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Effects of thermal vibrations on the valence-electron density and the forbidden x-ray reflections in C and Si

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The valence-electron density for diamond and silicon at finite, nonzero temperature has been calculated by using the first-principles pseudopotential method, where thermal effects are taken into account by averaging the valence-electron densities over all possible ion configurations at temperature T. The derived Debye-Waller factor for the valence electrons, $D(\mathbf{G})$, is given by a linear combination of the self-correlation and nearest-neighbor-pair correlation parameters of the ion displacement. The calculated values for Si(222) above room temperature are about 88% of the Debye-Waller factor for the core electrons, $D_C(\mathbf{G})$, in good agreement with experiment within experimental uncertainties.

I. INTRODUCTION

Recent progress of the x-ray diffraction technique (especially by using syncrotron radiation) has made it possible to measure weak forbidden reflections in diamond-type crystals precisely.[1-4] Since the forbidden reflection results from nonsphericality of the electron density, we can obtain valuable information on the bonding character in the crystal from these experiments.

For the electron density consisting of the core electrons that are tightly bound to the central nucleus, the temperature dependence of the Fourier components is well explained by the ordinary Debye-Waller factor for the core. However, it cannot be applied simply to the valence electrons, because they do not move with the central nucleus and deform their distribution according to the ion motion.

Yin and Cohen[5] calculated the valence-electron density for Si and Ge by using the first-principles pseudopotential method for a static lattice. However, they took the temperature effect into account by the ordinary Debye-Waller factor for the core. Using the same method, Van Camp, Van Doren and Devreese[6] calculated the pressure variation of 222 components of C and Si also in the static lattice, but they did not consider the temperature effect. The thermal reduction of the bond charge was calculated by Chelikowsky and Cohen,[7] using energy-dependent nonlocal pseudopotentials averaged over ion-core vibrations. Further, in order to take account of the bond thermal motion, they multiplied the calculated Fourier components by the Debye-Waller factor with one-half the ion-core value: the Debye-Waller factor for the core of Si used in their work[8] is too large when it is compared with the recent analyses,[9,10] as discussed in Ref. 11. The pseudopotentials used in their theory are empirical and are thought to be less suitable for calculating the valence-electron density than the more recently developed first-principles ones.

However, in order to correctly take into account the temperature effect, the valence-electron density should be averaged over all possible ion configurations at temperature T. As will be shown in this work, the temperature dependence is related to the nonlinear valence-electron-density deformation about the ion displacement mode at the Γ point. In the present paper we have calculated the valence-electron densities in C and Si at a finite, nonzero temperature based on the procedure mentioned above using the first-principles pseudopotential method. The obtained Debye-Waller factor for the valence electrons contains the self-correlation and nearest-neighbor-pair correlation parameters of the ion displacement, which have been calculated using a proper lattice-dynamical model. We will describe the formalism for the calculation of the valence-electron density at a finite, nonzero temperature in Sec. II and give the method of calculation and results in Sec. III. Our results will be discussed and compared with experimental data in Sec. IV.

II. FORMALISM

At a finite, nonzero temperature T the Fourier component of the valence-electron density with a reciprocal-lattice vector $\mathbf{G}$ can be written as

$$\tilde{\rho}_{v,T}(\mathbf{G})=\frac{1}{\Omega_c}\int_{\Omega_c}\langle\rho_v(\mathbf{r},\{\mathbf{u}_{n\nu}\})\rangle\exp(-i\mathbf{G}\cdot\mathbf{r})d\mathbf{r}\ . \quad (1)$$

