where $F_i^2(\text{obs})$ is the square of the observed structure factor, $F_i^2(\text{calc})$ the corresponding computed value and w_i the weight given to the observation. Estimation of w_i was made on the basis of the statistical errors

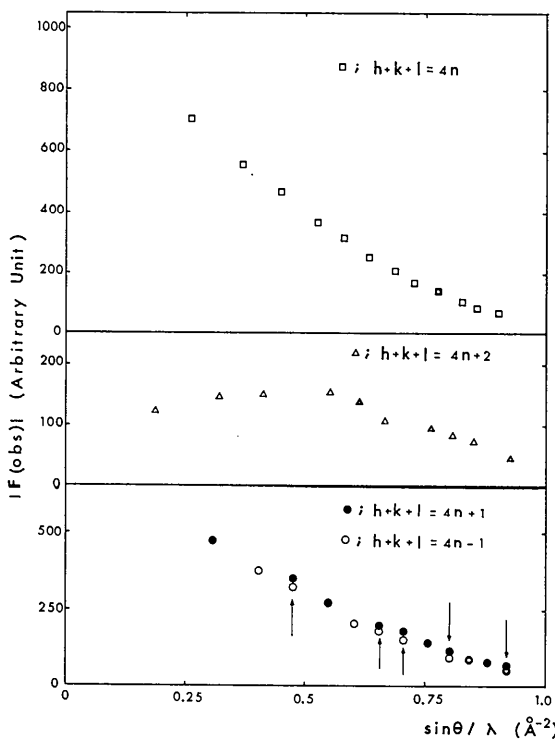


Fig. 2. Observed structure factors for the three types of reflexions as a function of $\sin \theta/\lambda$. \square , \triangle , \circ represent two reflexions with different indices.

in the measurements of integrated intensities, since they were larger than the discrepancies between two equivalent reflexions. The neutron scattering lengths used in the analysis are as follows (The Neutron Diffraction Commission, 1969):

$$b_{\text{Cu}} = 0.76 \times 10^{-12} \text{ cm}$$

and

$$b_{\text{Cl}} = 0.96 \times 10^{-12} \text{ cm}. \quad (24)$$

The results obtained from the analysis are listed in Table 1 for the three models. In the refinement of the anharmonic model, the anharmonic parameter β_{Cl} was found to have little effect on the R value, giving a very large standard deviation, while β_{Cu} was determined with the reasonable accuracy as listed in the Table. In order to clarify this situation a contour map giving equal R values was constructed in a space of the two parameters β_{Cu} and β_{Cl} , fixing other parameters at the values obtained from the least-squares analysis. The result is shown in Fig. 3. As seen in the Figure there is a deep minimum on the β_{Cu} axis, extending along the β_{Cl} axis, and a valley is formed in the map. The minimum position of the R value, however, is seen at

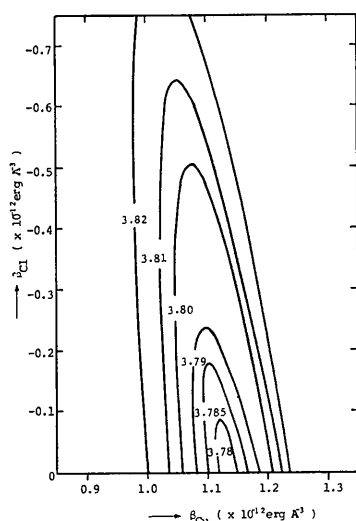


Fig. 3. Equi-contour map of R values in a space of the two parameters β_{Cu} and β_{Cl} . Numbers on the map represent R values as a percentage.

$\beta_{\text{Cl}} = 0$, $\beta_{\text{Cu}} = 1.14 \times 10^{-12} \text{ erg A}^{-3}$ which are in agreement with the least-squares results.

It is seen from Table 1 that the harmonic model is not fully successful in explaining the present neutron data at room temperature, as was predicted in the preliminary analysis described in §4. When the comparison is made between the other two models, however, it is difficult to conclude from the least-squares results alone which model, the anharmonic model or the disordered model, is suitable, although the R value for the anharmonic model is slightly lower than that for the disordered model.

