ANHARMONIC THERMAL VIBRATIONS OF BE METAL FOUND IN THE MEM NUCLEAR DENSITY MAP

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ABSTRACT

A direct observation of the thermal vibrations of Be metal was performed by the Maximum Entropy Method (MEM) using neutron single crystal data. In the previous study, the existence of the small but significant cubic anharmonicity of Be has been found by the conventional least squares refinement of the observed structure factors [Larsen, Lehmann & Merisalo(1980) Acta Cryst. A36, 159-163]. In the present study, the same data were used for the MEM analysis, which are comprised of 48 reflections up to sinθ/λ=1.41Å⁻¹ in order to obtain the high resolution nuclear density of Be without using any thermal vibrational model. It was directly visible in the MEM map that not only the cubic terms but also quartic anharmonicities exist in the thermal vibrations of Be nuclei. In order to evaluate thermal parameters of Be including anharmonic terms quantitatively, the least squares refinement of the effective one-particle potential (OPP) parameters up to quartic term was carried out by using the MEM nuclear densities around atomic sites as the data set to be fitted. It was found that the present treatment has a great advantage to decide the most appropriate model of OPP by visually comparing the model with MEM density map. As a result of the least squares refinement, the anharmonic thermal parameters are obtained as α₃₃ = -0.340(5)[eV/Å³], α₄₀ = 0, β₂₀ = 9.89(1)[eV/Å⁴] and γ₀₀ = 0. No other anharmonic term was significant.

INTRODUCTION

The Maximum Entropy Method (MEM) yields a high resolution electron or nuclear density distribution from even a limited number of diffraction data without using a structural model. Since X-rays are diffracted by electrons, the MEM analysis provides us with the electron density distribution from X-ray diffraction data. Recently, the direct investigations of the real space electronic structure by the MEM have been performed for several substances¹-⁷) in order to reveal the bonding natures of the crystalline materials.
The present theory of MEM is based on Collins’s formalism for present analysis. In order to get good spatial resolution, one pixel becomes 144.772 x 10^{-14}[m/A^3]. It is, in principle, possible to study thermal vibrations of crystalline materials directly in the real space without using a model by the MEM.

A conventional approach to describe the atomic thermal vibrations is to determine the parameters of an assumed effective one-particle potential (OPP) which is expanded according to the atomic site symmetry. Thus, the corresponding atomic thermal smearing function (TSF) and the Debye-Waller factor (DWF) can be formalized in terms of the OPP model. In order to determine the potential parameters, X-ray or neutron structure factors are used to be fitted to the calculated values. By using the nuclear densities produced by the MEM, which should be equivalent to the TSF, the thermal parameters of OPP can be determined by fitting MEM densities to densities calculated from OPP. This approach provides an alternative for the determinations of thermal parameters. In this work, such an analysis was done for the first time in the case of Be. For this purpose, it has an essential advantage to use a neutron diffraction data, since the thermal vibrations are well defined for nuclei.

It is well known that the Be metal is one of the most hard materials. Larsen, Lehmann and Merisalo (1980) have determined mean-square atomic displacements and antisymmetric atomic vibrations in Be by the conventional analysis by using a neutron diffraction data collected at room temperature with short wave length neutrons, which showed only modest extinction effects. They claimed that Be has a small but significant cubic anharmonic component of the thermal motion even at room temperature, although it is a very hard material. The interest of this study is focused whether the MEM analysis could also reveal the existence of anharmonic thermal motion of Be, of which contribution is not so big.

THE MEM ANALYSIS

In the present study, the lower angle 4θ reflections up to sinθ/λ<1.41[A^{-1}] are used for MEM analysis. The details of the procedure to obtain MEM density distributions are given in Sakata and Sato (1990). The present theory of MEM is based on Collins’s formalism. The MEM analysis was carried out by the computer program called MEED. In the present analysis, the unit cell was divided into 120 X 120 X 120 pixels in order to get good spatial resolution. Hence one pixel became 0.019[A] X 0.019[A] X 0.030[A]. The total computing time was 727 seconds for 10892 iterations by FACOM VP2600 vector computer.

