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Theory of Electric Field Gradient Due to a Point Defect in a Cubic Metal

M. J. Ponnambalam and P. Jena

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284

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With use of perturbed electron density, calculated self-consistently in the density-functional theory, and a new form for the strain tensor, quantitative agreement has been achieved for the first time with experiment for the electric field gradient and asymmetry parameter at various near-neighbor sites in Al containing vacancies. The implication of this theory in understanding lattice displacement around a point defect is discussed.

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It is well known that the loss of cubic symmetry due to a point defect in a cubic metal gives rise to electric field gradients (efg) which interact with the host nuclear quadrupole moments. Since the pioneering work of Bloembergen and Rowland[1] many sophisticated experiments[2] have been done and the efg at several near-neighbor (nn) sites around the defect have been measured. Unfortunately, no satisfactory theory exists that can account for the efg at nn host sites. The difficulty in achieving a quantitative theoretical understanding stems from the fact that a point defect in a metal not only perturbs the ambient electron distribution but, because of differences in size, it also introduces a strain in host lattice. These two effects are interrelated and both contribute to the efg.

In this Letter we report the first successful theoretical study of the efg distribution in a cubic metal. The theory which takes into account both charge screening and strain effects is applied to Al containing a monovacancy. We have achieved quantitative agreement with experiment for *all* near neighbors where experimental values are available. The screening of the defect charge is handled self-consistently with use of the density-functional theory. The conduction electron contribution to efg has been reformulated such that it is valid at short distances from the defect. In addition, a new form for the strain tensor is given which not only accounts for the lack of cylindrical symmetry of the efg tensor but also aids in our understanding of the lattice displacement around the point defect.

In the following we present the formulation of our theory, the motivation for choosing the Al-vacancy system for its application, a discussion of our results and finally the implications of the present work.

The asymptotic expression for the efg[3] is given by

$$q(r) = \tfrac{8}{3}\pi\alpha(k_F)\,\delta n_a(r), \tag{1}$$

where $\alpha(k_F)$ is the Bloch enhancement factor and $\delta n_a(r) = A\cos(2k_F r + \theta)r^3$ is the induced electron density in the asymptotic region. The difficulties in using Eq. (1) to interpret efg at nn sites in cubic metals are twofold: (1) The validity of Eq.

(1) for the first few neighbors is uncertain.
(2) Since $\delta n_a(r)$ is assumed to be spherically symmetric, Eq. (1) would predict the efg tensor to have cylindrical symmetry, in contradiction with experiments.[2]

Sagalyn and Alexander[4] have studied the contribution of the lattice strain to the efg following the elastic continuum model. As pointed out by these authors, the strain around the defect influences the efg in three different ways. The first two effects (the so-called indirect effect) originate from the displacement of the nn sites (giving rise to new equilibrium configurations of nn) and the local distortion around the defect (affecting the strength of electron-defect scattering[5]). A direct and somewhat more important contribution (usually referred to as the size effect) is a term proportional to the local strain. Using the point-ion model,[6] Sagalyn and Alexander[4] have calculated the local strain contribution to the efg tensor q_{ij} by relating it to a strain tensor ϵ_{mn} through a fourth-ranked tensor F. The strain-tensor is related to the displacement vector $\vec{u}$ through the relation, $\epsilon_{mn} = \frac{1}{2}(\partial u_m/\partial x_n + \partial u_n/\partial x_m)$ and $\vec{u}$ was assumed to have the following form,

$$\vec{u} = D\vec{r}/r^3, \tag{2}$$

where D is a constant and is a measure of the defect strength. The indirect contribution to efg due to lattice strain as well as the valence contribution were calculated by replacing the asymptotic charge density in Eq. (1) by the preasymptotic form.[7,8] By using the Bloch enhancement factor α and a strain-coupling constant λ (which can account for the inadequacy of the point-ion model[6] in determining the F tensor) as adjustable parameters, Sagalyn and Alexander[4] studied the efg's at first two near-neighbor sites in Cu-based alloys and obtained semiquantitative agreement with experiment. There are several drawbacks in this work. To list a few, we have the following:
(1) The variations in the adjustable parameters between different neighbors and different impurities were rather large. Furthermore, the magnitude of λ was as large as 87 whereas Faulkner[6] had predicted an upper limit of 7 for copper.
(2) Most of the conclusions regarding the importance of valence contribution are based upon the assumption that the preasymptotic form for the charge density is valid even at the first-neighbor site. Not only is the validity of such an approximation in doubt, but the preasymptotic form was obtained with use of empirical phase shifts.
(3) The spatial dependence of the displacement vector $\vec{u}$ in Eq. (2) used in their calculation suggests that all the neighbors would move along the same direction, in disagreement with earlier calculations.[9,10]

