

## Electric field gradient of single impurities in aluminum

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Single substitutional impurities of Mg, Zn, Ga, Ge, and Si in Al universally show very small electric field gradients at the second-nearest-neighbor sites, in obvious disagreement with theoretical calculations. We show that this does not likely reflect the neglect of nonspherical contributions to the induced charge density around the impurity.

The quadrupolar moment interaction of a host lattice nuclei with the electric field gradient (EFG) introduced by impurities provide detailed information about the shape of the screening charge density  $n(\vec{r})$  around such perturbations.<sup>1-8</sup> Since charge-density calculations for single impurities in metal hosts (and in particular in simple metals) have gained in sophistication<sup>9-12</sup> better agreements have been reported with such EFG measurements.<sup>7,8</sup> For an aluminum lattice with single substitutional impurities of Mg, Zn, Ga, Ge, and Si reasonable agreement between theory and experiment is found for first, third, and fourth neighbors from the impurity site. Invariably, however, all theoretical predictions grossly overestimate the EFG at the second-nearest neighbor, which experimentally is found to be much smaller (basically zero). Since this discrepancy persists for all of these impurities, with their expected different screening density  $n(\vec{r})$  (e.g., different phase of oscillations in the asymptotic limit) it is not likely a result of the impurity but rather that of the host Al lattice. This led to the suggestion that the anisotropy of  $n(\vec{r})$  (which is largely a property of the lattice) could account for these differences. However, the calculation of nonspherical corrections  $n_{ns}(\vec{r})$  to the charge density around an impurity is difficult and has been largely ignored. In this Brief Report we show that within our approximations such corrections are very small at the first few nearest neighbors, and therefore not likely to account for the discrepancy at the second-nearest neighbor.

For calculating the density  $n(\vec{r})$  around the impurity, two distinct approaches are possible. The first<sup>1</sup> starts with the Al lattice, and the corresponding Bloch states  $\phi_{\vec{k}}(\vec{r})$ , to which the effect of the *spherical* impurity potential  $V(r)$  is added. The second<sup>8</sup> focuses on the impurity potential, with its spherical wave functions, and charge density  $n_0(r)$ , and

corrects it by adding the effect of the lattice potential  $U(\vec{r})$  [the potential of the Al ion at the location of the impurity  $\vec{r} = 0$  is removed from  $U(\vec{r})$ ]. We assume that the environment around the impurity is the most important in determining the EFG at the few nearest-neighbor sites and that the lattice plays a secondary role, particularly in a weak scatterer such as Al. We therefore solve for  $n(\vec{r})$  using the second approach. We nevertheless hasten to add that since the Fermi surface of Al intersects the Brillouin-zone boundaries, the wave functions at these points will be Bragg scattered creating large corrections to the Bloch states at these points. Our calculation will fail to account for that but we expect such corrections to  $n(\vec{r})$  to be small, particularly close to the impurity. In fact, to some extent, our study of the density response to an impurity in copper<sup>13</sup> and also the density profile of the perfect Al lattice support this contention.

The calculation for the *nonspherical* corrections  $n_{ns}(\vec{r})$  to  $n(\vec{r})$  [ $n(\vec{r}) = n_0(r) + n_{ns}(\vec{r})$ ] proceeds as follows.<sup>12</sup> We decompose the potential  $U(\vec{r})$  in terms of the spherical harmonics  $Y_{lm}$ :

$$U(\vec{r}) = U_0(r) + U_{ns}(\vec{r}), \quad (1a)$$

where

$$U(\vec{r}) = \sum_{R_l \neq 0} U_p(\vec{r} - \vec{R}_l) \quad (1b)$$

and

$$U_{ns}(\vec{r}) = \sum_{\substack{l,m \\ l \neq 0}} U_{lm}(r) Y_{lm}(\theta, \phi), \quad (1c)$$