where $\rho_v(\mathbf{r},\{\mathbf{u}_{n\nu}\})$ is the valence-electron density in the ion-core configuration given by $\{\mathbf{R}_n+\mathbf{r}_\nu+\mathbf{u}_{n\nu}\}$ where $\mathbf{R}_n$, $\mathbf{r}_\nu$, and $\mathbf{u}_{n\nu}$ denote, respectively, a lattice vector of translation, the atomic position, and the displacement of the νth ion in the nth primitive unit cell with volume Ω_c. The diamond structure has two ion positions in the primitive unit cell and they are specified by $\nu=0$ or 1 in the following. We assumed the adiabatic approximation which is a reasonable assumption because the thermal energy k_BT under ordinary experimental conditions is much smaller than the energy band gaps and the electron- to ion-mass ratio is very small. Therefore the valence-electron density is a function of ion displacements $\{\mathbf{u}_{n\nu}\}$. In Eq. (1) $\langle\ \rangle$ denotes a thermal average taken over the lattice vibrations at temperature T. In the following we will express the subscripts (n,ν) collectively as i for brevity.

We now expand the valence-electron density up to second order in $\{\mathbf{u}_i\}$ as

$$\begin{aligned}\rho_v(\mathbf{r},\{\mathbf{u}_i\})=\rho_{v0}(\mathbf{r})&+\sum_{\alpha}\sum_{i}\frac{\partial\rho_v}{\partial u_{i\alpha}}u_{i\alpha}\\&+\tfrac{1}{2}\sum_{\alpha,\beta}\sum_{i}\frac{\partial^2\rho_v}{\partial u_{i\alpha}\partial u_{i\beta}}u_{i\alpha}u_{i\beta}\\&+\sum_{\alpha,\beta}\sum_{(i,j)}\frac{\partial^2\rho_v}{\partial u_{i\alpha}\partial u_{j\beta}}u_{i\alpha}u_{j\beta}\ ,\end{aligned}\tag{2}$$

where $\rho_{v0}(\mathbf{r})$ is the valence-electron density in the static lattice and derivatives are taken at all $\mathbf{u}_i=\mathbf{0}$ and α and β denote the Cartesian components of $\mathbf{u}_i$. In the last term of Eq. (2) we take only the nearest-neighbor pairs because as the valence-electron density has large amplitudes near the bond center, the density is affected strongly by the motion of the ion pairs related to the bond. We neglected other second-order terms.

We assume that the self-correlation and nearest-neighbor-pair correlation of the ion displacement can be written as

$$\begin{aligned}&\langle u_{i\alpha}u_{i\beta}\rangle=B_1\delta_{\alpha\beta}\ \ \text{(same ion)}\ ,\\&\langle u_{i\alpha}u_{j\beta}\rangle=B_2\delta_{\alpha\beta}\ \ \text{(nearest-neighbor pair)}\ .\end{aligned}\tag{3}$$

The off-diagonal correlation of the nearest-neighbor pair is neglected. The neglect is justified for the special case when the valence-electron density consists of spherically symmetric clouds moving with the bond centers. Using Eqs. (2) and (3), we get the valence-electron density at temperature T as

$$\rho_{v,T}(\mathbf{r})=\rho_{v0}(\mathbf{r})+B_1\mathrm{Tr}\underline{A}(\mathbf{r})+B_2\mathrm{Tr}\underline{B}(\mathbf{r})\ ,\tag{4}$$

where we used the relation $\langle\mathbf{u}_i\rangle=0$ and Tr means the trace, which is taken over a 3×3 matrix in Cartesian coordinates and the elements of matrices $\underline{A}(\mathbf{r})$ and $\underline{B}(\mathbf{r})$ are given, respectively, as

$$A_{\alpha\beta}(\mathbf{r})=\tfrac{1}{2}\left[\sum_{\nu=0}\frac{\partial^2\rho_v}{\partial u_{i\alpha}\partial u_{i\beta}}+\sum_{\nu=1}\frac{\partial^2\rho_v}{\partial u_{i\alpha}\partial u_{i\beta}}\right]\ ,\tag{5}$$

$$B_{\alpha\beta}(\mathbf{r})=\sum_{(i,j)}\frac{\partial^2\rho_v}{\partial u_{i\alpha}\partial u_{j\beta}}\ .\tag{6}$$