For the anharmonic model, the temperature parameter for the Cu atom is about twice as large as that for the Cl atom in spite of the fact that the Cu atom is much heavier than the Cl atom. Such a big difference between the temperature parameters for the two kinds of atom does not exist for the disordered model. This indicates that the disordered model obtained is not such that the approximation given in §2.3 can be applied. In fact, the value of 0.024 obtained for δ cannot be regarded as a small quantity. Hence, the disordered model is essentially different from the anharmonic one.

For the further study of the thermal vibration of atoms, it is worth while investigating the temperature dependence of the intensities of Bragg reflexion.

6. Temperature dependence

The temperature dependence of the integrated intensities for 13 Bragg reflexions was measured from room temperature to 523°K. Some of the results are shown in Fig. 4. The calculated values for the anharmonic model are shown by the solid curves in the figure. The calculations for the disordered model were carried out by assuming that δ is temperature independent (dashed curves in Fig. 4). For the normalization between the calculation and the observation, the scale factor obtained in the least-squares analysis at room temperature was used. As seen from the figure, the anharmonic model gives a very good fit to the observations, but the disordered model with fixed δ does not. It is found, however, that if we introduce a temperature-dependent δ shift (δ is assumed to be proportional to T^m and m is chosen as ~ 0.8) the disordered model also gives a good agreement with observations (dotted curves in Fig. 4).

Table 1. The final values of parameters and R values obtained from the least-squares refinements for the three models

Parameters	Harmonic model ($R = 5.2\%$)	Anharmonic model ($R = 3.7\%$)	Disordered model ($R = 4.0\%$)
$B_{\text{Cu}}(\text{Å}^2)$	4.4 ± 0.08	4.4 ± 0.08	2.9 ± 0.15
B_{Cl}	2.4 ± 0.04	2.4 ± 0.04	2.3 ± 0.04
$\alpha_{\text{Cu}}(10^{-12} \text{ erg Å}^{-2})$	0.74 ± 0.01	0.74 ± 0.01	1.12 ± 0.06
α_{Cl}	1.35 ± 0.02	1.35 ± 0.02	1.41 ± 0.02
$\beta_{\text{Cu}}(10^{-12} \text{ erg Å}^{-3})$	—	1.15 ± 0.66	—
β_{Cl}	—	0.0 ± 1.60	—
δ	—	—	0.024 ± 0.0006

7. Discussion

It was shown from the present analysis of the integrated Bragg intensities of CuCl that the anharmonic model and the disordered model with the temperature-dependent δ shift gave almost the same results in explaining the observed neutron diffraction data. This means that the potentials around the Cu site based on these two structure models are very alike, as seen from Fig. 1. In other words, it can be said that there is no essential difference between these two atomic potentials. In explaining the temperature dependence of the diffraction data, however, the disordered model requires a further parameter, *i.e.* the temperature dependence of the δ shift, while it is possible for the anharmonic model to anticipate the situation at the elevated temperature from the parameters obtained at room temperature. This is exactly the same situation as that for UO_2 and CaF_2 discussed by Dawson, Hurley & Maslen (1967). Thus, it should be understood that the potential of the Cu atom given by the disordered model is rather one approximation in describing the antisymmetric anharmonic potential of the Cu atom in CuCl. The large ionic conductivity of this crystal at high temperature can thus be understood in terms of the shallow anisotropic potential field for metal atoms which is characteristic of the zincblende-type cuprous halides.

Previously, it has been shown by Miyake & Hoshino (1958) from their X-ray studies that the temperature dependence of the intensities of Bragg reflexions showed curious behaviour for CuBr and CuI, which suggests an unrealistically large thermal vibration of the Cu atom at high temperature (for example, B_{Cu} for CuI is as large as 20 at 415°C). They interpreted this as the result of the asymmetric anharmonic thermal vibration of the Cu atoms. In the present analysis for CuCl at room temperature, it was shown that the asymmetric anharmonicity must be taken into account in order to explain the data well in spite of the smaller B value of the Cu atom in comparison with that of CuI at high temperature. Therefore, there is no doubt that the asymmetric anharmonic thermal vibrations exist for CuI and CuBr at high temperature.