THE MEM NUCLEAR DENSITY OF BE

The MEM nuclear density distribution of Be in the (110) plane and in the basal plane of hcp structure are shown in Fig.1(a) and (b), respectively. In these figures, the contour lines are drawn in logarithmic scale. At a first glance, it is understood that the nuclear densities of MEM map is concentrated in a small region around the atomic sites. The nuclear density at the peak maxima is 144.772 X 10^{-14}[m/A^3]. In the interatomic region,
the nuclear density is very close to zero. These features are very reasonable as a nuclear density distribution.

For Be, the MEM electron density distribution based on the X-ray powder data has been reported by Takata, Kubota & Sakata (1993)\(^7\). In order to compare nuclear and electron densities of Be, the MEM electron density

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**Fig. 1.** The MEM nuclear density distributions of Be at room temperature. (a) and (b) show maps on the (110) and basal planes, respectively. The contour lines are on a logarithmic scale with 0.05 X 2\(^n\) (n = 0,1,2,......) (X10\(^{-14}\) m/A\(^3\)). The tetrahedral and octahedral holes are marked T and O, respectively.
distribution is shown in Fig. 2 for the same planes as in Fig. 1. The contour lines are drawn only for the lower density region in linear scale to show a modulation of electron clouds. The nuclear densities are confined in a very limited region around atomic site and the peak shape of the atomic site is very sharp, whereas the electron densities are distributed somewhat diffusively as an nature of electrons. Furthermore, the surplus electron densities localized around the tetrahedral voids are clearly visible in Fig. 2, which have been believed to be a kind of the bonding electrons of Be. The MEM nuclear density, on the other hand, has no such a surplus density in the tetrahedral voids. This is an experimental confirmation that the surplus electron densities in the tetrahedral voids are purely due to an electronic origin and represent a kind of chemical bonding of Be metal.

THE ANHARMONIC THERMAL VIBRATIONS OF BE METAL

The nuclear densities in Fig. 1 show characteristic features deformed from the oblate expected from harmonic thermal vibrations, which indicate the existence of anharmonicites of Be thermal vibrations. In the basal plane, somewhat triangular distribution of nuclear densities is clearly recognized. According to the OPP-model of the thermal vibrations, the characteristic feature of nuclear density due to 3rd order anharmonic motion ought to appear in the basal plane for the hcp structure. Due to 3rd order anharmonic term the effective OPP will be distorted antisymmetrically and the equipotential contours are deformed into a triangular shape (9), (12) in the same manner as in Fig. 1(b). The nuclear densities of basal plane must be influenced by 3rd order anharmonicity, which was discussed in the previous studies (9), (13).

From a study of 4th order anharmonic motion in Zn (14), it is known in what way the nuclear densities deform when the contribution of 4th order anharmonic term in the OPP-model is significant. In Fig. 1(a), the Be MEM nuclear density shows significant deviations from the elliptical shape of harmonic vibrations. This deformation can be interpreted due to a quartic anharmonic term of the OPP function.

DIRECT FITTING OF MEM NUCLEAR DENSITY BY THE OPP MODEL

The MEM nuclear density shows a direct picture of the atomic thermal displacements and is not impaired by a particular electronic structure caused by, e. g. chemical bonding in a crystal. The obtained MEM nuclear densities, therefore, could be regarded as the TSF which is also known as the probability density function (p.d.f.) of Be. In a simple case like symmetric harmonic vibration, the mean-square atomic displacement can be derived directly from the half width at half maximum of the p.d.f. (15). The present case is not as simple as harmonic but it should be possible to evaluate the potential parameters of OPP, which describe the thermal atomic displacements of the point nuclei, by analyzing the shape of the nuclear density distribution. In this study, the potential parameters of an effective OPP for Be is determined for the first time by 3-dimensional function fitting to the real space MEM nuclear densities. In the OPP model, the anharmonic terms up to 4th order are considered.

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Fig. 2. The MEM electron density distributions of Be at room temperature based on X-ray powder diffraction data. (a) and (b) are the (110) and basal planes, respectively. The contour lines are drawn from 0.0 to 2.0 with intervals of 0.05(e/A^3) on a linear scale. The tetrahedral and octahedral holes are marked T and O, respectively.
The OPP model used in the present work is written as

\[
V(u) = \beta_1(u_1^2 + u_2^2) + \beta_2u_3^2
\]

\[
+ \alpha_{33}(2u_3^2 - 3u_1u_2)
\]

\[
+ \alpha_{40}/8(3u_1^4 + 3u_2^4 + 8u_3^4 + 6u_1u_2^2 - 24u_3^2u_1 - 24u_3^2u_2)
\]

\[
+ \beta_{20}/2(-u_1^2 - u_2^2 + 2u_3^2 - 2u_1u_2 - 2u_3u_1 - 2u_3u_2)
\]

\[
+ \gamma_{00}(u_1^2 + u_2^2 + u_3^2 + 2u_1u_2 + 2u_3u_1 + 2u_3u_2)
\]