From the Fourier transformation of Eq. (4), we can write

$$\tilde{\rho}_{v,T}(\mathbf{G})=\tilde{\rho}_{v0}(\mathbf{G})[1-D(\mathbf{G})]\sim\tilde{\rho}_{v0}(\mathbf{G})\exp[-D(\mathbf{G})]\ ,\tag{7}$$

$$D(\mathbf{G})=-B_1\frac{\mathrm{Tr}\underline{\tilde{A}}(\mathbf{G})}{\tilde{\rho}_{v0}(\mathbf{G})}-B_2\frac{\mathrm{Tr}\underline{\tilde{B}}(\mathbf{G})}{\tilde{\rho}_{v0}(\mathbf{G})}\ .\tag{8}$$

For a uniform translation $\mathbf{a}$ to every ion position, it is readily understood that the following relation holds:

$$\rho_v(\mathbf{r},\{\mathbf{u}_i=\mathbf{a}\})=\rho_v(\mathbf{r}-\mathbf{a},\{\mathbf{u}_i=\mathbf{0}\})\ .\tag{9}$$

Expanding both sides of Eq. (9) in the Taylor series of $\mathbf{a}$ and comparing the equal-power terms of $a_\alpha a_\beta$, we have

$$\tilde{A}_{\alpha\beta}(\mathbf{G})+\tilde{B}_{\alpha\beta}(\mathbf{G})=-\tfrac{1}{2}G_\alpha G_\beta\tilde{\rho}_{v0}(\mathbf{G})\ ,\tag{10}$$

where we use Eq. (2) and the underlying assumption.

If the valence-electron clouds around an ion move with it leaving the shape unchanged, $\tilde{B}_{\alpha\beta}(\mathbf{G})$ becomes zero and Eq. (8) is reduced to the ordinary Debye-Waller form of the core,

$$D_C(\mathbf{G})=\tfrac{1}{2}\mathbf{G}^2B_1\ .\tag{11}$$

On the other hand, if the valence-electron clouds move with the bond center, then

$$D_{BC}(\mathbf{G})=\tfrac{1}{4}\mathbf{G}^2B_1+\tfrac{1}{4}\mathbf{G}^2B_2\ .\tag{12}$$

When the Einstein model, i.e., $B_2=0$, is assumed for the lattice vibration, $D_{BC}(\mathbf{G})$ is reduced to one-half of $D_C(\mathbf{G})$, which is used in Ref. 7.

As is seen in the preceding discussions, the present method gives an improved method for the calculation of the temperature dependence of the valence-electron density and it does not include the uncertainty of whether the valence-electron clouds move with the center of the ion or with the bond center in contrast to previous treatments. This formalism can be applied to other simple crystals with some modifications.

III. METHOD AND CALCULATION

In calculating $\mathrm{Tr}\underline{\tilde{A}}(\mathbf{G})$ we adopt the following procedure. We calculate the valence-electron density in the lattice where the fcc sublattice of the $\nu=1$ ion is fixed and that of $\nu=0$ ion is displaced. There is no contribution from nearest-neighbor terms in Eq. (2) in this configuration because the nearest neighbor of the $\nu=0$ ion is the $\nu=1$ ion. Then we calculate second-order derivatives of the density with respect to the displacement of the $\nu=0$ ion and obtain $\mathrm{Tr}\underline{\tilde{A}}(\mathbf{G})$ by adding the contribution of the $\nu=1$ ion using inversion symmetry.

In practice, we have calculated the valence-electron densities in the following configurations:

$$\mathbf{u}_i=\begin{cases}(\Delta,0,0)&\text{for }\nu=1\text{ ions}\\(-\Delta,0,0)&\text{for }\nu=0\text{ ions}\ ,\end{cases}$$

where we take Δ to be the sets of values -0.10, -0.05, 0.00, 0.05, and 0.10 a.u. for C, and of -0.10, -0.05, 0.00, 0.05, and 0.10 Å for Si. In Ref. 12 similar configurations are used to calculate the anharmonic couplings at the Γ point.