In our theory we have tried to remedy all these shortcomings. We begin with the calculation of the valence contribution to efg. If we assume that the induced charge density and the potential are spherically symmetric around the defect, Poisson's equation yields

$$d^2V/dr^2 + 2r^{-1}dV/dr = 4\pi e[\delta n(r) - \delta n_{\rm ext}(r)], \tag{3}$$

where e is the magnitude of the electron charge. $\delta n_{\rm ext}$ and δn are, respectively, the perturbations caused in the positive and negative charge distribution of the metal due to a defect. If the z axis is chosen along the direction connecting the impurity and the host ion under consideration, the traceless efg tensor is given by

$$eq_{zz} = d^2V/dr^2 - \tfrac{1}{3}\nabla^2 V. \tag{4}$$

With use of Eqs. (3) and (4) and the notations in Ref. 4, it can be shown after some algebraic manipulation that

$$q_{\parallel}{}^{V}(r) = \tfrac{8}{3}\pi\,\alpha(k_{\rm F})\{\delta n(r) + (3/4\pi r^3)[Z_{\rm eff} - Z(r)]\}, \tag{5}$$

where $Z(r) = \int_0^r \delta n(r) d^3r$ is the induced electron charge within a sphere of radius r around the point defect. Thus for $r \to \infty$, $Z(r) \to Z_{\rm eff}$, the effective charge on the defect ion. In the asymptotic region, the second term inside the curly brackets in Eq. (5) is zero, and one recovers the usual formula of Kohn and Vosko.[3] It can be easily shown that if the potential and induced charge density are kept to the order r^{-4} (preasymptotic) one recovers the expression of Jensen, Nevald, and Williams exactly.[8] It should be emphasized that the charge density $\delta n(r)$ in Eq. (5) is obtained self-consistently in the density-functional theory and is valid at *all* distances from the point defect. Thus the efg in Eq. (5) does not suffer from the shortcomings associated with the validity of the asymptotic and preasymptotic form at first few nn sites. It should also be pointed out that the contributions to the efg from outside the host atomic sphere (the so-called distant contribution) have been calculated with use of the geometry prescribed by Sagalyn and Alexander.[4]

For computation of the strain tensor, we have considered a different form for the displacement

vector

$$\vec{u} = A\cos(2k_F r + \varphi)\vec{r}/r^n, \quad (6)$$

where A and φ are constants. This choice was motivated by the well-known oscillatory dependence of the scattering charge density and potential at large distance from the point defect. The exponent n in Eq. (6) is assigned a value of 3, which is consistent with Eq. (2) as well as computer simulation studies[10] in fcc crystals. The constant A is chosen such that the displacement of the nearest neighbor agrees with either experimental value (if available) or with first-principles theory. The constant φ is determined from the equilibrium conditions of the continuum theory of elasticity[11] and thus is not an adjustable parameter.

Using Eq. (6), we have solved the traceless efg tensor equation $eq_{ij}{}^s = V_{ij}{}^s - \frac{1}{3}\delta_{ij}\nabla^2 V^s$ for the strain along with $V_{ij}{}^s = \sum_{m,n}\epsilon_{mn}F_{ijmn}$ and obtained

$$q_{ij}{}^s = [(F_{11}-F_{12})\delta_{ij} + 2(1-\delta_{ij})F_{44}]\left(\frac{A\cos(2k_F d_\nu + \varphi_\nu)}{2d_\nu{}^3 e}\right)\left(\frac{n(n-1)+4k_F{}^2 d_\nu{}^2}{(n-2)d_\nu{}^{n-3}}\right)\left(\frac{1}{3}\delta_{ij} - \frac{x_i x_j}{d_\nu{}^2}\right). \quad (7)$$

Here, ν refers to the configuration (i.e., first nn, second nn, etc.) of the near neighbor at a distance of d_ν from the point defect. In the point ion model,[6] $F_{11}-F_{12} = 9\lambda e/d_1{}^3$, and $F_{11}-F_{12} = -3F_{44}$. Here λ, as mentioned earlier, is a dimensionless strain-coupling parameter which corrects for the fact that a solid is idealized by point charges. This concludes our discussion of the formalism.

