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Role of Conduction Electrons in Electric-Field Gradients of Ordered Metals

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Measurements of the electric-quadrupole interaction of V^{51} nuclei in the ordered β-wolfram structure V_3X (X=Ga, Si, Au, etc.) intermetallic compounds suggest a correlation between the magnitudes of the electric-field gradients at the vanadium sites and the density of electronic states at the Fermi energy $\eta(E_F)$. The conduction-electron contributions to an electric-field gradient in a metal have been inspected and the results indicate that the above correlation can indeed be expected and that conduction-electron field-gradient terms which are linearly related to $\eta(E_F)$ are of experimental significance in many metals, ordered and disordered. In these investigations, the sources of the field gradient have been divided into three terms: (1) the lattice contribution, q_{latt}, arising from the electronic and nuclear charge external to an atomic sphere drawn about the nuclear site in question, (2) a local contribution, q_{loc}, arising from conduction electrons within the sphere, and (3) Sternheimer antishielding contributions arising from the distortions of the ionic core. Attention is focused on q_{loc} and, in particular, on those contributions coming from electron states in the vicinity of the Fermi surface. This is done by inspecting the change q' in q_{loc} associated with the repopulation of Bloch states of different symmetries at the Fermi surface when q_{latt} *and* its associated potential of $Y_2^0(\theta,\phi)$ symmetry within the sphere are turned on (or off). Although this effect does not include all Fermi-surface contributions to q_{loc}, a "coherence" due to the common symmetry of the perturbing potential and the gradient operator tends to make this term important. It is linearly related to both q_{latt} and $\eta(E_F)$, and tends to strongly shield the lattice gradient. For example, a maximum estimate of its value for V_3Ga is in excess of $-100q_{\text{latt}}$. Thus, we are dealing with an "overshielding" which, contrary to traditional expectations, can cause a field gradient which is linearly related to q_{latt} to be ***opposite in sign*** to it. The investigation suggests that this term will be of experimental significance in p band as well as high $\eta(E_F)$ transition metals. Self-consistent effects have been included in the calculation and do not destroy the tendency toward strong shielding. The electron-phonon interaction is inspected and found not to play a role in these terms [i.e., a "bare" $\eta(E_F)$ should be used]. Finally, the effect of thermal repopulation on the temperature dependence of q_{loc} is considered.

I. INTRODUCTION

NUCLEAR-QUADRUPOLE interactions in metals have been the object of considerable investigation in recent years. Of particular interest has been the source(s) of the electric-field gradient q which interacts with the nuclear-quadrupole moment. In the earliest work, surprisingly[1] good predictions of experimental q values were obtained with simple lattice sums over point charges assumed due to the positive ion cores of the other atomic sites of the metal (which are incompletely screened by the system's conduction electrons). More recently, attention[2] has centered on the contributions to q from the conduction electrons in the immediate vicinity of the nucleus in question and it is to this matter that the present paper will be addressed. Emphasis will be placed on the role played by the conduction electrons which are in the immediate vicinity of the Fermi surface and on the implications of such behavior for all metals (ordered *or* disordered) with high densities of electronic momentum states $\eta(E_F)$ at the Fermi energy. We will concentrate on temperature-independent effects but temperature-dependent terms associated with the Fermi surface will be considered.

The present work was stimulated by the experimental results plotted in Fig. 1, where we see the V^{51} nuclear-quadrupole interaction as measured by nuclear magnetic resonance, plotted versus $\eta(E_F)$, as deduced from electronic specific-heat data, for several of the V_3X (where X=Si, Ge, Ga, As, etc.) intermetallic compounds.[3] The figure shows a correlation between the field gradients and the $\eta(E_F)$ which suggests that the Fermi-surface electrons may play a role in determining the field gradient in a metal. Note that only the magnitude of the gradients is plotted. The figure suggests that the gradient appropriate to V_3Ir (and perhaps

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[1] W. D. Knight, Phys. Rev. **92**, 539 (1953); T. J. Rowland, *Nuclear Magnetic Resonance in Metals* (Pergamon Press, Inc., New York, 1961), p. 27 and references cited therein.

[2] M. Pomerantz and T. P. Das, Phys. Rev. **119**, 70 (1960); R. R. Hewitt and T. T. Taylor, *ibid.* **125**, 524 (1962); W. J. O'Sullivan and J. E. Schirber, *ibid.* **135**, A1261 (1964); E. H. Hygh and T. P. Das, Bull. Am. Phys. Soc. **9**, 264 (1964); E. H. Hygh, Ph.D. thesis, University of California, Riverside, 1964 (unpublished); and P. Tobin and G. Benedek, Bull. Am. Phys. Soc. **10**, 75 (1965).

[3] The regions indicated for V_3Pt, V_3Sn, and V_3As are due to the lack of knowledge of their $\eta(E_F)$ behavior.

