Towards an *ab initio* theory for the temperature dependence of electric-field gradient in solids: application to hexagonal lattices of Zn and Cd

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Based on *ab initio* band structure calculations we formulate a general theoretical method for description of the temperature dependence of electric field gradient in solids. The method employs a procedure of averaging multipole electron density component \((L \neq 0)\) inside a sphere vibrating with the nucleus at its center. As a result of averaging each Fourier component \((K \neq 0)\) on the sphere is reduced by the square root of the Debye-Waller factor \([\exp(-W)]\). The electric field gradient expressed as a sum of \(K^{-}\)components most frequently decreases with temperature \((T)\), but under certain conditions it can also increase with \(T\). The method is applied to calculations of the temperature evolution of the electric field gradients of pristine zinc and cadmium crystallized in the hexagonal lattice. For calculations within our model of crucial importance is the temperature dependence of mean-square displacements which can be taken from experiment or obtained from the phonon modes in the harmonic approximation. For the case of Zn we have used data obtained from single crystal x-ray diffraction. In addition, for Zn and Cd we have calculated mean-square displacements with the phonopy package. With the experimental data for displacements in Zn the calculation of electron band structure parameters reproduces the temperature dependence of the electric field gradient very accurately. Within the harmonic approximation of the phonopy package the decrease of electric field gradients in Zn and Cd with temperature is overestimated. Our calculations indicate that the anharmonic effects are of considerable importance in the temperature dependence of electric field gradients.

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I. INTRODUCTION

The electric field gradient (EFG) is a very sensitive characteristic of electron structure [1–4]. It is directly measured by the family of methods experiencing quadrupole hyperfine interactions, such as nuclear quadrupole resonance (NQR), Mössbauer spectroscopy (MS) and perturbed angular correlation (PAC) spectroscopy [4–6]. Nuclear probes in these techniques are exposed to the local electronic and molecular structure via the electric interaction between the nuclear quadrupole moment and the surrounding electronic charge distribution providing a spectroscopic fingerprint of the electron environment.

The methods are utilized in a wide range of applications. The time differential perturbed \(\gamma-\gamma\) angular correlation (TDPAC) spectroscopy [6, 7] for example can be used in biochemistry characterizing interactions between metal ions and proteins [7], point defects in metals and recently in semiconductors [8], surface and interface properties, detecting charge density wave formations and structural phase transitions [9] in various materials. Although the TDPAC spectroscopy has been known for more than 40 years, it still has a rich potential for solid state physics and novel materials [6, 8].

On the other hand EFGs measured by these techniques, can be confronted with theoretical values obtained from *ab initio* calculations [10–12] which should give a thorough picture of microscopic properties of the investigated material. Recently, such a comparison has lead to an improved value of the nuclear quadrupole moment of cadmium [13, 14]. The problem is however that in many cases there is a strong temperature \((T)\) dependence of EFGs [1–3, 15], discussed in detail in Sec. II A below, which is often not taken into account. In contrast to *ab initio* calculations of EFGs, first principles studies of the \(T\) dependence of EFGs are very rare [2, 16]. Several models put forward in the past (see Sec. II A) rely heavily on phenomenological parameters [1, 3].

In the present paper following the *ab initio* path we formulate a novel theoretical approach to this problem, which on the basis of crucial band structure parameters
can describe the $T$ evolution (i.e., decrease or increase) of EFG in detail. We demonstrate our method by applying it to the hexagonal close packed (hcp) structure of zinc and cadmium both of which show the characteristic temperature decrease of EFG [18].

The paper is written as follows: in the section II we give details of our approach, in section III we describe our results for the $T$ reduction of EFG in hcp zinc and cadmium, discussing separately the possibility of increasing EFG with $T$ in Sec. III C. Our conclusions are summarized in section IV.

II. THEORETICAL MODEL

A. Theoretical background and models of the $T$ dependence

The EFG tensor $V_{ij}$ is defined as the second partial spatial derivatives of an electric mean-field potential $V$ evaluated at the nuclear site, i.e.

$$V_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j},$$

where $i = x, y, z$. Since $V_{ij}$ is a symmetric (traceless) second rank tensor, it can be further diagonalized by transforming coordinates to the principal system of axes where $V_{zz} \geq V_{xx} \geq V_{yy}$. (Thus, the number of independent parameters for EFG is reduced to two.) The largest component ($V_{zz}$) is called the electric field gradient, and the second independent parameter is the asymmetry $\eta$ defined as $\eta = (V_{xx} - V_{yy})/V_{zz}$ ($0 \leq \eta \leq 1$).

Very often EFGs demonstrate a strong temperature ($T$) dependence which was first approximated by

$$V_{zz}(T) = V_{zz}(T = 0)(1 - BT^n),$$

where the coefficient $B > 0$ implying smaller EFG with increasing $T$, and the coefficient $\alpha$ is usually $3/2$ [18]. Later however this “universal” form of the $T$ dependence was corrected [20]: it was attributed to normal ($sp$) metals, while for transition metals deviations from the $T^{3/2}$ law were notable (down to $\alpha \approx 0.8$). In some cases, the quadratic approximation, $V_{zz}(T) = V_{zz}(0)\left(1 + C_1 T + C_2 T^2\right)$, also gave good quality fits [21]. Even in classical systems like $^{67}$Zn in zinc metal or $^{111}$Cd probes in cadmium metal there were found deviations from the $T^{3/2}$ law at low temperatures [20].