(1)

where \(u_1=<210>, u_2=<010>\) and \(u_3=<001>\) are the Cartesian components of the atomic displacement. In equation (1), \(\beta_1\) and \(\beta_2\) are the harmonic parameters, and \(\alpha_{ij}, \beta_{ij}\) and \(\gamma_{ij}\) are the anharmonic (third and fourth order) parameters. Then, the p.d.f., \(P(u_1,u_2,u_3)\), becomes

\[
P(u_1,u_2,u_3) = N \cdot \exp\{-V(u_1,u_2,u_3)/k_BT\}
\]

(2),

where \(N\) is the normalization factor.

In the conventional method, it is absolutely necessary to calculate the temperature factor by performing a Fourier transformation of p.d.f. to be included in the structure factor expression. In this process, an approximation is usually introduced such as Taylor expansion of the exponential term, \(\exp[-V(u)/k_BT]\). In the present method, the potential parameters can be determined by a direct least-squares fitting of the MEM densities with p.d.f. without using any approximation for OPP.

FITTING RESULTS OF THE MEM MAP

The least-squares fitting was carried out as increasing anharmonic terms. In the equation (1), there are three kinds of anharmonic parameters for the 4th order anharmonic vibration. First two terms, \(\alpha_{40}\) and \(\beta_{20}\), are for anisotropic anharmonic vibrations and last one, \(\gamma_{00}\), is for isotropic one. As for 4th order parameters, the potential model with individual 4th order parameters are examined as well as with all combinations of the three 4th order parameters. Whenever any 4th order parameter is refined, the harmonic and third order anharmonic parameters are always included in the potential model. The values of the cubic anharmonic parameters \(\alpha_{33}\) and R-factors, defined as \(\Sigma | \rho_{\text{MEM}}(u) - \rho_{\text{cal}}(u)|^2/\Sigma | \rho_{\text{MEM}}(u)|^2\) for the nuclear density, for each of the model did not differ significantly. The R-values were dropped to the order of 2% by introducing any 4th order anharmonic term.

It was very difficult to decide which 4th order anharmonic model is most appropriate only from R-factor. Any 4th order model did not change significantly the nuclear densities on basal plane. The nuclear densities on (110) plane shows considerable difference depending on the potential model. With the visual aid of (110) plane densities, it was concluded that the \(\beta_{20}\) parameter is the most significant and important among 4th order anharmonic parameters. The final values for all the parameters of the present refinement are listed in Table 1. The calculated nuclear density
from OPP model using the final parameters are shown in Fig. 3. In the figure, the MEM nuclear densities are well reproduced for both basal and (110) plane.

From Fig. 1 (b), it can be easily and visually concluded that due to cubic anharmonic term the potential is softened in the +[210] direction and hardened in the opposite direction. This is consistent with the previous result \(^9\) and similar to that for the other hcp metals, Mg\(^{16}\) and Zn\(^{12,17}\).

Fig. 3. The nuclear densities calculated with the final parameters obtained by the direct fitting with the effective OPP model up to 4th order anharmonic term for sections (a) (110) and (b) basal plane.
This corresponds to a negative sign of $a_{33}$ as listed in Table 2. The value of $a_{33}$, $-0.340(5)$, show slight different value from the previous result, $-1.0(3)$. This seemed to be caused by exclusion of fourth order term from the potential model in the previous analysis. Thus, the discrepancy between these two values is of no importance.

**Table 1** Final values of potential parameters for Be.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (eV/$\AA^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_1$</td>
<td>2.7902(5)</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>2.7763(8)</td>
</tr>
<tr>
<td>$a_{33}$</td>
<td>-0.340(5)</td>
</tr>
<tr>
<td>$a_{40}$</td>
<td>0</td>
</tr>
<tr>
<td>$\beta_{20}$</td>
<td>0</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>9.89(1)</td>
</tr>
</tbody>
</table>

$R(\rho^2) = 0.024$

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**REFERENCES**