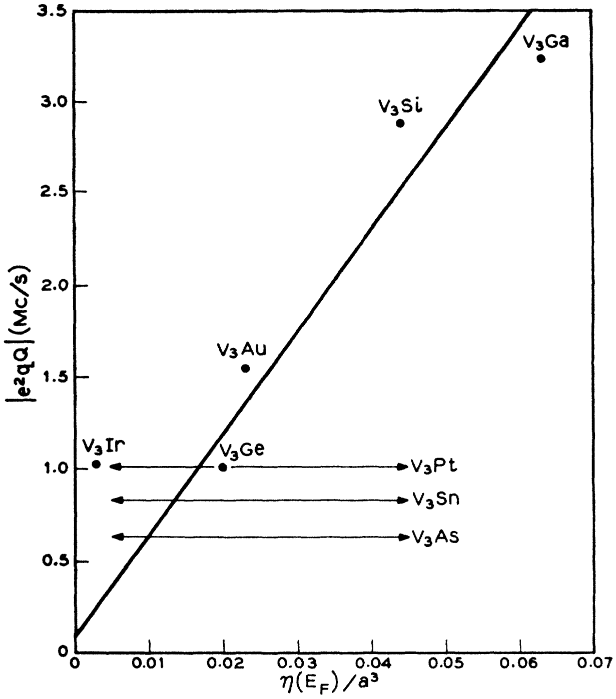

FIG. 1. The *magnitude* of the V^{51} electric-quadrupole interaction $|e^2qQ|$ plotted as a function of the density of states at the Fermi surface, $\eta(E_F)$, as deduced from electronic-specific-heats measurement (and normalized to the lattice cell volume) for various $V_3X(X=\mathrm{Si}$, Ge, Ga, etc.) compounds. In the cases of V_3Pt, V_3Sn, and V_3As, $\eta(E_F)$ has not been obtained experimentally.

several others) is opposite in sign to that for V_3Ga and V_3Ge, causing a negative intercept.

In this paper we will consider a field-gradient contribution which samples the behavior of electrons at the Fermi surface and which is linearly related to ***both*** $\eta(E_F)$ and the field gradient, q_{latt}, arising from the lattice external to the ion site. This contribution will in general be of opposite sign to q_{latt} and may be larger in magnitude than q_{latt}. This conduction-electron contribution is estimated in Sec. III and the results suggest that it may dominate for metals with large $\eta(E_F)$ and orbitally degenerate conduction bands. The results also indicate that this term may be very significant for p-band metals despite their comparatively small $\eta(E_F)$ values. Questions concerning self-consistency arise for such a gradient contribution and these are considered in Sec. IV. There is also the question of whether an $\eta(E_F)$ deduced from electronic specific-heat data and involving electron-phonon enhancement is appropriate to the quadrupole effects considered in this paper or whether one should utilize the "bare" electron $\eta(E_F)$. In Sec. V we conclude that the bare $\eta(E_F)$ should be used. The temperature dependence of the electric-field gradient due to Fermi-surface electrons is discussed in the conclusion and is considered in greater detail in an Appendix. In another Appendix we consider the V_3X structure, the q_{latt} which might be appropriate to it, the energy-band results Mattheiss[4] has obtained for these compounds and finally the question of the value of the V^{51} nuclear-quadrupole moment Q.

The V_3X compounds will be the particular object of attention in this paper but crude estimates will be made for a large number of pure metals. Some evidence will emerge suggesting that the ideas developed in this paper may very well be more appropriate for some of these other metals. Exact statements will not be made for any particular metal because of insufficient knowledge of Fermi-surface conduction-electron character. Our purpose in the paper is to provide a qualitative picture of the effect of Fermi-surface electrons on electric-field gradients. In the process we have used what might be called a tight-binding—augmented-plane-wave model of conduction-electron behavior in order to segregate what we believe to be the most interesting features of the conduction-electron contribution to a field gradient.

II. ELECTRIC-FIELD GRADIENTS IN METALS

The electric-field gradient at a nucleus arises from the distribution of charge (both electronic and nuclear) about it in space and is given by

$$eq=2\int_{\text{all space}}\rho(\mathbf{r})\frac{1}{r^3}P_2{}^0(\cos\theta)d\tau. \qquad (1)$$

However, for convenience it is useful to consider a field gradient in a metal as arising from three separate sources. Let us draw a sphere about the nuclear site at which we wish to evaluate q as is done in Fig. 2. The sphere radius can be chosen so that spheres touch for near neighboring atomic sites. The first gradient contribution is q_{latt} arising from the region outside of the sphere, namely

$$eq_{\text{latt}}=2\int_{\text{outside atomic sphere}}\rho(\mathbf{r})\frac{1}{r^3}P_2{}^0(\cos\theta)d\tau, \qquad (2)$$

where ρ is the nuclear plus electronic-charge density. The integral can be replaced by a lattice sum over point charges and higher multipoles centered at the various lattice sites. Multipoles as high as the hexadecapole can be experimentally significant.

The second contribution comes from the conduction electrons within the atomic sphere, i.e.,

$$eq_{\text{loc}}=2\int_{\text{atomic sphere}}\rho_{\text{cond}}(\mathbf{r})\frac{1}{r^3}P_2{}^0(\cos\theta)d\tau, \qquad (3)$$

$$\equiv 2\sum_{i}^{\substack{\text{occupied conduction-}\\ \text{electron states}}}\int_{\text{atomic sphere}}\rho_i(\mathbf{r})\frac{1}{r^3}P_2{}^0(\cos\theta)d\tau, \qquad (3a)$$

where ρ_i is the charge density of conduction electron i. It is the behavior of q_{loc}, and the question of how this

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[4] L. F. Mattheiss, Phys. Rev. **138**, A112 (1965).

may be correlated with $\eta(E_F)$, and other features of Fermi surface electrons which will preoccupy us in this paper.