Since the discovery of strong $T$ dependence of EFG, the problem has been considered theoretically [16, 22, 24]. Two main approaches have been put forward in the past: one is based on electron band structure methods [22, 23, 24], while the other used screened charged potential formalism [24]. A starting point of both methods is in fact the phenomenological expression for $V_{zz}$ [24],

$$V_{zz} = (1 - \gamma) V_{zz}^{latt} + (1 - R) V_{zz}^{el},$$

where $V_{zz}^{latt}$ is the field gradient due to the non-cubic arrangement of ions in the lattice (excluding the central site), corrected by the antisheilding factor $\gamma$ and $V_{zz}^{el}$ is due to the conduction electrons corrected by the shielding factor $R$. The screened charged method works with $V_{zz}^{latt}$ calculating lattice sums over vibrating ions, while the first approach works with the electron contribution ($V_{zz}^{el}$) and considers $V_{zz}^{latt}$ as virtually temperature independent. Nowadays however we do not analyze EFG in terms of $V_{zz}^{latt}$, $V_{zz}^{el}$, $\gamma$ and $R$. With the success of $ab$ initio all-electron methods for electronic structure of solids [10–12] capable of treating the electron potential of general shape, the electric field gradient $V_{zz}$ at zero temperature can be found directly from the obtained self-consistent potential. Eq. (3) then should be rewritten in a general form as

$$V_{zz} = V_{zz}^{out} + V_{zz}^{in},$$

where $V_{zz}^{in}$ is the local contribution due to EFG, for example, from the charges inside a muffin-tin (MT) sphere, whereas $V_{zz}^{out}$ is from the charges outside the MT-sphere [more details on Eq. (4) are given below in Sec. II C]. Moreover, $V_{zz}^{in}$ and $V_{zz}^{out}$ can be calculated and we know that by far the leading term is $V_{zz}^{in}$ [18]. In our case $V_{zz}^{in}/V_{zz}$ amounts only to $-2.6\%$ for Zn and $-1\%$ for Cd. (The minus sign of $V_{zz}^{out}$ is discussed in Ref. [3]).

In Ref. [22] Jena started with $V_{zz}^{in}$ and used reduced matrix elements $M' = M \cdot \exp(-W)$ of pseudopotential which appeared as a result of averaging $M$ over the lattice vibrations [28]. Notice that $\exp(-W)$ is a square root of the Debye-Waller factor (SRDWF) $\exp(-2W)$. Keeping in $\exp(-W) \approx 1 - W$ only the first order term in $W \ll 1$, he finally arrived at

$$V_{zz} = V_{zz}(0)[1 - \beta \varphi(T/T_D)].$$

Here $T_D$ is an effective Debye temperature and the function $\varphi$ is the Debye integral [29] and $\beta$ is an adjustable constant. Since at low $T$, $\varphi(T/T_D)$ approaches the zero-point value as $T^2$ and at high $T$ increases linearly with $T$, in the region of $0 < T/T_D < 2$ a $T^{3/2}$ behavior is approximately followed. The concept of Ref. [22] continued in a number of publications on the $T$ dependence of EFG [23, 25, 26]. These studies can not be attributed to a true $ab$ initio approach, although elements of it are present in Refs. [26, 28]. While the $T$ curves for $V_{zz}$ can be reproduced in some cases, one should be aware that in Eq. (5) $T_D$ and especially $\beta$ are fitting parameters of the model. Explicit EFG computation in these models has been avoided in favor of finding expected trends with temperature.

Nowadays, while we can successfully obtain the $T = 0$ value of $V_{zz}$ by performing $ab$ initio band structure calculations, the problem of finding its $T$ dependence from first principles remains. It is a difficult and laborious problem because it requires an accurate calculation of both electronic and phonon properties. Probably, the first attempt is done by Torumba et al. in Ref. [16], who used
molecular dynamics and a supercell calculations of pristine cadmium. For the $T$ dependence of $V_{zz}$ atoms in the supercell were displaced according to the values of mean-square displacements at this temperature, after which the value of $V_{zz}(T)$ was obtained by averaging over various displcive configurations. The authors have observed the decrease of EFG with $T$ in the supercell approach, although their data deviate from the experimental curve at $T > 500$ K.

Surprisingly, in some studies an increase of $V_{zz}$ with $T$ has been reported. For example, in 5% Fe-doped $\text{In}_2\text{O}_3$ [30], in the rutile modification of $\text{TiO}_2$ [31, 32] and in tetrahedrally coordinated Fe sites in $\text{Bi}_2(\text{Fe}_x\text{Ga}_{1-x})_4\text{O}_9$ [17]. In the rutile structure the situation is in fact probe-dependent: while EFG measured at $^{47,49}\text{Ti}$ or substitutional $^{181}\text{Ta}$ and $^{44}\text{Sc}$ increases with $T$, it changes in the opposite direction for $^{111}\text{Cd}$ probes [31, 32]. The increase of EFG is in disagreement with the classical treatment [33, 34] of the evolution of EFG in ionic and molecular crystals based on small rotations of the gradient tensor in respect to a fixed system of axes, according to which the electron density of a solid

$$\langle V_{zz} \rangle = V_{zz}(0) \left[ 1 - \frac{3}{2} \left( \langle \theta_x^2 \rangle + \langle \theta_y^2 \rangle \right) \right].$$

(6)

Here $\theta_x$ and $\theta_y$ are small rotations about the $x-$ and $y-$axis, respectively, and $\langle \theta_x \rangle = \langle \theta_y \rangle = 0$. Notice that Eq. (6) always leads to a decrease of EFG with $T$.

Below we formulate a novel theoretical approach to this problem, which depending on specific conditions can result both in temperature decrease or increase of EFG with temperature. It establishes a close relation between the values of the mean-squared displacements and the evolution of EFG, and also uses the square root of the Debye-Waller factor $\exp(-W)$ which lies at the center of early phenomenological models [1, 22, 24]. The method is applied to the temperature decrease of $V_{zz}$ in hcp zinc and cadmium [1, 18].