The densities in the lattice where the $\nu=1$ ions are fixed and the $\nu=0$ ions are displaced can be obtained by coordinate transformation from them. Using these electron densities, we constructed the fourth-order polynomials of Δ which express the Fourier components of the densities as functions of Δ. From the second-order parts of the polynomials, we can get $\mathrm{Tr}\underline{\tilde{A}}(\mathbf{G})$. The quantity $\mathrm{Tr}\underline{\tilde{B}}(\mathbf{G})$ is obtained through Eq. (10). The lattice con-

TABLE I. Fourier components of $\tilde{\rho}_{v0}(\mathbf{G})$, $\mathrm{Tr}\underline{\tilde{A}}(\mathbf{G})$, and $\mathrm{Tr}\underline{\tilde{B}}(\mathbf{G})$ for three forbidden reflections.

Reflection	$\tilde{\rho}_{v0}(\mathbf{G})$ (Å^{-3})	$\mathrm{Tr}\underline{\tilde{A}}(\mathbf{G})$ (Å^{-5})	$\mathrm{Tr}\underline{\tilde{B}}(\mathbf{G})$ (Å^{-5})
		Diamond	
222	1.977×10^{-2}	-2.656×10^{-1}	-1.025×10^{-1}
442	-1.411×10^{-3}	5.475×10^{-2}	2.404×10^{-2}
622	-4.858×10^{-4}	2.885×10^{-2}	4.307×10^{-3}
		Silicon	
222	8.854×10^{-3}	-5.667×10^{-2}	-1.444×10^{-2}
442	-6.769×10^{-4}	1.832×10^{-2}	-2.010×10^{-3}
622	-1.745×10^{-4}	7.386×10^{-3}	-2.225×10^{-3}

stants of the cubic unit cell are taken to be 6.7403 a.u. for C and 10.2625 a.u. for Si.

In calculating the valence-electron densities, we used the first-principles pseudopotential method with the Bachelet-Hamman-Schlüter potential[13,14] in the local-density approximation scheme with the Wigner correlation energy. For the **k**-space integration over the Brillouin zone we adopted the special point technique[15] with two points $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$ and included 350 and 348 plane waves[16] for each **k** point. The number of the waves used to expand the electron density is 1989. The calculated values of $\tilde{\rho}_{v0}(\mathbf{G})$, $\mathrm{Tr}\underline{\tilde{A}}(\mathbf{G})$, and $\mathrm{Tr}\underline{\tilde{B}}(\mathbf{G})$ for the forbidden reflections of (222), (442), and (622) for C and Si are tabulated in Table I.

Due to the cubic symmetry of the diamond-type lattice the self- and nearest-neighbor-pair correlations of ion displacements are written as

$$\langle u_{n0\alpha}u_{n0\beta}\rangle=\langle u_{n1\alpha}u_{n1\beta}\rangle=B_1\delta_{\alpha\beta}\,,$$
$$\langle u_{n0\alpha}u_{n1\beta}\rangle=\begin{bmatrix}B_2 & C & C\\ C & B_2 & C\\ C & C & B_2\end{bmatrix}, \tag{13}$$

where the subscripts 0 and 1 denote the fcc sublattice to which the ions belong. The correlation parameters B_1, B_2, and C have been calculated by using the model potential given by Goldammer *et al.*[17] In the calculation we neglected the temperature variations of the lattice constants and force parameters and used the special point scheme with 2992 points: we checked the results by comparing them with those calculated with 408 points. The convergence is satisfactory. The calculated values of B_1, B_2, and C are tabulated in Table II as functions of temperature. We confirmed that our values of B_1 are in good agreement with those found in recent experimental analyses[9,10] and the other model calculations discussed in Ref. 11.

TABLE II. Calculated self-correlation and nearest-neighbor-pair correlation parameters of ion displacement in units of 10^{-2} Å^2. The number of used special points is 2992.

