is concluded that better estimates are obtained 
with anharmonic temperature factors if a signi-
ficance level in fitting the experimental data with the anharmonic model is obtained.

Anharmonic temperature factors were programmed 
for structures where the anharmonicity is due 
to librations of (rigid) molecules. Here only 
three anharmonic parameters are needed (three 
parameters of the (supposed) principal libra-
tions about a supposed origin). The anharmonic 
third order vibration tensors of the individual 
atoms concerned are all calculated from these 
three librational parameters. In refinements 
with the structures of thiophyridone and nitro-
ic acid (room temperature X-ray data) the 
weighted R values were significantly lowered 
(significance level < 0.005) with these three 
extra parameters. The values of the librational 
parameters obtained do not always agree with 
those obtained from a TLS analysis of the har-
monic vibration tensors. For the anharmonic 
model the distances between the mean positions 
were always shorter than those for the harmonic 
model. For thiophyridone the decreases were 
< 0.0012 Å, for nitric acid < 0.0060 Å. For 
urea, thiourea and p-dicyanobenzene at low tem-
perature, deformation densities were calculated 
with only harmonic and with the three addition-
al anharmonic parameters. Comparison of the 
maps shows that the effect of the anharmonic 
nature of the density distribution is small and 
rarely exceeds 0.1eÅ⁻³. For heavier atoms the 
effect may well be larger.

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06.5-2 X-RAY DIFFRACTION STUDY ON THE ANHARMONIC
THERMAL VIBRATIONS OF ATOMS IN ZnX(Y=S,Se,Te) 
T. Yamanka, Y. Tekkuchi and M. Tokonami, Faculty of 
Science, University of Tokyo, Tokyo, Japan

In relation to our previous study on the temperature 
dependence of the anharmonic thermal vibration of atoms 
by high temperature refinements of MgAl₂O₄ up to 1933 K 
(Yamanka et al. Acta Crystal. (1964) 20) an investigation 
between valence charge density and the anharmonicity has 
been elucidated by X-ray structure refinements of ZnX (X= 
S,Se,Te). In a monoclinic structure (R, m), Zn in 
ZnS at 0,0,0 and X on Zn at 1/4,1/4,1/4. 

Spherical samples of ZnS, ZnSe, ZnTe were prepared 
from grinding the crystals grown by the chemical transport 
method. X-ray diffraction intensity measurement at 20°C 
were carried out with a four-circle diffractometer using 
Mono-Ka radiation monochromated by pyrolytic graphite. 
Intensities measured in the range 0.12<sinθ<1.32 were 
correction for Lorentz and polarization effects and 
for absorption. This study was initiated by the refinement 
of the temperature factor T(θ) 
based on the harmonic oscilla-
tion model besides the isotro-
ic extinction parameter.

Difference Fourier syntheses 
based on the structure factors 
revised from the harmonic 
refinements of ZnS(R=1.74%), 
ZnSe(1.68%) and ZnTe(1.43%) 
revealed the residual electron 
density around atoms, as shown 
in Fig. 1. A tetrapod shape 
structure was found in the 
anharmonic thermal vibration 
in consideration of 3D Rush of 
Zn giving spherical electron 
densities around X(S,Se,Te) ascribe to both effects of 
the anharmonicity and valence electron density given by 
the pseudopotential calculation (Cohen, Science (1973) 
179, 1189). These features are more remarkable in ZnTe 
having a covalent bonding character stronger than those of 
ZnS or ZnSe.

Before the anharmonic refinement, the effect of thermal 
diffuse scattering (TDS) was taken into account for the 
diffraction intensity correction. A theoretical approach 
for the TDS correction derived from Mannisalo and Kurrits 
(J. Appl. Crystal. (1978) 11, 179) was employed. The evalua-
tion of the TDS correction factor in the equation of 
\[\log_{10} I_{\text{TDS}}(\theta) = c \] 
was conducted in terms of not only elastic constants of ZnX 
but also scanning modes and scattering vector defined by the 
"S matrix. The TDS correction resulted in the improvement of the reliability (R-factor) 
of the refinement.

For the anharmonic refinement, a cumulant expansion 
of (10) in the form \[T(\theta) = \exp \left[ \sum_{i=1}^{n} \right] \] 
The coefficients of the higher order anharmonic tensors 
of atoms in ZnTe are exceedingly larger than those in 
ZnS(Table 1), probably resulting form the difference 
in the nature of chemical bonding unlike the results of a 
neutron diffraction study by Cooper et al. (Acta Crystal. 
(1973) A29, 49).

After the anharmonic refinements, the 
residual electron densities 
mentioned disappeared in 
differences 
Fourier maps of ZnX.

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06.5-3 ANHARMONICITY OF CUBIC CaPbCl₃ NEAR 
THE PHASE TRANSITION By M. Sakata, H. Miyatake 
and J. Harada, Faculty of Engineering, Nagoya 
University, Chikusa-ku, Nagoya, Japan

CaPbCl₃ exhibits a cubic to tetragonal phase 
transition at 320K due to the condensation of 
M₃ phonons in perovskite structure. If a 
connection with this phase transition an anom-
alous temperature dependence of the tempera-
ture parameters of Cl ion has been known to 
exist in the cubic phase, besides a very big 
anisotropy B₁₃(Cl)<B₂₃(Cl). An analysis of 
this behavior has been made by the present au-
thors and others(Sakata et al. Acta Crystal. ( 
1980) A36, 99) in terms of one particle poten-
tial approximation including higher order an-
harmonisities. Harmonic potential model is, 
however, shown to be insufficient if potential 
parameter is regarded as temperature dependent 
Further least square refinements were then carried 
out for the following three potential 
models to Cl ion:

Model A: \[V_0 = V_0 + (1/2)\alpha U_0^2 \]

Model B: \[V_0 = V_0 + (1/2)\alpha U_0^2 + \beta U_0^4 \]

Model C: \[V_0 = V_0 + (1/2)\alpha U_0^2 + \beta U_0^4 + \gamma U_0^6 \]

with \(U_0^2 = U_0^2 + U_0^2 \) where \(\alpha,\beta,\gamma \) are potential 
parameters and \(U_0, U_0 \) etc are the displace-
ments of the ion on the plane. In the analy-
sis a direct numerical integration method was