B. Reduced quadrupole potential and density on the displaced MT-spheres

The temperature dependence of EFG is clearly a manifestation of both electron and phonon properties. To evaluate correctly $V_{zz}$ we have to effectively average it over atomic vibrations, because a typical frequency of the lattice vibrations (1 THz = $10^{12}$ Hz) is large compared to a typical quadrupole frequency (100 MHz = $10^8$ Hz) experienced by nuclear probes in solids.

The electron density of a solid $\rho(\vec{R})$ is a translationally invariant quantity,

$$\rho(\vec{R} + \vec{a}_i) = \rho(\vec{R}),$$

(7)

where $\vec{a}_i$ ($i=1, 2, 3$) are the basis vectors of the Bravais lattice. Therefore, $\rho(\vec{R})$ can be expanded in Fourier series,

$$\rho(\vec{R}) = \sum_{\vec{K}} \rho(\vec{K}) e^{i \vec{K} \cdot \vec{R}},$$

(8)

where the vectors $\vec{K}$ belong to the reciprocal lattice. Fourier components $\rho(\vec{K})$ are usually found quite naturally from solutions of the Schrödinger (or Dirac) equation for an electron in a periodic mean field potential of the solid. According to the Bloch theorem, the solution for the electron band $n$ has the form

$$\Psi_{\vec{k}, n}(\vec{R}) = \sum_{\vec{K}} c_{\vec{k}, n}(\vec{K}) \phi_{\vec{K} + \vec{k}}(\vec{R}),$$

(9)

where the vector $\vec{k}$ lies in the first Brillouin zone, $\phi_{\vec{K} + \vec{k}}$ are basis functions and $c_{\vec{k}, n}(\vec{K})$ are the coefficients of expansion in the basis set. Almost in all computational methods the basis functions are modified plane waves, which in the interstitial region are simply $\phi_{\vec{K} + \vec{k}}(\vec{R}) \sim \exp(i(\vec{K} + \vec{k}) \cdot \vec{R})$. Substituting Eq. (9) in

$$\rho(\vec{R}) = \sum_{\vec{K}, n: E(\vec{k}, n) \leq E_F} |\Psi_{\vec{k}, n}(\vec{R})|^2,$$

(10)

where $E_F$ is the Fermi energy, we obtain Eq. (8), with the Fourier coefficients $\rho(\vec{K})$ given by

$$\rho(\vec{K}) = \sum_{\vec{K}, n: E(\vec{k}, n) \leq E_F} \sum_{\vec{K}'} c_{\vec{k}, n}^* (\vec{K}') c_{\vec{k}, n}(\vec{K} + \vec{k} \cdot \vec{R}).$$

(11)

In the following we consider a model of vibrating spheres [called below muffin-tin or MT-spheres], Fig. 1.
which are immersed in the interstitial region with fixed values of \( \rho(\vec{K}) \), Eq. (11). It turns out that at a finite and even zero temperature \( T \) the quantities \( \rho(\vec{K}) \) on vibrating MT-spheres are effectively reduced. To demonstrate it we consider a simple case of a single atom in the primitive unit cell. (This avoids unnecessary technical complications whereas the generalization for the case of few atoms is straightforward.) The electron density on an MT-sphere of the radius \( R_{MT} \) centered at a site \( n \) and displaced from the equilibrium position \( \vec{X}(n) = \{X_x(n), X_y(n), X_z(n) \} \) by the vector \( \vec{u}_n \) can be expanded in the multipole series

\[
\rho(\vec{u}_n, r = R_{MT}, \theta, \phi) = \sum_{\Lambda} \rho_{\Lambda}(\vec{u}_n) S_{\Lambda}(\theta, \phi), \tag{12}
\]

where \( \Lambda \equiv (l, \tau) \) stays for \( A_{1g} \) irreducible representations of the crystal point group, \( S_{\Lambda}(\theta, \phi) \) are corresponding symmetry adapted functions (SAFs), \( L \) is the multipole orbital index and \( \tau \) counts functions with the same \( L \) (if there are few such functions). The polar angles \( \Omega = (\theta, \phi) \) are specified by the vector \( \vec{r} \) from the nuclear position \( (\vec{X} + \vec{u}) \). \( S_{\Lambda}(\theta, \phi) \) are linear combinations of real spherical harmonics \( (Y^{m,c}_l \sim \cos m\phi \text{ and } Y^{m,s}_l \sim \sin m\phi) \) defined by the crystal site symmetry and tabulated in [35]. The first function with \( \Lambda = 0 \) \( (l = 0, \tau = 1) \) is the spherically symmetric (monopole) contribution, \( S_0 = Y_{l=0}^{m=0} = 1/\sqrt{4\pi} \). For the hexagonal close packed structure defined by the basis vectors specified in [35] the other multipole functions are: \( Y_{l=1} = Y_{l=3} \), \( Y_{l=4} = Y_{l=5} \), \( Y_{l=6} = Y_{l=6} \), etc. Thus, we have only one quadrupolar function \( S_Q \equiv S_{l=2} = Y_{l=2}^{m=0} \), which explicitly reads as

\[
S_Q(z) = \frac{1}{4} \sqrt{\frac{5}{\pi}} (3z^2 - 1), \tag{13}
\]

where \( z = \cos \theta \). From Eq. (8) we obtain for the coefficients \( \rho_{\Lambda} \) in Eq. (12),

\[
\rho_{\Lambda}(\vec{u}) = 4\pi i \sum_{\vec{K}} j_l(KR_{MT}) S_{\Lambda}(\vec{K}) \rho_{\vec{u}}(\vec{K}). \tag{14}
\]