T (K)	B_1	B_2	C
		Diamond	
0	0.1630	0.026 67	0.006 82
300	0.1862	0.044 93	0.008 37
500	0.2278	0.069 33	0.012 10
700	0.2804	0.095 70	0.016 49
1000	0.3688	0.136 10	0.023 34
		Silicon	
0	0.2337	0.049 04	0.025 54
300	0.6060	0.252 24	0.090 07
500	0.9621	0.419 64	0.149 61
700	1.3277	0.587 37	0.209 37
1000	1.8819	0.839 05	0.299 06

IV. RESULTS AND DISCUSSION

There are some uncertainties regarding the values of the Debye-Waller factor for the valence electron as was mentioned in several works.[3,7] From a simple consideration that the valence-electron clouds are localized near the bond center and follow its motion with their shapes unchanged, $D(\mathbf{G})$ is estimated to be $\frac{1}{2}D_C(\mathbf{G})$, assuming the Einstein model for lattice vibrations.[7] However, in reality, the valence electrons are not so much tightly bound to the bond center as are the core electrons to the central nucleus and so they redistribute accordingly as the ions move and therefore these effects cannot be included in such a simple model. In Table III we tabulated the values of the ratio $D(\mathbf{G})/D_C(\mathbf{G})$ for the forbidden reflections. In Table IV we tabulated the ratios of $\tilde{\rho}_{v,T}(\mathbf{G})$ at $T=1000$ K to $\tilde{\rho}_{v,T}(\mathbf{G})$ at $T=300$ K for the reflections. They are calculated by the last expression in Eq. (7). In Table V we tabulated $F^{\mathrm{bond}}(\mathbf{G})$ in the static lattice. Note that all the values in this section are taken in the cubic unit cell with eight atoms. For Si(222), $D(\mathbf{G})$ above room temperature is about 88% of $D_C(\mathbf{G})$. Though it is generally believed that $\frac{1}{2}D_C(\mathbf{G})<D(\mathbf{G})<D_C(\mathbf{G})$,[3] our results show that it is not the case for higher-order reflections of Si and that the ratio $D(\mathbf{G})/D_C(\mathbf{G})$ varies strongly with **G**.

In the above calculation, we did not consider the variations of $\tilde{\rho}_{v0}(\mathbf{G})$ by thermal expansion. We estimated this effect to be negligible using the thermal-expansion coefficients and the variation of $\tilde{\rho}_{v0}(\mathbf{G})$ due to volume changes given in Ref. 6.

From the experimental results presented in Table II of Ref. 1, we estimated the ratio of $\tilde{\rho}_{v,T}(\mathbf{G})$ at $T=1000$ K to $\tilde{\rho}_{v,T}(\mathbf{G})$ at $T=300$ K, of Si(222) to be $(90.2\pm0.9)\%$. Our

TABLE III. Temperature dependence of the ratio $D(\mathbf{G})/D_C(\mathbf{G})$ for three forbidden reflections. The values are given in %.

	222		442		622	
T (K)	C	Si	C	Si	C	Si
0	76.7	84.0	74.5	109.7	89.1	134.6
300	78.9	88.1	76.8	107.2	90.1	125.7
500	80.6	88.6	78.8	107.0	90.9	124.8
700	81.7	88.7	79.9	106.9	91.4	124.6
1000	82.4	88.8	80.7	106.8	91.8	124.4

TABLE IV. The ratio of the Fourier components of the valence-electron density at $T=1000$ K to that at $T=300$ K for three forbidden reflections. D_C means the Debye-Waller case, and D_{BC} means the case in which the valence-electron density consists of the density moving with the bond center and leaving its shape unchanged. The values are given in %.

Reflection	This work	D_C case	D_{BC} case	This work	D_C case	D_{BC} case
		Diamond			Silicon	
222	97.12	96.66	97.49	91.28	90.26	92.79
442	91.73	90.32	92.65	72.04	73.53	79.90
622	89.01	88.30	91.09	62.85	68.68	76.01

TABLE V. Comparison of the theoretical values of F^{bond} per cubic unit cell with the experimental ones at room temperature. Parentheses denote the static-lattice values.