As seen in Table 1, the present analysis at room temperature shows that the B values in the anharmonic model are the same as those in the harmonic model. Therefore, the B values are not affected even if the additional anharmonic temperature parameters, β_j , are introduced in the least-squares refinement. This seems to suggest that the large B value of the Cu atom is not due to the neglect of cubic anharmonicity, but to the harmonicity itself. It could be concluded in general that the large B value indicates the necessity of the introduction of anharmonic terms in accurate structure analysis.

It is conceivable that the isotropic quartic anharmonicity of the Cu atoms may contribute to the large B value. However, because the temperature dependence

of the Bragg intensities can be well explained by introducing only third-order anharmonic terms in the potential field, we see that such a quartic anharmonicity of the Cu atom is not important as far as the present case of CuCl is concerned.

Very recently, the anharmonicity for the atomic potentials in the zincblende structure (ZnS and ZnTe) was studied by Cooper, Rouse & Fuess (1973). They pointed out that in this type of structure it was possible to determine only one effective anharmonic parameter defined by $\beta' = \beta_S - (\alpha_S/\alpha_{Zn})^3 \beta_{Zn}$, and that the anharmonic temperature parameters β_{Zn} and β_S could not be determined separately. In the present study of CuCl, however, β_{Cu} and β_{Cl} were determined independently. This is because in the analysis of ZnS and ZnTe the square terms of the antisymmetric temperature factor $[T_{aj}(\mathbf{Q})]$ were neglected, while in the present study of CuCl these terms were not neglected since the temperature parameters for CuCl were much larger than those for ZnS and ZnTe.

The present results suggest that a lattice-dynamical treatment of this type of crystal will be affected by the considerable contribution of cubic anharmonicity to the atomic potential. It seems interesting, therefore, to perform a lattice-dynamical study by paying particular attention to the line broadening and the peak shift in the phonon scattering cross section of the

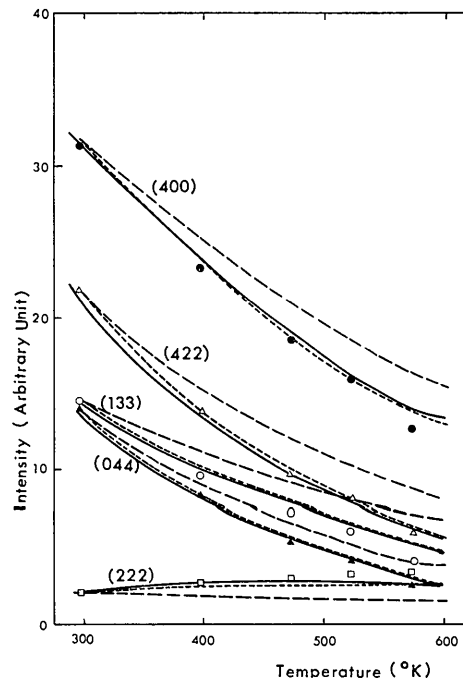


Fig. 4. Temperature dependence of integrated intensities for some Bragg reflexions. The solid curves represent the calculation for the anharmonic model, the dashed curves that for the disordered model with temperature-independent δ shift and the dotted curves that for the disordered model with temperature-dependent δ shift.

neutron inelastic scattering,* although no anomalies have been reported in the recent studies of the phonon dispersion relations for CuCl (Carabatos, Hennion, Kunc, Moussa & Schwab, 1971), CuBr (Prevot, Carabatos, Schwab, Hennion & Moussa, 1973) and CuI (Hennion, Moussa, Prevot, Carabatos & Schwab, 1972).

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* Very recently, the temperature dependence of the dispersion relation for CuBr was investigated and a distinct anharmonic effect even at room temperature was found (Hoshino, Fujii, Axe, Shirane & Harada, 1974).

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