Here \( j_l \) are spherical Bessel functions and \( \vec{K} \) specifies the direction of \( \vec{K} \), i.e., \( \vec{K} \equiv (\theta_K, \phi_K) \). In the case \( \vec{u} = 0 \) (i.e., at the equilibrium position \( \vec{X}(n) \)) we get \( \rho_{\vec{u}}(\vec{K}) = \rho(\vec{K}) \), where \( \rho(\vec{K}) \) is defined by Eq. (11). If, however, the nucleus and the MT-sphere \( n \) are displaced by the vector \( \vec{u}_n \), we obtain

\[
\rho_{\vec{u}}(\vec{K}) = e^{i\vec{K} \cdot \vec{u}_n} \rho(\vec{K}), \tag{15}
\]

Averaging over the displacements at the chosen site \( n \) we arrive at

\[
\rho_{\Lambda} = \langle \rho_{\Lambda}(\vec{u}) \rangle = 4\pi i \sum_{\vec{K}} j_l(KR_{MT}) S_{\Lambda}(\vec{K}) \langle \rho(\vec{K}) \rangle, \tag{16}
\]

where

\[
\langle \rho(\vec{K}) \rangle = \langle e^{i\vec{K} \cdot \vec{u}} \rangle \rho(\vec{K}), \tag{17}
\]

Notice that we have dropped the index \( n \) in Eq. (17) because the thermal averages \( \langle \rho(\vec{K}) \rangle \equiv \langle \rho_{\vec{u}_n}(\vec{K}) \rangle \) and \( \langle e^{i\vec{K} \cdot \vec{u}_n} \rangle \) are the same for all equivalent atoms \( n \).

As has been proved by Glauber [36], the thermal average on the right hand side of Eq. (17) can be transformed to

\[
\langle e^{i\vec{K} \cdot \vec{u}} \rangle = e^{-W(\vec{K}, T)}, \tag{18}
\]

where

\[
W(\vec{K}, T) = \frac{1}{2} \langle (\vec{K} \cdot \vec{u})^2 \rangle. \tag{19}
\]

Since the usual Debye-Waller factor is \( \exp(-2W) \) [29], the temperature function \( \exp(-W) \), Eq. (18), is the square root of the Debye-Waller factor (SRDWF). Such a function has been used by Kasowski for the description of the temperature-dependent Knight shift in cadmium [28]. The function \( W \) can also be written in the familiar form

\[
W(\vec{K}, T) = \frac{1}{2N} \sum_{\vec{k}, s} \langle (\vec{k} \cdot \vec{u}_s(\vec{k}))^2 \rangle, \tag{20}
\]

where the summation runs over all vectors \( \vec{k} \) in the first Brillouin zone and the phonon branches \( s \), while \( u_s(\vec{k}) \) stands for the corresponding phonon amplitudes. From space symmetry considerations it follows that the function \( W(\vec{K}) \) is the same for all vectors \( \vec{K} \) belonging to the same star. In the harmonic approximation \( W \) implicitly depends on the temperature through the number of thermally excited phonons \( n_{\vec{K}, s} \). In the Debye approximation at high temperatures \( (T \gg T_D) \) \( W \sim T \).

Since for all \( \vec{K} \) we have \( W(\vec{K}) > 0 \) even for zero temperature, all averaged Fourier components \( \langle \rho(\vec{K}) \rangle \) in Eqs. (16) and (17) are effectively reduced. Is is also worth noting that the \( \vec{K} = 0 \) harmonic is unaffected by the vibrations, Eq. (17), and the total electron charge is conserved. Multipole components \( \rho_{\Lambda} \) with \( l = 2, 4, 6 \) etc. are also often reduced, that is \( \langle \rho_{\Lambda}(\vec{u}) \rangle < \rho_{\Lambda}(\vec{u} = 0) \). However, in some rare cases the opposite can occur. Such a situation is discussed below in Sec. III C.

In the following we shall apply our approach to the case of the hexagonal close packed structure, although in principle the consideration is general and can be used for other non-cubic lattices.

C. EFG and quadrupole (\( L = 2 \)) expansion of the electron potential around the nucleus

Similarly to the density expansion, Eq. (12), the electron mean-field potential of the general form around
Notice that the coefficients $V_r(r)$ of electron density (top panel) and the corresponding potential $V_Q(r)$ (bottom panel) inside the MT-sphere of the hcp structure of Zn ($a = 2.659\ \text{Å}, \ c = 4.851\ \text{Å}, \ R_{MT} = 1.33\ \text{Å} \ or\ 2.51\ \text{a.u.}$).

A nucleus, employed for example in the full potential linearized augmented plane wave method (FLAPW) \textsuperscript{37, 38}, also can be expanded in multipolar series,

$$V(r, \theta, \phi) = \sum_\Lambda V_\Lambda(r) S_\Lambda(\theta, \phi). \quad (21)$$

Notice that the coefficients $V_\Lambda(r)$ for the potential and $\rho_\Lambda(r)$ for electron density, Eq. \textsuperscript{12}, can be obtained from the \textit{ab initio} electron band structure calculations. In Figs. 2 and 3 we reproduce such dependencies for the quadrupole component, $L = 2$.