	This work		Van Camp[a]	Expt.
$F_{\mathrm{C}}^{\mathrm{bond}}(222)$	0.872(0.897)		(0.896)	1.152[b]
$F_{\mathrm{C}}^{\mathrm{bond}}(442)$	−0.0591(−0.0640)		(−0.0654)	
$F_{\mathrm{C}}^{\mathrm{bond}}(622)$	−0.0196(−0.0220)		(−0.0220)	
	This work	Yin and Cohen[c]	Van Camp[a]	Expt.
$F_{\mathrm{Si}}^{\mathrm{bond}}(222)$	1.36(1.42)	1.36	(1.38)	1.35[d] 1.46[e]
$F_{\mathrm{Si}}^{\mathrm{bond}}(442)$	−0.0927(−0.1084)	−0.084	(−0.1034)	−0.0635[f]
$F_{\mathrm{Si}}^{\mathrm{bond}}(622)$	−0.0223(−0.0279)	−0.020	(−0.0273)	−0.0046[f]

[a] Reference 12.
[b] Reference 19.
[c] Reference 11.
[d] Reference 20.
[e] Reference 21.
[f] Reference 4.

result, 91.28%, is in agreement with the experimental value. We note that the reported experimental values for C(222) (Ref. 18) have errors that are too large to get a correct answer.

In order to look into the effects of the motion of the ion center and the bond center separately, we write Eq. (4) as

$$\begin{aligned}\rho_{v,T}(\mathbf{r}) &= \rho_{v0}(\mathbf{r}) + \sum_{\alpha,\beta}[A_{\alpha\beta}(\mathbf{r}) - B_{\alpha\beta}(\mathbf{r})]\langle u_{i\alpha}u_{i\beta}\rangle \\ &\quad + \sum_{\alpha,\beta} 2B_{\alpha\beta}(\mathbf{r})\left\langle \frac{u_{i\alpha}+u_{j\alpha}}{2}\,\frac{u_{i\beta}+u_{j\beta}}{2}\right\rangle \\ &= \rho_{v0}(\mathbf{r}) + B_1\mathrm{Tr}[\underline{\boldsymbol{A}}(\mathbf{r}) - \underline{\boldsymbol{B}}(\mathbf{r})] \\ &\quad + \frac{B_1+B_2}{2}2\mathrm{Tr}\underline{\boldsymbol{B}}(\mathbf{r})\;, \qquad (14)\end{aligned}$$

where we neglected the off-diagonal terms in the pair correlation. The last two terms in Eq. (14), which are plotted in Fig. 1, represent the density changes due to the motion of the ion center and the bond center, respectively. The temperature dependence of the valence-electron density at the bond center is affected not by the thermal motion of the ion center but that of the bond center. In C, $B_1\mathrm{Tr}[\underline{\boldsymbol{A}}(\mathbf{r}) - \underline{\boldsymbol{B}}(\mathbf{r})]$ near ions is fairly symmetric with respect to the ion center compared with that in Si. If we assume that the valence-electron density is expressed by the superposition of the part moving with the ion center and that moving with the bond center, this suggests that the former has a fairly spherically symmetric profile in C, but not in Si. The decomposition of the valence-electron density into two parts is plotted in Fig. 2 and the method is explained in the Appendix. For (222) reflections, the ratio $\mathrm{Tr}[\tilde{\underline{\boldsymbol{A}}}(\mathbf{G}) - \tilde{\underline{\boldsymbol{B}}}(\mathbf{G})]$ to $2\mathrm{Tr}\tilde{\underline{\boldsymbol{B}}}(\mathbf{G})$ is 44:56 for C and 59:41 for Si. For C the contribution due to the part moving with the ion core is smaller than that with the bond center, but not for Si. This is consistent with the picture stated above.