Finally there are contributions from the closed-shell core electrons at the atomic site in question. In first approximation they are spherical and make no contribution to q but they become distorted under the influence of their aspherical environment and interact in turn with the nuclear-quadrupole moment. These distorted *core* interactions may be accounted for in terms of the familiar Sternheimer antishielding factors[5] γ_∞ and R_Q appropriate to

$$q=q_{\text{latt}}(1-\gamma_\infty)+q_{\text{loc}}(1-R_Q). \tag{4}$$

For the V core appropriate to the V_3X compounds, we estimate $(1-\gamma_\infty)\sim 8\pm 2$ and $(1-R_Q)\sim 1.0\pm 0.2$. We will assume values of 8 to 15 for $(1-\gamma_\infty)$ and of 1 for $(1-R_Q)$ for the V_3X compounds *and* other metals considered henceforth in this paper.

The electric-field gradient (EFG) in a metal is typically 5 to 20% of what a single valence electron would produce in the free-parent ion. For example, for pure indium the gradient is of the order of 2% while for tin it is somewhere between 8 and 25%. In other words, a gradient arises from rather severe cancellation, a fact which makes serious theoretical estimates most difficult.

Matters are further complicated by the fact that one experimentally observes e^2qQ, where Q is the nuclear-quadrupole moment. An experimental estimate of q requires knowledge of Q, a quantity based on someone else's estimate of q for a system where they had measured e^2qQ. The V^{51} moment, of interest in this paper, provides a good example of what can happen and a review of estimates of its value appears in Appendix I. Also appearing in the Appendix is a discussion of the structure of the V_3X compounds shown in Fig. 3 and of the q_{latt} associated with them.

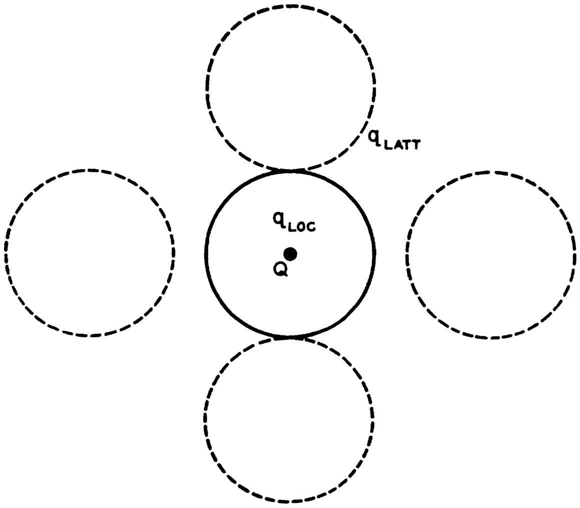

FIG. 2. Atomic spheres for a hypothetical metal with q_{loc} arising from the conduction-electron charge within the sphere and q_{latt} from the nuclear and electronic charge outside.

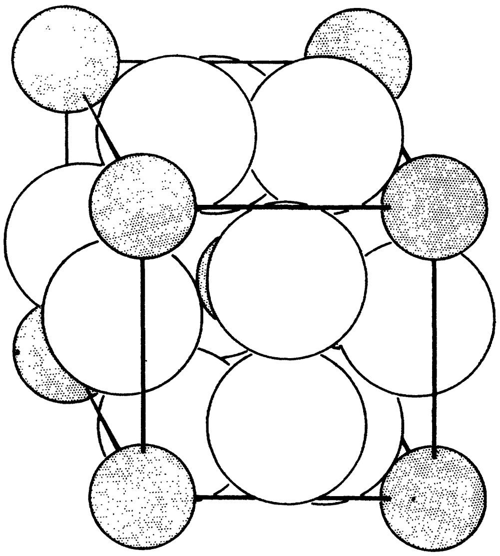

FIG. 3. The unit cell for the V_3X(X=Si, Ge, Ga, etc.) compounds having the β-wolfram structure, the X atoms being shaded. The V atoms form nearest-neighbor chains lying in the x, y, or z direction.

III. THE DENSITY-OF-STATES DEPENDENCE OF q

One would expect dependence of the field gradient on $\eta(E_F)$ to be primarily associated with q_{loc}, the contribution to the EFG from conduction electrons within the atomic sphere. Actually, q_{latt} may also show such dependence[6] but we expect it to be much weaker. We will, therefore, concentrate on q_{loc} in this section, with a few observations concerning q_{latt} appearing later.

For convenience we will quite arbitrarily divide q_{loc} into three terms

$$q_{\text{loc}}=q^0+q'+q'' \tag{5}$$

which arise in the following way. As our starting point, let us assume that we have a set of Bloch functions which are eigenfunctions of a crystal potential which is spherical within atomic spheres about each atomic site as in Fig. 2. The Bloch functions will have the symmetry of the crystal since the array of atomic spheres has that symmetry. Given the Bloch functions and their energy eigenvalues, one can construct the Fermi surface and in turn evaluate Eq. (3) obtaining a local gradient, which we will call q^0.