From a scrupulous analysis of the multipolar components of the potential (see Appendix A and Ref. \textsuperscript{34}) it follows that in the neighborhood of the nucleus (when $r \ll 1$) the radial dependence of the function $V_{r, \tau}$ reads as

$$V_\Lambda(r) = v_\Lambda r^\Lambda, \quad (22)$$

where $v_\Lambda$ is a constant. This in particular implies that for quadrupolar component ($Y_{l=2}^m=0$) we have $V_Q = V_{(2,0)}(r) = v_{(2,0)} r^2$, for the component $\Lambda = (4, 0)$ we have $V_{(4,0)}(r) = v_{(4,0)} r^4$, etc. This dependence of $V_Q$ is illustrated in Fig. 3. It is worth noting that the quadrupolar electron density component also follows the same law close to the nucleus, i.e. $\rho_Q = \rho_{(2,0)} r^2$, Fig. 3.

Taking Eq. \textsuperscript{22} into account, we obtain for the electric field gradient,

$$V_{zz} = \frac{\partial^2 V_Q}{\partial z^2} = \sqrt{\frac{5}{\pi}} v_{(2,0)}. \quad (23)$$

Details are given in Appendix A. Notice that Eq. \textsuperscript{23} gives a temperature independent EFG.

The quadrupole potential on the MT-sphere, $V_Q^S$, consists of two contributions,

$$V_Q^S = V_Q^{S, \text{out}} + V_Q^{S, \text{in}}. \quad (24)$$

Here, $V_Q^{S, \text{out}}$ and $V_Q^{S, \text{in}}$ are the potentials due to all charges outside the MT-sphere and inside it, respectively. Correspondingly, for the quadrupole potential $V_Q$ at any point $\vec{r} = (r, \theta, \phi)$ inside the MT-sphere we have

$$V_Q(\vec{r}) = V_Q^{S, \text{out}}(\vec{r}) + V_Q^{S, \text{in}}(\vec{r}), \quad (25a)$$

where

$$V_Q^{S, \text{out}}(r, \theta, \phi) = V_Q^{S, \text{out}} \frac{r^2}{R_{MT}^2} S_Q(\theta, \phi), \quad (25b)$$

(for hcp lattices $S_Q = Y_2^0$) and

$$V_Q^{S, \text{in}}(r, \theta, \phi) = \frac{4\pi}{5} \left( \frac{\rho_Q(r)}{r^4} + r^2 q_Q(r) \right) S_Q(\theta, \phi). \quad (25c)$$
Here
\[ q_Q(r) = \int_0^r \rho_Q(r') r'^3 dr', \] (26a)
\[ q'_Q(r) = \int_r^{R_{MT}} \frac{\rho_Q(r')}{r'} dr', \] (26b)
Since \( q_Q(R_{MT}) = 0 \), we find \( V_Q^{S, \text{in}} = 4\pi q(R_{MT})/R_{MT}^3 \).
Notice that \( V_Q^{\text{out}} \) is explicitly proportional to \( r^2 \), Eq. (25b). It can be shown \[39\] that the same holds for \( V_Q^{\text{in}} \).
From Eqs. (22), (23) we then arrive at
\[ V_{zz} = \sqrt{\frac{5}{\pi}} \left( v_{(2,0)}^{\text{out}} + v_{(2,0)}^{\text{in}} \right), \] (27)
Here \( v_{(2,0)}^{\text{out}} \) and \( v_{(2,0)}^{\text{in}} \) are obtained from \( V_Q^{\text{out}}/r^2 \) and \( V_Q^{\text{in}}/r^2 \) when \( r \to 0 \). As a result of the reduction of \( \rho_Q(r) \) with temperature, \( v_{(2,0)}^{\text{out}} \) and \( v_{(2,0)}^{\text{in}} \) also become reduced, and \( V_{zz} \) decreases with temperature.

### D. Temperature dependence of EFG

As shown in Sec. [II B] the quadrupole density component \( \rho_Q(R_{MT}) \) on the vibrating MT-sphere is often reduced, Eqs. (18), (17). However, to calculate exactly the effect of the reduction on EFG, we have to know \( \rho_Q(r) \) at all values \( r \leq R_{MT} \), see Sec. [II C]. In a straightforward approach we should perform a set of calculations taking all values of \( r \) as MT-radii. In practice, this approach does not work because due to the Coulomb divergence at nuclei, we can not take MT-radii very small.

However, by changing \( R_{MT} \) in a range of relatively large values close to \( R_{MT} \), we have found that the reduction of the quadrupolar density component, \( \rho_Q(r, T)/\rho_Q(r, T = 0) \), is approximately constant. We then in a first approximation assume that for all \( r \leq R_{MT} \)
\[ \frac{\rho_Q(r, T)}{\rho_Q(r, T = 0)} = \frac{\rho_Q(R_{MT}, T)}{\rho_Q(R_{MT}, T = 0)} = R_{in}^3(T). \] (28)

According to Eqs. (26a) and (26b), the reduced quadrupolar density component \( \rho_Q(r, T) \) for all \( r \leq R_{MT} \) changes the quadrupole charges as \( q_Q(r, T) = R_{in}^3(T)q_Q(r) \) and \( q'_Q(r, T) = R_{in}^3(T)q'_Q(r) \). This in turn leads to the reduction of \( V_Q^{\text{in}}(T) = R_{in}^3(T)V_Q^{\text{in}} \), Eq. (25a), and \( v_{(2,0)}^{\text{in}}(T) = R_{in}^3(T)v_{(2,0)}^{\text{in}} \). We then for the temperature evolution of EFG have
\[ V_{zz}(T) = \sqrt{\frac{5}{\pi}} \left( R_{in}^3(T)v_{(2,0)}^{\text{out}} + R_{in}^3(T)v_{(2,0)}^{\text{in}} \right), \] (29)
[compare with Eq. (27)]. Here the factor \( R_{in}^3(T) \) accounts for the change of the potential due to all charges outside the MT-sphere, while \( v_{(2,0)}^{\text{out}} \) and \( v_{(2,0)}^{\text{in}} \) are temperature independent (calculated with an \textit{ab initio} electron band structure method). In practice, \( v_{(2,0)}^{\text{out}} \) is found to be small (1-3 \%) compared to \( v_{(2,0)}^{\text{in}} \). Since, in addition the difference between \( R_{out} \) and \( R_{in} \) is not essential, in the following we take \( R_{out} \approx R_{in} \). Then the temperature dependence of EFG is completely due to the change of \( \rho_Q \) inside the MT-sphere and
\[ V_{zz}(T) \approx R_{in}^3(T)V_{zz}. \] (30)