If we take $\mathrm{Tr}\underline{\boldsymbol{B}}(\mathbf{r}) = 0$ in Eq. (10), we can see that Eq. (8) reduces to the ordinary $D_C(\mathbf{G})$. As is shown in Fig. 1, the thermal change of the valence electron described by $D_C(\mathbf{G})$ leads to a large error at the bond center, because $\mathrm{Tr}\underline{\boldsymbol{B}}(\mathbf{r})$ has a large value at the bond center. We think that we can observe the difference through the (222) reflection by the more precise measurements.

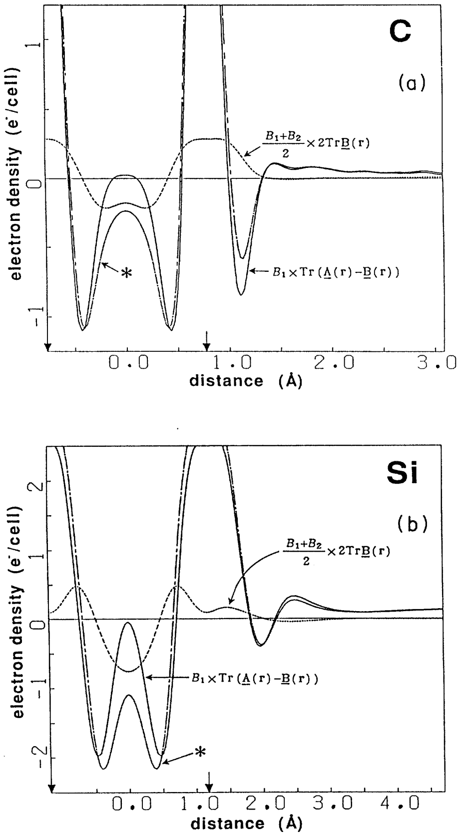

FIG. 1. $B_1\mathrm{Tr}[\underline{\boldsymbol{A}}(\mathbf{r}) - \underline{\boldsymbol{B}}(\mathbf{r})]$ and $\frac{1}{2}(B_1+B_2)\times 2\mathrm{Tr}\underline{\boldsymbol{B}}(\mathbf{r})$ at 1000 K along the [111] direction. For comparison, we plot the valence-electron density change for the case in which its temperature dependence is affected by the ordinary Debye-Waller factor for the core $D_C(\mathbf{G})$, which is denoted by *. Points indicated by arrows on the horizontal axis denote ion equilibrium positions.

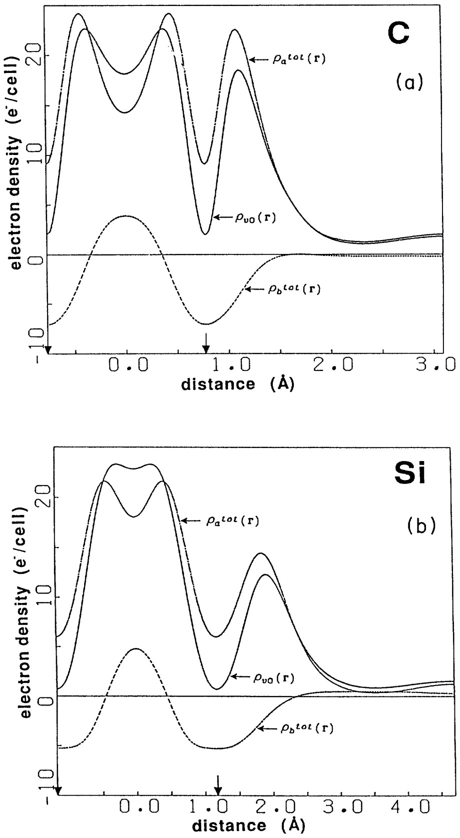

FIG. 2. Total valence-electron density $\rho_{v0}(\mathbf{r})$ and its decomposition to the part moving with the ion center $\rho_a^{\mathrm{tot}}(\mathbf{r})$ and that with the bond center $\rho_b^{\mathrm{tot}}(\mathbf{r})$ along the [111] direction. The method of decomposition is explained in the Appendix. Points indicated by arrows on the horizontal axis denote ion equilibrium positions.