We have applied this theory to calculate the efg distribution around a monovacancy in Al. This choice was dictated by the following reasons: (1) Recent single-crystal NMR data[12] are available up to fourth nn sites. Also a large asymmetry parameter ($\eta = 0.65$) was observed in the efg tensor at the first nn site. (2) Al is a simple metal and the assumptions made here are believed to be reasonable for Al. (3) A monovacancy in Al corresponds to a charge difference of $\Delta Z = 6$ between the point defect and the host ion and thus constitutes a large perturbation on the electronic environment. (4) First-principles calculation of lattice displacement around a monovacancy in Al is also available.

The charge screening and the valence contribution to efg were calculated self-consistently in the density-functional theory.[13,14] We have compared our calculated induced electron density $\delta n(r)$ with the asymptotic and preasymptotic forms which were computed from our calculated phase shifts for $0 \le l \le 6$. We find that the true induced charge is very different from the approximate forms at the first few nn sites. Thus any conclusion drawn from the use of approximate charge densities is deemed to be unreliable. We have found that the correction to the Kohn-Vosko form in Eq. (5) is important up to as far as fourth-neighbor sites. Also the size of the distant contribution[4] as mentioned earlier is comparable to that in Eq. (5).

The strain contribution in Eq. (7) was calculated by first determining A in Eq. (6) such that the displacement of the first nn is in agreement with Singhal's calculated 1.74% inward displacement. With the value of φ determined from the equilibrium conditions,[11] as discussed above, Eq. (6) predicts the displacements of the 2nd, 3rd, and 4th neighbors to be -0.42%, -0.19%, and -0.10%, respectively. These have to be compared with Singhal's values[9] of -0.93%, -0.23%, and -0.07%, respectively.

In Table I our results for the largest component

TABLE I. Electric field gradient q(Å^{-3}) and asymmetry parameter η at four nn sites due to a monovacancy in Al with the antishielding factor $(1-\gamma_\infty)$ from Ref. 16 and the Bloch enhancement factor α from Ref. 17. Here $q = q^\nu + q^s$. The values for q^s, q, and η from theory are calculated with use of Eq. (7) and $\lambda = -1.7$.

	Theory				Experiment	
nn	q^ν	q^s	q	η	$\lvert q\rvert$	η
1	0.037	−0.314	−0.277	0.78	0.28	0.65
2	0.008	−0.199	−0.191	0	•••	•••
3	≈0	−0.092	−0.092	0.76	0.093	•••
4	−0.002	−0.074	−0.076	0.24	0.069	•••

of the efg tensor and asymmetry parameter are compared with the experimental values. Several comments have to be made:

(i) The strain coupling parameter λ was chosen to fit our computed efg at first-nn site so that it agrees with experimental value. This led to a value of $\lambda = -1.7$. It should be pointed out that Chakraborty, Pickett, and Siegel[15] have carried out a supercell calculation of the lattice displacement around a monovacancy in Al. Their result for the first-nn displacement is 2.5% inward. If we use this displacement instead, a value of $\lambda = -1.2$ is obtained since the leading term in the strain contribution to efg is proportional to the fractional displacement. It should be emphasized that the calculated efg in Eq. (7) is independent of how the amplitude A in Eq. (6) is fitted to various calculated displacements since $q_{ij}{}^{s} \propto A\lambda$. Thus the strain coupling parameter λ can be adjusted to accommodate any variation in the value of A.

(ii) The valence contribution to the efg for all the neighbors considered here is small in comparison to the strain contribution.

(iii) Our computed efg at other nn sites is in quantitative agreement with experiment.

(iv) When the efg due to strain is calculated using the radial displacement in Eq. (2), we find that $\lambda = -29$ is needed to obtain agreement even for the first-nn site. This value of λ is much larger compared to that obtained using the form of the displacement vector in Eq. (6). This large difference in the values of λ is a consequence of the additional term $4k_F{}^2 d_\nu{}^2$ in Eq. (7) which is absent if the displacement vector in Eq. (2) is used. Furthermore, the form which uses Eq. (2) predicts the efg at 2nd, 3rd, and 4th neighbor to be -0.134, -0.054, and -0.039 Å^{-3}, respectively, in worse agreement with experiment. The asymmetry parameters, η, on the other hand, for the first four nn are 0.78, 0, 0.76, and 0.18, respectively.

(v) The computation of the efg for the third nn is much more complicated than for the other nn sites considered here. This is because of the fact that the principal axes of the valence-effect and the size-effect tensors do not coincide. Fortunately, the valence contribution to the efg at the third nn is nearly zero and the above problem does not concern us for this particular application.

(vi) If the valence contribution to the efg were also zero for the first and fourth nn, it can be shown that the asymmetry parameter $\eta = 0.33$ for both the neighbors. The large difference between the calculated value of η in Table I for these two nn's is due to the role of valence effect. This clearly illustrates the need for a better understanding of the valence contribution even though its influence in determining the efg for any nn seems to be less important for the present application.