Now, if the external environment is such as to pro-

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[5] For example see R. M. Sternheimer, Phys. Rev. **80**, 102 (1950); **84**, 244 (1952); **86**, 316 (1954); **95**, 736 (1954); **96**, 951 (1954); **105**, 158 (1957); **130**, 1423 (1963).

[6] This will arise from polarization contributions to Eq. (2) which are similar to the q_{loc} terms considered in this section, see e.g., M. Pomerantz and T. P. Das, Phys. Rev. **119**, 70 (1960).

duce a nonzero q_{latt}, it will also produce a potential term within the atomic sphere of the form

$$V_2(\mathbf{r}) = -(e^2/2)q_{\text{latt}}r^2P_2{}^0(\cos\theta)\,. \tag{6}$$

Let us add this term to the potential seen by the Bloch electrons and reevaluate Eq. (3). There will then be two gradient contributions in addition to q_0. First, the V_2 potential will contribute first-order shifts to the Bloch-function energies causing a redistribution of occupied states in the immediate vicinity of the old Fermi surface. The gradient contribution associated with this redistribution is q'. Secondly, there is q'' which is associated with spatial distortions of the Bloch functions. This includes terms which are linear in V_2 and are analytically similar to the familiar Sternheimer antishielding of core electrons. Experience with Sternheimer antishielding suggests that these lowest order terms form the dominant part of q''.

Of the three terms, q' samples function character only in the region of the Fermi surface and can be expected to depend on $\eta(E_F)$ while q^0 and q'' measure the behavior of *all* occupied conduction-electron states. The q^0 and, in particular, q'' are not expected to be strongly correlated with $\eta(E_F)$.

The breakdown of q_{loc} into three terms has been done deliberately in order to segregate q' from the remaining contributions. The starting point yielding this segregation was the use of a spherical potential within the atomic sphere. Just such a potential is used in many current energy band efforts (in particular with integral techniques such as the augmented plane-wave method.[7]) This coincidence is of no significance to us here. What is important is that V_2 was omitted, rather than that the potential was spherical, when q^0 was obtained.

It is convenient to normalize our Bloch functions to a single atomic sphere[8] when estimating q'. Doing this and designating that fraction of states at the Fermi surface having particular spatial character by f_i, the change in population of these states is

$$\begin{aligned}\Delta n_i &= -2\eta(E_F)f_i\{\langle V_2\rangle_i - \delta E_F\}\\ &= -2\eta(E_F)f_i\{[-(e^2/2)q_{\text{latt}}]\\ &\qquad\times\langle r^2P_2{}^0(\cos\theta)\rangle_i - \delta E_F\}\,,\end{aligned} \tag{7}$$

where $\langle\ \ \rangle_i$ is the expectation value for an orbital with spatial character i; the factor 2 accounts for the fact that, by convention, $\eta(E_F)$ is defined for electrons of a single spin m_s; δE_F is the shift in the Fermi energy required by the conservation of particles, i.e.,

$$\textstyle\sum_i \Delta n_i = 0 \tag{8}$$

yielding

$$\begin{aligned}\delta E_F &= [-(e^2/2)q_{\text{latt}}]\textstyle\sum_i f_i\langle r^2P_2{}^0(\cos\theta)\rangle_i\\ &\equiv [-(e^2/2)q_{\text{latt}}]\langle\langle r^2P_2{}^0(\cos\theta)\rangle\rangle\,.\end{aligned} \tag{9}$$

The ith component contribution to q' is

$$(q')_i = -2\Delta n_i\langle r^{-3}P_2{}^0(\cos\theta)\rangle_i \tag{10}$$

where the minus sign is associated with the electronic charge. Summing to obtain q' we have

$$\begin{aligned}q' = -2e^2q_{\text{latt}}\eta(E_F)&\textstyle\sum_i f_i\langle r^{-3}P_2{}^0(\cos\theta)\rangle_i\\ &\times\{\langle r^2P_2{}^0(\cos\theta)\rangle_i - \langle\langle r^2P_2{}^0(\cos\theta)\rangle\rangle\}\,.\end{aligned} \tag{11}$$

In this and the preceding expressions, the f_i sampling and sum over i could be replaced by an integration, $\int dS_{\mathbf{k}}$, over the sheets(s) of the Fermi surface. The latter choice involves a more detailed sampling over the Fermi surface than is required for the problem at hand. We are not involved with such matters as the topology of the Fermi surface, the energy dependence of the energy bands in the vicinity of ϵ_F, or where a particular orbital lies on the Fermi surface. We are instead interested only in how much of each sort of spatial character is associated with the Bloch orbitals at the Fermi surface.