### E. Mean-square displacements

The SRDW factor, Eqs. (18) and (19), depends crucially on the mean square displacements \( \langle u_x^2 \rangle, \langle u_y^2 \rangle \) and \( \langle u_z^2 \rangle \), which are functions of temperature. For the hcp lattice \( \langle u_x^2 \rangle = \langle u_y^2 \rangle \), and for calculations of SRDWF we need to know only two functions: \( U_{11}(T) = \langle u_z^2 \rangle \) and \( U_{33}(T) = \langle u_z^2 \rangle \) (for hcp lattice \( U_{33} > U_{11} \)),
\[ W(K, T) = \frac{1}{2} \left( (K_x^2 + K_y^2)U_{11}(T) + K_z^2U_{33}(T) \right). \] (31)
The functions \( U_{11}(T) \) and \( U_{33}(T) \) can be calculated within the harmonic approximation or extracted experimentally as illustrated in Fig. 4 for the hcp lattice of Zn.

In Fig. 5 we plot individual SRDW factors, \( \exp(-W(K, T)) \), for the hcp structure of Zn, which are responsible for the temperature reduction of the quadrupole density and potential, Sec. [II B]. With the increase of \( T \) the SRDW factors get shifted to lower values. A finite width of SRDWF for reciprocal vectors with close
The number of $k_{\text{MT}}$ basis state cut-off parameter was increased to 3000. The typical nuclear region to obtain the electric field gradient accurately was formed with the Moscow-FLAPW code [17]. The code with the local density approximation within the density functional theory (DFT) [43].

Electron density functional calculations have been performed with the Moscow-FLAPW code [17]. The code explicitly takes into account the nuclear size and the change of the potential and the wave function inside the nuclear region to obtain the electric field gradient accurately. In addition, the number of radial points inside the MT-region has been increased to 3000. The typical LAPW basis state cut-off parameter was $R_{\text{MT}}K_{\text{max}} = 9$, the number of $k$ points was $\sim 500$. For calculation of the exchange-correlation potential and the exchange-correlation energy contribution we have used a variant of the local density approximation within the density functional theory (DFT) [43].

The temperature evolution of the tensor of mean-square displacements can be obtained by three different ways: (1) from a direct experimental parametrization of the displacements $\langle u_{x}^{2}(T) \rangle$ and $\langle u_{z}^{2}(T) \rangle$ as given in Ref. [21] for Zn; (2) from calculations of the phonon frequencies and eigenvectors (for example, with the open source package phonopy [40]); (3) from effective Debye temperature $T_{D}(T)$ which appear as a result of experimental parametrization [42, 44]. The strict harmonic approximation is adopted only in (2), while in (1) and (3) an anharmonic effects such as thermal expansion of solids and phonon softening are effectively taken into account. Experimentally, the values of $\langle u_{x}^{2}(T) \rangle$ and $\langle u_{z}^{2}(T) \rangle$ (or directly related to them temperature factors $B_{z}(T)$ and $B_{z}(T)$ [42] are found from the temperature evolution of the x-ray diffraction spectra.

### A. Zinc

Mean-square displacements for hcp structure of zinc are shown in Fig. 4. First, we notice that in the harmonic approximation in the region of $T$ from 60 K to 500 K, $U_{11}(T)$ and $U_{33}(T)$ obtained with the package phonopy [40] are practically linear in $T$. Such behaviour is also expected in the Debye model for $T > T_{D}$. Experimentally, however we observe that $U_{11}(T)$ and $U_{33}(T)$ deviate from the linear law. As shown in Ref. [21] $U_{11}(T)$ and $U_{33}(T)$ are approximated by quadratic functions of $T$ for all data in the range from 40 K to 500 K. In addition, in the harmonic approximation values of $U_{33}$ are consistently overestimated, which results in a considerable suppression of the SRDF factors and the calculated temperature dependence of EFGs, Fig. 4.

On the other hand, our calculations of the temperature evolution of EFG using experimental data for $U_{11}(T)$ and $U_{33}(T)$ demonstrate a good correspondence with the measured values of $V_{zz}$, Fig. 6. We have also found that the $T$ dependence of $V_{zz}$ is extremely sensitive to the ratio $\mathcal{R} = U_{33}/U_{11}$. To demonstrate it we have computed the evolution of $V_{zz}$ with $T$ with reduced values of $\mathcal{R}$, Fig. 7 (upper panel). It turns out that if $\mathcal{R} = 1$ [i.e. $U_{33}(T) = U_{11}(T)$] there is virtually no temperature decrease of EFG, although we have kept the average value of mean-squared displacements

$$U_{av} = (2U_{11} + U_{33})/3$$

The temperature evolution of zinc is highly nonlinear in contrast to the simple linear increase of the lattice constant ratio $c/a$ [21]. On the other hand, in the harmonic approximation $U_{33}/U_{11}$ should be almost independent of $T$, at least for $T > T_{D} \sim 200$ K [41]. Therefore, in the $T$ dependence of $U_{33}/U_{11}$ and consequently of EFG there is a substantial anharmonic contribution.