the  $\vec{R}_l$  are the lattice sites of the unrelaxed Al host, and  $U_p(\vec{r})$  is a pseudopotential representation of the Al-ion potential. For  $U_p(\vec{r})$  we choose the smooth Heine-Abarenkov form<sup>14,15</sup>

$$U_p(\bar{r}) = - \int \frac{d^3q}{(2\pi)^3} e^{i\bar{q} \cdot \bar{r}} \frac{4\pi Z e^2}{q^2} \left( \frac{D \sin(qR_c)}{qR_c} + (1-D) \cos(qR_c) \right) e^{-(q/q_0)^2}, \quad (2)$$

with  $Z = 3$ , core radius  $R_c = 1.09$  a.u., well depth  $D = 0$ , and damping parameter  $q_0 = 5.5k_F$ . The spherical density  $n_0(r)$ , induced by the impurity, is now solved by first calculating the self-consistent charge density  $n_1(r)$  for the potential  $U_0(r) + V(r)$  [ $V(r)$  is the full potential of an aluminum ion,  $V(r) = -Z^*e^2/r$  with  $Z^* = 13$ ]. The numerical solution of such a charge density is well documented in previous papers.<sup>9-12</sup> We next replace  $V(r)$  by the

full impurity potential (e.g.,  $Z^* = 12$  for Mg) and repeat the calculation for  $n_2(r)$ . The results are displayed in Fig. 1 along with Zn, Ga, Ge, and Si.  $n_0(r)$  is now given by  $n_2(r) - n_1(r)$ . To calculate  $n_{ns}(\bar{r})$  we follow Ref. 12. Briefly we introduce  $U_{ns}(\bar{r})$  [Eq. (1c)] as a linear perturbation in the presence of  $n_1(r)$  and  $n_2(r)$  and calculate the response using a statistical form for the kinetic and exchange energy, i.e.,<sup>12,16,17</sup>

$$G[n(\bar{r})] \approx \frac{3}{10} (3\pi^2)^{2/3} \int d^3r n^{5/3}(\bar{r}) + \frac{1}{72} \int d^3r \frac{|\bar{\nabla} n(\bar{r})|^2}{n(\bar{r})} - \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int d^3r n^{4/3}(\bar{r}). \quad (3)$$

If we take the functional derivative and linearize it around  $n_1(r)$  [or  $n_2(r)$ ], the following equation for  $n_{ns}(\bar{r})$  results,

$$U_{ns}(\bar{r}) + \int d^3r' \frac{n_{ns}(\bar{r}')}{|\bar{r} - \bar{r}'|} + \left[ (3\pi^2)^{2/3} n(r)^{-2/3} - \frac{1}{3} \left( \frac{3}{\pi} \right)^{1/3} n(r)^{-2/3} - \frac{|\bar{\nabla} n(r)|^2}{36n^3(r)} + \frac{\nabla^2 n(r)}{36n^2(r)} \right] n_{ns}(\bar{r}) - \frac{1}{36n(r)} \nabla^2 n_{ns}(\bar{r}) + \frac{\nabla n_{ns}(\bar{r}) \cdot \nabla n(r)}{36n^2(r)} = \mu_{ns}, \quad (4)$$

where  $n(r)$  is either  $n_1(r)$  or  $n_2(r)$ . For each component  $U_{l,m}(r)$  [Eq. (1c)], Eq. (4) produces the same  $l$  and  $m$  components of  $n_{ns}^l(\bar{r})$ , i.e.,

$$n_{ns}^l(\bar{r}) = \sum_{l',m'} n_{l',m'}^l(r) Y_{l',m'}(\theta, \phi). \quad (5)$$

The nonspherical screening charge is given by  $n_{ns}(\bar{r}) = n_{ns}^2(\bar{r}) - n_{ns}^1(\bar{r})$ . In Fig. 2 we display Eq.