A nonzero δE_F tends to reduce q', i.e., the greater $|\delta E_F|$, the smaller the fraction of $\langle \mathrm{V}_2\rangle$ energy contributing to repopulation. As we are interested in gaining some insight into the extreme behavior allowable for q' let us assume, for the moment, that $\delta E_F = 0$ and, for convenience, that individual Bloch orbitals within the sphere can be expressed as a product of a radial function times an angular part.[9] With these assumptions

$$q' \to -2e^2q_{\text{latt}}\eta(E_F)\textstyle\sum_i f_i\langle r^2\rangle_i\langle r^{-3}\rangle_i(\langle P_2{}^0(\cos\theta)\rangle_i)^2 \tag{12}$$

and in this form the essential properties of Eq. (11) become prominent. First, we are involved with the square of the $\langle P_2{}^0(\cos\theta)\rangle_i$ matrix elements because of the common angular symmetry of the V_2 and field-gradient operators. This leads to a "coherence" in the contributions from the different terms in the i summation, a coherence which is one reason for our preoccupation with q'. Secondly, the individual factors multiplying q_{latt} are all positive. Therefore q' is of opposite sign to q_{latt}, shielding it. On going from Eq. (12) back to (11), this tendency will hold. Shielding will generally persist,[10] through Fermi energy shifts, δE_F (and perhaps by mixtures of s and d character in the orbitals) will reduce its effectiveness. Thirdly, we see that q' is linearly dependent on $\eta(E_F)$ while also

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[7] J. C. Slater, Phys. Rev. **51**, 846 (1937); **92**, 603 (1953).

[8] It might seem more appropriate to replace the atomic spheres by atomic polyhedra. For present purposes it makes no significant difference.

[9] Note that this does not imply an angular function which is a spherical or cubic harmonic involving a single l value.

[10] Under special circumstances q' can reverse sign and become antishielding. Typically this would involve a set of Fermi-surface Bloch functions with identical or almost identical angular behavior [otherwise the angular character of Eqs. (11)–(12) will cause shielding] and appreciably differing radial behavior. This, with an associated, and substantial, δE_F could lead to antishielding. We doubt that the necessary conditions would ever be met by a set of Bloch functions for a solid and if by chance they were, the antishielding would be several orders of magnitude smaller than the shielding considered in this paper. A set of predominantly s-like Fermi surface orbitals with small d admixing *might* yield a negative sum in Eq. (11). If so, it would be small in magnitude and would have a small $\eta(E_F)$ associated with it again yielding a weak antishielding.

TABLE I. Expressions for q' for several simple choices of the f_i and of the spatial d- or p-electron character associated with them. Orbitals are assumed to be purely d (or p) like and to have common radial behavior. Estimates (see text) of q'/q_{latt} for V_3Ga are also listed.

Case	Band	Orbital symmetry	$q'/e^2q_{\text{latt}}\eta(E_F)\langle r^2\rangle\langle r^{-3}\rangle$	q'/q_{latt} as estimated for V_3Ga
a	d	$d_{xy}+d_{yz}+d_{zx}$; $f_i=1/3$ for each	$-4/49$	-110
	p	$p_x+p_y+p_z$; $f_i=1/3$ for each	$-4/25$	$\cdots$
b	d	Spherical bands where	$-8/245$	-44
	p	$\Phi_{l,\mathbf{k}}\sim\sum_{m=-l}^{l} Y_l^{-m}(\theta_k\varphi_k)\Psi_{l,m}$	$-8/125$	$\cdots$
c	d	$d_{3z^2-r^2}+d_{x^2-y^2}$; $f_i=1/2$ for each	$-8/49$	-220

taking a detailed sampling of the spatial character of the Fermi-surface orbitals. It does not, of course, depend on the geometric shape of the Fermi surface. In general one would expect changes in the sum in Eqs. (11) or (12) to be as important as changes in $\eta(E_F)$ on going from one metal to another. The V_3X compounds may provide a minor exception. Their Fermi surfaces lie on a common peak of the density of states curve (assuming a rigid band model for these metals) and inspection of Mattheiss's energy band results[4] suggests that there will be very similar functional character on going from V_3Ga to V_3Ge, though not so, on going further to V_3As. In other words, q' may show a strong linear dependence on $\eta(E_F)$ here. There remains, of course, the question of whether q' is a significant fraction of the total V_3X vanadium gradient.

A detailed quantitative estimate[11] of q' for a particular metal is at best formidable due to the lack of sufficient knowledge of Fermi-surface orbital character. We will not attempt a "realistic" calculation based on the band structure of a particular metal but will instead inspect three simple cases of spatial distribution which should give some indication of q' behavior. In all three cases δE_F equals zero and for all three we will assume that the orbitals are purely d like[12] (or for p-electron metals, p like) within the atomic sphere, with common radial behavior so that the $\langle r^2\rangle\langle r^{-3}\rangle$ product may be brought outside the summation of Eq. (12). The three cases are indicated in Table I. Case (b) was suggested by the Rayleigh plane-wave expansion, where θ_k and φ_k are the angles taken by $\mathbf{k}$. The other cases involve the cubic p- and d-electron representations. Case (a) represents the largest p band, case (c) the largest d band, q' compatible with the requirement of common orbital radial behavior at the Fermi surface. We would like to use the expressions, given for these three cases, to estimate q' for various pure metals and for the V_3X compounds in particular. In this, we will use $\eta(E_F)$ values as deduced from electronic-specific-heats measurements and will, for the moment, ignore any question of the appropriateness of this choice. We obtain $\langle r^2\rangle\langle r^{-3}\rangle$ values from free-ion Hartree-Fock wave functions (integrated to infinity) with some effort at choosing the atomic configuration most appropriate to the metal.[13] Having not integrated out to just our sphere radius, these $\langle r^2\rangle\langle r^{-3}\rangle$ will tend to overestimate the magnitude but not the sign of q'.

