Towards an ab initio theory for the temperature dependence of electric field gradients in solids:
Application to hexagonal lattices of Zn and Cd

A.V. Nikolaev[1], N.M. Chtchelkatchev[2], D.A. Salamatin[2], A.V. Tsvyashchenko[2]
[1]Skobeltsyn Institute of Nuclear Physics Moscow State University, 119991 Moscow, Russia
[2]Institute of High Pressure Physics, Russian Academy of Sciences, 108840 Moscow, Russia

Based on ab initio band-structure calculations we formulate a general theoretical method for description of the temperature dependence of an 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 effectively reduced by the square root of the Debye-Waller factor [exp(−W)]. The electric-field gradient related to a sum of K components most frequently decreases with temperature (T), but under certain conditions because of the interplay between terms of opposite signs, 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 density-functional perturbation treatment of the quantum espresso package. With the experimental data for displacements in Zn, our calculations reproduce the temperature dependence of the electric-field gradient very accurately, see Fig.1. Within the harmonic approximation of the quantum espresso package, the decrease in 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 [1].

The EFG tensor V_{ij} is defined as the second partial spatial derivatives of an electric self-consistent-field potential V evaluated at the nuclear site (where i = x,y,z):

$$V_{ij} = \frac{\partial^2 V}{\partial i \partial j}$$

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 $|V_{zz}| > |V_{yy}| > |V_{xx}|$. (Thus, the number of independent parameters for the EFG in the principal axis system is reduced to two.) The principal component (V_{zz}) is called the electric-field gradient, and the second independent parameter is the asymmetry η defined as η = ($V_{xx} - V_{yy}$)/V_{zz} (0 <η <1). Very often, EFGs demonstrate a strong temperature (T) dependence which can be described by a equation of this form $V_{zz}(T) = V_{zz}(T=0)\left(1 - BT^{\alpha}\right)$ where the coefficient B > 0 implying a smaller EFG with increasing T and the coefficient α is usually 3/2. Later, however, this "universal" form of the T dependence was corrected: It was attributed to normal (sp) metals, whereas for transition metals, deviations from the 3/2-law were notable (down to α ≈ 1). In some cases, the quadratic approximation, also gave good quality fits. Even in classical systems, such as ^{67}Zn or ^{111}Cd probes in cadmium metal, there were found **pronounced deviations** from the $T^{3/2}$ law at low temperatures.

The temperature dependence of the 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.
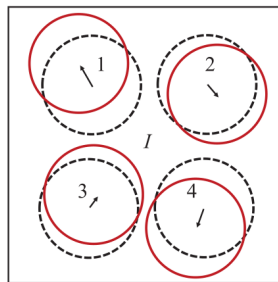

FIG. 1. Vibrations of MT-spheres $n = 1-4$ and the interstitial region (I). The dashed lines: averaged surfaces positions in the ideal structure; the full (red) lines: instantaneous sphere positions; the arrows indicate the sphere displacements u_n, $n = 1-4$. As a result of sphere vibrations, the averaged quadrupole potential $\langle V_Q \rangle$ on the sphere surfaces is reduced, see the text for details.

$$V_{zz}(T) = \sqrt{\frac{5}{\pi}} \left[R^{\text{out}}(T) v_{(2,0)}^{\text{out}} + R^{\text{in}}(T) v_{(2,0)}^{\text{in}} \right]$$

Here, the factor $R^{\text{out}}(T)$ accounts for the change in the potential due to all charges outside the MT sphere, whereas $v_{(2,0)}^{\text{out}}$ and $v_{(2,0)}^{\text{in}}$ are temperature independent (calculated with an *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, for simplicity, we take $R^{\text{out}} \approx R^{\text{in}}$. Then, the temperature dependence of the EFG is completely due to the change in ρ_Q inside the MT sphere and

$$V_{zz}(T) \approx R^{\text{in}}(T) V_{zz}.$$

The quadrupole potential on the MT-sphere consists of two contributions,

$$V_Q^S = V_Q^{S, \text{out}} + V_Q^{S, \text{in}}$$

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

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

$$V_Q^{\text{out}}(r, \theta, \phi) = V_Q^{S,\text{out}} \frac{r^2}{R_{\text{MT}}^2} S_Q(\theta, \phi),$$
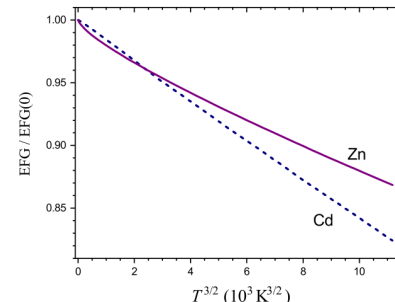
(for hcp lattices $S_Q = Y_2^0$) and

$$V_Q^{\text{in}}(r, \theta, \phi) = \frac{4\pi}{5} \left(\frac{q_Q(r)}{r^3} + r^2 q_Q'(r) \right) S_Q(\theta, \phi).$$

Here,

$$q_Q(r) = \int_0^r \rho_Q(r') r'^3 \, dr',$$

$$q_Q'(r) = \int_r^{R_{\text{MT}}} \frac{\rho_Q(r')}{r'} \, dr'.$$

Here, v_Q^{out} and v_Q^{in} are obtained from V_Q^{out}/r^2 and V_Q^{in}/r^2 when $r \to 0$.

Plots of the T dependence of electric-field gradient $V_{zz}(T)/V_{zz}(T=0)$ for Zn and Cd as functions of $T^{3/2}$.

1. A.V. Nikolaev, N.M. Chtchelkatchev, et al, *Phys. Rev. B 101, 064310 (2020).*

Conclusions. We have presented a method which can describe the temperature evolution of electric-field gradient V_{zz} in metals.