(5) for Mg in an Al host for  $l = 4, m = 4$ . From symmetry

$$n_{4,-4}^1(r) = n_{4,4}^1(r)$$

and

$$n_{4,0}^1(r) = \left( \frac{5}{14} \right)^{1/2} n_{4,4}^1(r).$$

$n_{ns}(\bar{r})$  is also plotted in Fig. 2 and clearly its contribution is very small.  $n_{ns}(\bar{r})$  is of course the pseudo-density but the core orthogonalization factor

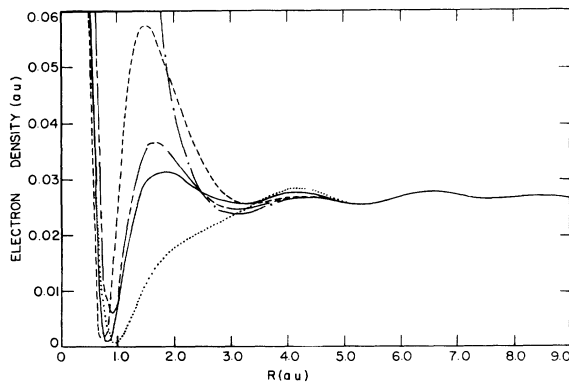


FIG. 1. Solid curve is the spherical charge density around an aluminum ion in pseudopotential representation of the remaining lattice [i.e.,  $V(r) + U_0(r)$  in the text]. The other curves represent the same calculation with  $V(r)$  the full potential for Mg ( $\cdots$ ), Zn ( $-\cdot-$ ), Ga ( $---$ ), and Si ( $----$ ) (Ge results were nearly identical to those of Si and therefore have not been plotted separately). The induced charge density  $n_0(r)$  for the different impurities is given by subtracting the solid curve from the rest.

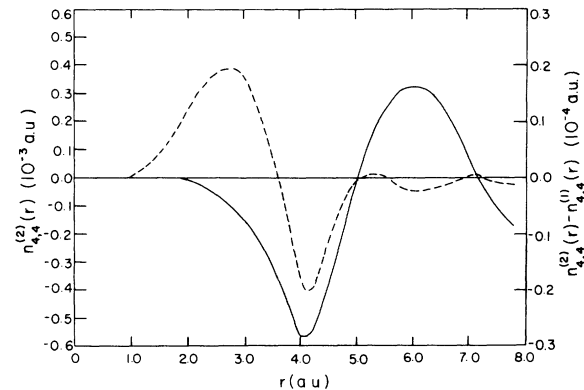


FIG. 2. The contribution of the  $l = 4$  and  $m = 4$  component to the nonspherical charge density  $n_{ns}(\bar{r})$ . The solid curve is the  $n_{4,4}^{(2)}(r)$  corresponding to a full magnesium potential  $V(r)$  and a pseudopotential lattice  $U_0(r)$ . The dashed curve is the difference in  $n_{ns}^{(2)}(\bar{r}) - n_{ns}^{(1)}(\bar{r})$  when  $V(r)$  is replaced by Al. The scale for the solid curve is on the left and the dashed on the right ordinate.

does not change this result. We have carried Eq. (5) to  $l = 12$  and the same conclusions persist. The EFG necessary to explain the above discrepancy at the second-nearest neighbor is of the order of  $10^{13}$  cgs units and  $n_{ns}(\bar{r})$  of Fig. 2 provides at best  $10^{10}$  cgs units. We must conclude that nonspherical contributions of the screening charge density to EFG are too small and we do not expect our approximations (see above) to be off by a factor of  $10^3$ .

The universal behavior of the EFG at second-nearest-neighbor sites of Mg, Zn, Ga, Ge, and Si in Al obviously cannot depend strongly on the properties of the impurity. Aside from possible pathological clustering configurations, which would have to signi-

ficantly reduce the EFG only at the second-nearest neighbors, and which are *highly* unlikely for such small concentrations, our experience<sup>18</sup> suggests that lattice relaxation may account for the discrepancy. We are pursuing such lattice relaxation calculations and their effect on the corresponding EFG.

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