Using the observed[14] V_3Ga $\eta(E_F)$ of 7.1 states of one spin per vanadium per electron volt, and a $\langle r^2\rangle\langle r^{-3}\rangle$ of 7 atomic units (a.u.) we obtain the results appearing in Table I. These suggest that not only is q' opposite in sign to q_{latt} but that it can be one or two orders

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[11] When estimating q's with Eqs. (7) to (12), one assumption should be borne in mind, namely that we assume that the repopulation effects do not distort the Fermi surface too severely, for otherwise one cannot simply sample wave function character at the Fermi surface. In other words the number of states populated (or depopulated), i.e.,

$$\tfrac{1}{2}\sum_i |\Delta n_i|,$$

should not be too large. Exactly what constitutes too large, is best suggested by the exact expression for Δn_i, i.e.,

$$\Delta n_i = 2\int_{E_F}^{E_F+\delta E_F-\langle V_2\rangle_i} \eta(E) f_i dE,$$

where f_i and the integration-limit contribution $\langle V_2\rangle_i$ are, themselves, functions of E. In using Eqs. (7) and (10) we assume that $\langle V_2\rangle_i$, the product $\eta(E)f_i$ and $\langle r^{-3}P_2^0(\cos\theta)\rangle_i$ do not vary too severely as one moves a distance $\delta E_F-\langle V_2\rangle_i$ off of the original Fermi surface. For high $\eta(E_F)$ metals one would suspect that $\eta(E)f_i$ is most liable to vary and comparison of the $\Sigma|\Delta n_i|$ with $\eta(E)$ behavior in the vicinity of the Fermi surface, provides a crude check on the seriousness of this. We should note that $\Sigma|\Delta n_i|$ is linearly dependent on $\eta(E_F)$ and q_{latt}.

[12] Mattheiss's energy-band results (Ref. 4) indicate that this is true to something like 98% in the V_3X compounds.

[13] For the V_3X compounds with their two constituent atoms, we must make further assumptions concerning Fermi-surface orbital character. First, we will assume that the Fermi-surface character, i.e., $\eta(E_F)$, is entirely associated with vanadium sites, an assumption which Mattheiss's calculations show to hold to better than ninety percent. Secondly, with three types of V sites (on the x, y, and z lines, respectively), there arises the question of whether interference can occur between the polarization associated with different sites. We will avoid this by assuming that one-third of the Fermi-surface Bloch electrons can be entirely associated with one set of vanadium lines. Within the nearest-neighbor tight-binding approximation, this assumption is rigorously justified but in actual fact this can be only approximately done (see Appendix I).

[14] F. J. Morin and J. P. Maita, Phys. Rev. 129, 1115 (1963).

TABLE II. Values of q'/q_{latt}, and the $\langle r^2\rangle\langle r^{-3}\rangle$ and $\eta(E_F)$ on which they are based, for various metals. Case (a) was assumed throughout (see Table I).

Metal	q'/q_{latt}	$\langle r^2\rangle\langle r^{-3}\rangle$ a.u.	$\eta(E_F)$[a] States per electron volts per metal atom
Sc 3*d*	-37	~ 7[g]	2.4[b]
Ti 3*d*	-10	~ 7[g]	0.7
Co 3*d*	-20	~ 9[g]	1.0
Y 4*d*	-50 to -55	11–12[g]	2.1[b,d]
Zr 4*d*	-10 to -15	~ 12[g]	0.4 to 0.6
Ru 4*d*	-8	~ 15[g]	0.2_5
Nb in Nb_3Sn	-145	~ 15[g]	4.4[d]
La 5*d*	-650	~ 140[f]	2.1[c]
Re 5*d*	-165	~ 150[f]	0.5[d]
Os 5*d*	-65	~ 150[f]	0.2
Ga 4*p*	-17	~ 40[e]	0.1
In 5*p*	-110 to -150	75 to 100[f]	0.3_5
Sn 5*p*	-140 to -170	90 to 110[f]	0.3_5
Sb 5*p*		100 to 125[f]	
Tl 6*p*	-260	~ 200[f]	0.3
Bi 6*p*	-8	~ 200[f]	0.01

[a] Except where otherwise noted, these data come from J. G. Daunt, Progr. Low Temp. Phys. **I**, 202 (1955).
[b] H. Montgomery and G. P. Pells, Proc. Phys. Soc. **78**, 622 (1961).
[c] A. Berman, M. W. Zemansky, and H. A. Boorse, Phys. Rev. **109**, 70 (1958).
[d] F. J. Morin and J. P. Maita, Phys. Rev. **129**, 1115 (1963).
[e] From A. J. Freeman and R. E. Watson (unpublished).
[f] Relativistic and nonrelativistic Hartree results of J. Waber, D. Liberman, and D. T. Cromer (to be published).
[g] From A. J. Freeman and R. E. Watson, *Treatise of Magnetism*, edited by H. Suhl-G. T. Rado (Academic Press Inc., New York, 1965), Vol. II.

larger in magnitude as well. In such a case, $q_{\text{latt}}(1-\gamma_\infty)$ is overpowered. If we assume that q' dominates over q^0 and q'' and that the angular $\sum [P_2{}^0(\cos\theta)]^2$ character is much the same among the V_3X compounds, we find the result quite consistent with Fig. 1 and in particular with the possibility that e^2qQ changes sign as we approach zero $\eta(E_F)$. Figure 1 is thus consistent with, but by no means conclusive evidence of, an important density of states dependent q' in the V_3X's.