V. SUMMARY

We have given a formalism to calculate the valence-electron density at a finite, nonzero temperature. This method is more reliable than the previous theories and is easily applied to other simple crystals. For the Si(222) reflection, the calculated values of the Debye-Waller factor for the valence electrons are nearly equal to that for the core. This is in agreement with reported experimental results. However, the calculated valence-electron densities at the bond center are small compared with the case using the Debye-Waller factor for the core. This will be proved experimentally by precise measurements of (222) reflections.

APPENDIX

We try to decompose the valence-electron density to the part moving with the ion center and that moving with the bond center. We assume that the valence-electron density as a function of $\mathbf{u}_i$ can be decomposed into the part moving with the ion center and the part moving with the bond center. That is,

$$\rho_v(\mathbf{r},\{\mathbf{u}_i\})=\sum_i \rho_{a,i}(\mathbf{r}-\mathbf{R}_i-\mathbf{u}_i) + \sum_{(i,j)} \rho_{b,(i,j)}(\mathbf{r}-\mathbf{R}_{ij}-(\mathbf{u}_i+\mathbf{u}_j)/2) \ , \tag{A1}$$

where $\mathbf{R}_{ij}$ means the equilibrium position of the bond center specified by (i,j). We define $\rho_a^{\mathrm{tot}}(\mathbf{r})$ and $\rho_b^{\mathrm{tot}}(\mathbf{r})$ as

$$\begin{aligned} \rho_a^{\mathrm{tot}}(\mathbf{r}) &= \sum_i \rho_{a,i}(\mathbf{r}-\mathbf{R}_i) \ , \\ \rho_b^{\mathrm{tot}}(\mathbf{r}) &= \sum_{(i,j)} \rho_{b,(i,j)}(\mathbf{r}-\mathbf{R}_{ij}) \ . \end{aligned} \tag{A2}$$

Then using $\tilde{\rho}_{v0}(\mathbf{G})=\tilde{\rho}_a^{\mathrm{tot}}(\mathbf{G})+\tilde{\rho}_b^{\mathrm{tot}}(\mathbf{G})$ and the relation about the second-order derivatives with respect to $\mathbf{u}_i$ [$\mathrm{Tr}\underline{\tilde{A}}(\mathbf{G})$ can be expressed by $\tilde{\rho}_a^{\mathrm{tot}}(\mathbf{G})$ and $\tilde{\rho}_b^{\mathrm{tot}}(\mathbf{G})$], we can obtain

$$\begin{aligned} \tilde{\rho}_a^{\mathrm{tot}}(\mathbf{G}) &= -\tilde{\rho}_{v0}(\mathbf{G})-\frac{4}{\mathbf{G}^2}\mathrm{Tr}\underline{\tilde{A}}(\mathbf{G}) \ , \\ \tilde{\rho}_b^{\mathrm{tot}}(\mathbf{G}) &= 2\tilde{\rho}_{v0}(\mathbf{G})+\frac{4}{\mathbf{G}^2}\mathrm{Tr}\underline{\tilde{A}}(\mathbf{G}) \ . \end{aligned} \tag{A3}$$

They are plotted in Fig. 2 [the $\mathbf{G}=\mathbf{0}$ component cannot be determined uniquely in this method and set as $\tilde{\rho}_b^{\mathrm{tot}}(0)=0$]. This decomposition corresponds to the physical picture of Eq. (14). The term proportional to B_1 in Eq. (14) is the contribution of ρ_a and the term proportional to $(B_1+B_2)/2$ is the contribution of ρ_b. The density $\rho_b^{\mathrm{tot}}(\mathbf{r})$ has a reasonable profile that has a peak at the bond center. [Note that holes near an ion position are a superposition of four equivalent contributions of $\rho_{b,(i,j)}(\mathbf{r})$]. We can see that the shape of the part moving with the ion core is fairly different between C and Si as discussed in Sec. IV.

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