(vii) The value of η for the third nn is rather large and is independent of λ as well as of the form for the lattice displacement vector $\vec{u}$ as long as the valence contribution is zero. Thus, an experimental determination of η for the third and fourth nn will serve as a further check on the quantitative accuracy of this theory.

(viii) The valence effect is expected to die out faster than the size effect as one goes further away from the point defect since the latter is a mechanical property while the former is an electrical property which is screened out in a metal. This is reflected in our results in Table I.

In conclusion, we have presented a complete theory for efg in cubic metals due to point defects which is valid at nn sites. The conduction-electron contribution was calculated in a self-consistent theory and the strain contribution with use of a new form for the displacement vector. While the quantitative agreement achieved here is gratifying, the reader must be cautioned against premature optimism unless the theory is capable of explaining efg systematically in several cubic metal alloys. It is our hope that this paper will stimulate further work in both theory and experiment.

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Bardeen-Cooper-Schrieffer Pairing in Antiferromagnetic Superconductors

M. J. Nass and K. Levin
The James Franck Institute and Department of Physics, The University of Chicago, Chicago, Illinois 60637

and

G. S. Grest
Department of Physics, Purdue University, West Lafayette, Indiana 47907

(Received 21 November 1980)

The mean-field theory of an antiferromagnetic superconductor is solved and some fluctuation effects are discussed. In contrast to claims of other authors, it is found that the pairing is of the usual BCS type, $\Delta = \langle C_{\vec{k},\uparrow}^{\dagger} C_{-\vec{k},\downarrow}^{\dagger} \rangle$. Results for the gap parameter $\Delta(T)$ and $H_c(T)$ are presented. The latter is similar to the measured $H_{c2}(T)$. The ratio $\Delta(0)/T_c$ and the (nonmonotonic) temperature T dependence of H_c and $\Delta(T)$ are shown to deviate markedly from BCS theory.

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The recent discovery of antiferromagnetic (AF) superconductors[1] has revived interest in the problem of coexistent magnetic and superconducting order. In this Letter we present a mean-field theory and discuss some fluctuation effects for a system of superconducting electrons interacting with antiferromagnetically ordered localized spins. While we treat a somewhat idealized three-dimensional system, our qualitative results are relevant to the Chevrel-phase and rare-earth rhodium boride AF superconductors.

One purpose of this paper is to establish the nature of the (most favorable) Cooper pairs: We find, in contrast to a previous claim,[2] that the order parameter is of the usual BCS type, $\langle C_{\vec{k},\uparrow}^{\dagger} C_{-\vec{k},\downarrow}^{\dagger} \rangle = \Delta_0 \equiv \Delta$. Another aim is to calculate the thermodynamic variables Δ, T_c, and H_c. In particular, we find a nonmonotonic temperature T dependence of Δ and H_c. The latter quantity, which is related to the difference of the free energies in the normal and superconducting phases, is found to have a T dependence rather similar to that of the measured upper critical field H_{c2} (Ref. 3) for the Chevrel-phase AF superconductors.

The importance of doing a mean-field calculation should be emphasized. First, it is essential in order to properly characterize the Cooper pairs. Second, it is a necessary first step in any treatment of fluctuation effects. Using mean-field theory as a basis, we can then obtain the Eliashberg-like equations for the renormalized gap function $\tilde{\Delta}$ and effective mass from which we derive the superconducting density of states and an effective spin-flip lifetime τ_s. We will discuss this briefly at the end of this paper and in more detail in a subsequent work.

Our Hamiltonian contains the d-electron kinetic energy, the d-electron–f-electron exchange interaction J^{df} (assumed constant for simplicity), and the d-d interaction arising from the phonons. In our mean-field theory we replace the Fourier transform of the f-electron spin operator S_i by a temperature-dependent molecular field $H_Q \equiv J^{df}\langle S_Q \rangle / 2N$, where $\vec{Q}$ is the wave vector of the antiferromagnetic order. The electron-electron term, which is written as

$$-\sum_{\substack{\vec{k},\vec{k}',\vec{q},\\ \sigma,\sigma'}} V_{\vec{k}\vec{k}',\vec{q}} C_{\vec{k}+\vec{q},\sigma}^{\dagger} C_{\vec{k}',-\vec{q},\sigma'}^{\dagger} C_{\vec{k}',\sigma'} C_{\vec{k},\sigma},$$

allows electron pairing with $q = 0$ and $q = \pm Q$, all of which must be included in order to proceed in the most general way.