Notice, that even at zero temperature the value of EFG is slightly reduced because of the zero point vibra-
and 13.42 MHz for $Q$ quadrupole frequency 11.18 MHz for phonopy. The refined calculated absolute value of EFG square displacements from Ref. [21] and 1% according to calculations. The calculated reduction is 0.6% with the mean square displacements from Ref. [21] and 1% according to phonopy. The refined calculated absolute value of EFG at $T = 0$, $V_{zz} = 3.70 \times 10^{21} \text{ V/m}^2$, corresponds to the quadrupole frequency 11.18 MHz for $Q(\text{Zn}) = 0.125 \text{ b}$ [14] and 13.42 MHz for $Q(\text{Zn}) = 0.15 \text{ b}$, both of which compare well with the experimental value of 12.34 MHz at 4.2 K [16].

B. Cadmium

Results for cadmium are given in Figs. 8 and 9. As for the zinc calculation we observe that the mean-squared displacements $U_{33}$ are greatly overestimated by the phonopy calculations, which leads to a drastic decrease of $V_{zz}$ with temperature. In general, our calculations of the temperature evolution of $V_{zz}$ have turned out to be quite sensitive to values of mean square displacements $U_{11}$ and $U_{33}$. It is worth noting that with the mean-square values obtained by Torumba et al [16] with the Phonon program [47], we have obtained reduced EFGs which compares well with the experimental results of Ref. [18] at 280 K and 430 K, Fig. 8. However, our calculations also show that these values of $U_{11}$ and $U_{33}$ somewhat underestimate the reduction of $V_{zz}$ at 430 K and especially at 570 K (not shown in Fig. 8). We believe that this is related to the softening of the Cd lattice [11] and increase of the ratio of $R = U_{33}/U_{11}$ with temperature which lays beyond the harmonic approximation. In fact, as we know from experimentally deduced values of $U_{11}$ and $U_{33}$ [21] both effects are clearly present in the case of Zn lattice, Fig. 4. Since at the moment there are no experimental data for the mean-square displacements of cadmium, we have performed a number of model calculations, Fig. 9. The averaged mean square displacement $U_{av} = (2U_{11} + U_{33})/3$ has been calculated within the Debye lattice model with a temperature dependent Debye temperature $T_D$. The lattice softening has been modelled by a linear decrease of $T_D$, from 140 K (at $T = 0$ K) to 115 K (at $T = 500$ K), with the averaged value of $T_D^{av} = 127.5$ K. These value is very close to $T_D = 131 \pm 7$ K given in Ref. [18] for Cd. In addition, we consider an anharmonic effect modelled by a linear change of $\mathcal{R}$ from 1.5 (at $T = 0$ K) to 2.7 (at $T = 500$ K) with the averaged value of $\mathcal{R} = 2.1$. Correspondingly, we have performed four model calculations shown in Fig. 9: (1) with the lattice softening and the temperature increase of $\mathcal{R}$ (black curve in Fig. 9), (2) without softening and $\mathcal{R}$ fixed (yellow curve), (3) with the softening and $\mathcal{R}$ fixed (blue dotted line), (4) without softening and the temperature increase of $\mathcal{R}$ (dashed green line). The results clearly demonstrate that the best fit is achieved with the lattice softening and the temper-
calculations \[18\]. Purple triangles are our calculations with temperature increase of \(T\) (see text for details), dark cyan dash line – phonopy calculations \[40\]. Purple triangles are our calculations with temperature increase of \(T\) (see text for details), dark cyan dash line – phonopy calculations \[40\]. Purple triangles are our calculations with temperature increase of \(T\) (see text for details), dark cyan dash line – phonopy calculations \[40\].

mean-field displacements of Table II of Ref. \[16\] (the Phonon effects improve the comparison with the experiment.

proof, the important finding is that both unharmonic effects improve the comparison with the experiment. Al- though these arguments can not be considered as a solid proof, the important finding is that both unharmonic effects improve the comparison with the experiment. Al-

The mean-square displacements of Table II of Ref. \[16\] (the Phonon effects improve the comparison with the experiment. Al-

C. Mechanism of increase of EFG with \(T\)

The most important factor in the \(T\) dependence of EFG is \(\mathcal{R} = U_{33}/U_{11}\). As discussed in Sec. III A B and shown in Fig. 7 the ratio \(\mathcal{R}\) has a pronounced influence on the shape of the \(V_{zz}(T)\) curve. A reduction of \(\mathcal{R}\) in cadmium also has an immediate and sizeable effect on \(V_{zz}(T)\), Fig. 7. Interestingly, for \(\mathcal{R} = 1\) \([U_{11} = U_{33}]\) we observe in cadmium a rare effect of a weak increase of \(V_{zz}\) with \(T\) (orange plot in Fig. 4). At first sight, this does not seem compatible with the apparent reduction of \(\langle \rho_Q \rangle\), Eqs. \[17\] and \[18\], caused by \(\exp(-W)\). Notice however, that in the sum of Eq. \[19\] individual contributions proportional to \(j l (KR_{MT}) S_{\Lambda}(\vec{K}) \langle \rho(\vec{K}) \rangle\) are of different signs. Two terms of different signs can be schematically written as

\[ V_{zz}(T) \propto \langle \rho_Q \rangle = \sum c_l \mathcal{W}(\vec{K}_1) \rho(\vec{K}_1) - c_2 \mathcal{W}(\vec{K}_2) \rho(\vec{K}_2). \]

Here the \(T\) dependent SRDWFs are incorporated in the weight factors \(\mathcal{W} = \exp(-W)\) and \(c_1 > 0\), etc. Both \(\mathcal{W}(\vec{K}_1)\) and \(\mathcal{W}(\vec{K}_2)\) reduce with \(T\), but if \(\mathcal{W}(\vec{K}_2)\) drop fast enough in comparison with \(\mathcal{W}(\vec{K}_1)\), one can have a resulting increase of the expression in square brackets and of the whole sum.