Estimates of q' for other metals, along with the $\eta(E_F)$ and $\langle r^2\rangle\langle r^{-3}\rangle$ values which were used, appear in Table II. These are for the pure metals with the exception of Nb in Nb_3Sn (which was treated in the same way as V_3X's).[13] For the pure metals it was assumed that $\eta(E_F)$ is associated entirely with the predominant *d* or *p* band. This should be a good approximation for the *d* metals and less so for *p* band metals where, in general, $\eta(E_F)$ is smaller. Case (a) was used throughout the table. Large $\langle r^2\rangle\langle r^{-3}\rangle$ values, rather than large $\eta(E_F)$'s cause large q'/q_{latt} ratios for some of the *p*-shell metals. This is associated with the fact that the noded valence *p* electrons penetrate close to the nucleus causing $\langle r^{-3}\rangle$ to remain large for an "outer" electron which already has an appreciable $\langle r^2\rangle$.

We have seen crude estimates of a q' term which suggest that it may, on occasion, be larger in magnitude and opposite in sign to $q_{\text{latt}}(1-\gamma_\infty)$. Its magnitude suggests that a linear theory is inadequate and that one must consider self-consistency, particularly since the repopulation will make a contribution to the potential within the sphere which is of $P_2{}^0(\cos\theta)$ symmetry and which opposes $V_2(\mathbf{r})$. Self-consistent or saturation effects are considered in the following section but before we go on to them let us consider a feature of the total field gradient, of q', and of the polarization process. Our approach was to consider a set of Bloch functions which were obtained with V_2 set equal to zero within the atomic sphere and to inspect the effect on the gradient due to turning V_2 on. This led to repopulation (q') and changes in the spatial behavior of the Bloch functions (q''). Repopulation and spatial change would also occur if a different aspherical potential (say cubic, if we are dealing with *d* bands) were turned on or, under certain circumstances,[15] if the spherical potential were merely modified. The resulting repopulation would have associated with it a change in field gradient which would be analytically similar to Eq. (11) in its dependence on the Fermi surface. The important difference is that the driving potential would not be of the same symmetry as the gradient operator and the two terms would therefore not act *coherently* when summed over Fermi-surface orbitals. Therefore, by concentrating on a q' which is driven by a $V_2(\mathbf{r})$ potential, we have not isolated the entire dependence of our total gradient q on Fermi-surface behavior. We have, though, isolated the term in this dependence which will normally tend to dominate. This term is also of interest because, like the more familiar Sternheimer core antishielding, it is linearly related to q_{latt}.

IV. SELF-CONSISTENCY

If one includes the self-consistent effects associated with repopulation, Eq. (7) becomes

$$\Delta n_i = -2f_i\eta(E_F)[\langle V_2\rangle_i - \delta E_F + \textstyle\sum_j \Delta n_j f(i,j)], \quad (13)$$

where $f(i,j)$ is the interaction of an electron of orbital character j with orbital character i. Consistent with Fig. 2 and the convention of the preceding section we will include in $f(i,j)$ only that part of the interaction which occurs when electron j, as well as electron i, is within the atomic sphere (or polyhedron). The interactions from electrons outside the atomic sphere provide an electrostatic repopulation contribution to q_{latt} and V_2 which we shall ignore.[16] The interaction $f(i,j)$ is, in principle, the full interaction between electrons but we will limit attention to direct and exchange Coulomb terms. Then, if the orbital character is entirely *p*-like or *d*-like, and has common radial character (within the sphere) and if we make the usual multipole expan-

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[15] Namely if the set of Fermi surface Bloch functions vary in radial behavior.

[16] Providing that repopulation does not involve a transfer of charge from one sphere to another (something which we are neglecting in this paper), it will only contribute to the multipole terms of Eq. (2). In such a case, we believe it to be relatively unimportant.

sion of $1/r_{12}$, we have

$$f(i,j)=\int\int|\varphi_i(\mathbf{r}_1)|^2\frac{e^2}{r_{12}}|\varphi_j(\mathbf{r}_2)|^2d\tau_1d\tau_2-\frac{1}{2}\int\int\varphi_i^*(\mathbf{r}_1)\varphi_j(\mathbf{r}_1)\frac{e^2}{r_{12}}\varphi_i(\mathbf{r}_2)\varphi_j^*(\mathbf{r}_2)d\tau_1d\tau_2$$

$$=e^2\sum_k F^k\sum_m\frac{(k-m)!}{(k+m)!}[\langle P_k{}^m(\cos\theta)e^{im\phi}\rangle_i\langle P_k{}^m(\cos\theta)e^{-im\phi}\rangle_j-\tfrac{1}{2}|\langle P_k{}^m(\cos\theta)e^{im\phi}\rangle_{ij}|^2],\quad(14)$$

where the first term in the bracket is the direct Coulomb interaction involving diagonal matrix elements of the angular operators whereas the second term involving off-diagonal elements is the exchange term. The one-half multiplying the exchange term arises because we have assumed the metal to be nonmagnetic. The F^k is the familiar radial Slater integral

$$F^k\equiv\int\int R(r_1)^2R(r_2)^2\frac{r_<{}^k}{r_>{}^{k+1}}r_1{}^2dr_1\,r_2{}^2dr_2,\quad(15)$$

where the R is the radial part (and φ the total spatial part) of the Bloch orbital within the sphere. The radial integrations should be out to the sphere radius.[17]