Our detailed numerical analysis for the situation is illustrated further in Fig. 10. One can see that at \(T = 300\) positive contributions to the gradient (red circles) although appreciably suppressed by negative contributions (blue diamonds), finally prevail, which leads to a small positive net contribution to EFG (the \(n = 120\) value of

FIG. 8: Temperature evolution of \(V_{zz}\) in Cd (upper panel) determined by the mean-square displacements \(U_{11}\) and \(U_{33}\) (lower panel). Red circles stand for experimental measurements \[18\], black line – for a model calculation taking into account softening of the lattice and an increase of \(U_{33}/U_{11}\) with \(T\) (see text for details), dark cyan dash line – phonopy calculations \[40\].

FIG. 9: Model mean-square displacements \(U_{11}\) and \(U_{33}\) in Cd (lower panel) and corresponding temperature dependencies of \(V_{zz}\) (upper panel). Red circles stand for experimental measurements \[18\], black line – for a model calculation taking into account the softening of the lattice and the increase of \(U_{33}/U_{11}\) with \(T\). Yellow solid line – calculations without softening and a fixed \(U_{33}/U_{11}\) ratio, blue dotted line – with the softening and the fixed \(U_{33}/U_{11}\) ratio, and green dashed line – without softening and the increased \(U_{33}/U_{11}\) ratio, see text for details. Purple triangles are our calculations with mean-field displacements of Table II of Ref. \[16\].
nature softening (modelled by a decrease of the Debye temperature) are also present in zinc.[21] In addition, we have performed calculations of the mean-square displacements in Zn and Cd in the harmonic approximation by using the package Phonopy.[40] In that case for both metals the decrease of EFG has been grossly exaggerated, and the shape of the calculated $V_{zz}$ curves has been incorrect. In case of cadmium, using the mean-square displacements calculated at $T = 280$ and 430 K by Toramba et al.[19] with the package Phonon,[47] we have obtained reduced values of EFG which lie not far from the experimental data.

In our studies we have not found an intrinsic mechanism for the $T^{3/2}$ dependence of EFG, Eq. (2). Nevertheless, the $T^{3/2}$ plots, Fig. 11 indicate that an approximate $T^{3/2}$ law for Zn and Cd holds. For Cd the dependence is almost perfect, for Zn it deviates from $T^{3/2}$ at low temperatures which can be partially explained by the fact that the experimental data for mean-square displacements[21] are available only for $T > 40$ K. In any case, even experimental data for EFG of Zn and Cd deviate from the $T^{3/2}$ law at low temperatures[20]. We therefore conclude that the mechanism of the temperature dependence of $V_{zz}$ in Zn and Cd is complex, with a substantial contribution from anharmonic effects. An approximate correspondence with the $T^{3/2}$ dependence is probably due to the $T$ behavior of SRDW factors, $\exp(-W(T))$.[22]

Finally, we mention that even at zero temperature the measured EFGs are smaller than $V_{zz}$ calculated by \textit{ab initio} methods. The zero temperature reduction however is small: 0.6% in Zn and 1% in Cd.

Acknowledgments

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Appendix A: Quadrupolar potential and the tensor of EFG

The asymptotic behavior of the potential close to the nucleus, Eq. (22), can be understood from the two center expansion of the Coulomb potential in double multipolar series,

\[
\frac{1}{|\vec{R}(\vec{n}) - \vec{R}(\vec{n}')}} = \sum_{\Lambda\Lambda'} v_{\Lambda\Lambda'}(\vec{n}, \vec{n}'; r, r') \mathcal{S}_\Lambda(\vec{r}(\vec{n})) \mathcal{S}_{\Lambda'}(\vec{r}'(\vec{n}')) ,
\]

where the interaction strength \(v_{\Lambda\Lambda'}\) is given by

\[
v_{\Lambda\Lambda'}(\vec{n}, \vec{n}'; r, r') \sim \frac{(r)^{l}(r')^{l'}}{|X(\vec{n}) - X(\vec{n}')|^{l+l'+1}}. \tag{A2}
\]

Here \(\vec{R}(\vec{n}) = \vec{X}(\vec{n}) + \vec{r}(\vec{n})\) is the radius vector close to the crystal site \(\vec{n}\). For \(r \ll 1\) we arrive at Eq. (22) which holds both for the contributions from the electron density around the site \(\vec{n}\) and the contributions from the densities on the other sites \(\vec{n}' \neq \vec{n}\).

As follows from Eqs. (21), (22), the quadrupolar component of the potential for the hexagonal lattice can be written as

\[
V_Q(r, \theta, \phi) = v_{(2,0)} r^2 Y_{l=2}^m=0(\theta, \phi) = v_{(2,0)} \frac{1}{4} \sqrt{\frac{5}{\pi}} (3z^2 - r^2). \tag{A3}
\]

From this relation we obtain that the tensor of EFG is diagonal in the Cartesian system of axis and

\[
V_{zz} = \frac{\partial^2 V_Q}{\partial z^2} = \frac{\sqrt{5}}{\sqrt{\pi}} v_{(2,0)}, \tag{A4}
\]

\[
V_{zx} = \frac{\partial^2 V_Q}{\partial z \partial y} = -\frac{1}{2} \frac{\sqrt{5}}{\sqrt{\pi}} v_{(2,0)}. \tag{A5}
\]
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