For d-like electrons, k will equal 2 and 4 while for p-like orbitals it will equal 2 alone. If we had allowed either variation in radial behavior or a transfer of charge in or out of the sphere during the repopulation process, a spherical, $k=0$, term would also contribute to $f(i,j)$. Such a term could make a significant contribution but since its evaluation requires an even more detailed knowledge of the conduction-band wave-function character appropriate to a specific metal than do the terms which we consider here, we will ignore it. We will, in fact, concentrate on the $k=2$ term whose direct Coulomb part should act coherently with V_2.

One can simplify the $k=2$ term of Eq. (14) if we note that the local symmetry in which our ion will normally find itself is such that x-like and y-like wave-function character (the gradient axis being parallel to z) will enter equally. One then obtains the same result for Eq. (13) if one replaces $f(i,j)$ by $f'(i,j)$ where

$$f'(i,j)=e^2F^2\Big[\langle P_2{}^0(\cos\theta)\rangle_i\langle P_2{}^0(\cos\theta)\rangle_j-\tfrac{1}{2}\sum_m\frac{(2-m)!}{(2+m)!}|\langle P_2{}^m(\cos\theta)e^{im\phi}\rangle_{ij}|^2\Big].\quad(16)$$

It is to be emphasized that this is not identical to Eq. (14) but that, subject to the above observation, it yields identical results on insertion into Eq. (13). Let us make this insertion, and, considering only the direct Coulomb term, observe the effect of self-consistency on q'. One first obtains from Eq. (8) that

$$\delta E_F=e^2\Big[-\frac{q_{\text{latt}}}{2}\langle r^2\rangle+\sum_j\Delta n_jF^2\langle P_2{}^0(\cos\theta)\rangle_j\Big]\times\langle\langle P_2{}^0(\cos\theta)\rangle\rangle,\quad(17)$$

where

$$\langle\langle P_2{}^0(\cos\theta)\rangle\rangle\equiv\textstyle\sum_i f_i\langle P_2{}^0(\cos\theta)\rangle_i.\quad(18)$$

Substituting this back into Eq. (13) we have

$$\Delta n_i=-2e^2\eta(E_F)f_i(\langle P_2{}^0(\cos\theta)\rangle_i-\langle\langle P_2{}^0(\cos\theta)\rangle\rangle)\times\Big[-\frac{q_{\text{latt}}}{2}\langle r^2\rangle+\sum_j\Delta n_jF^2\langle P_2{}^0(\cos\theta)\rangle_j\Big].\quad(19)$$

On introducing a small self-energy error by letting the j sum span all repopulated orbitals, we see that the square bracket is independent of i and

$$\frac{\Delta n_l}{\Delta n_k}=\frac{f_l(\langle P_2{}^0(\cos\theta)\rangle_l-\langle\langle P_2{}^0(\cos\theta)\rangle\rangle)}{f_k(\langle P_2{}^0(\cos\theta)\rangle_k-\langle\langle P_2{}^0(\cos\theta)\rangle\rangle)}.\quad(20)$$

Using this relation to express the Δn_j of Eq. (19) interms of Δn_i, we obtain

$$\Delta n_i=-\frac{2e^2\eta(E_F)f_i(-q_{\text{latt}}/2)\langle r^2\rangle(\langle P_2{}^0(\cos\theta)\rangle_i-\langle\langle P_2{}^0(\cos\theta)\rangle\rangle)}{1+2e^2\eta(E_F)F^2\Omega}\quad(21)$$

and in turn

$$q=-\frac{2e^2\eta(E_F)q_{\text{latt}}\langle r^2\rangle\langle r^{-3}\rangle\Omega}{1+2e^2\eta(E_F)F^2\Omega},\quad(22)$$

where

$$\Omega\equiv\textstyle\sum_i f_i\langle P_2{}^0(\cos\theta)\rangle_i\times(\langle P_2{}^0(\cos\theta)\rangle_i-\langle\langle P_2{}^0(\cos\theta)\rangle\rangle).\quad(23)$$

The F^2 term in the denominators is, of course, the self-consistent-field term and it inhibits the polarization. In

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[17] We will use free-ion values where the integration actually is to infinity (as with the r^n integrals) in what follows.

TABLE III. $[\langle r^2\rangle\langle r^{-3}\rangle/F^2]$ values for the valence electrons of various ions.

Ion	$[\langle r^2\rangle\langle r^{-3}\rangle/F^2]$
$\mathrm{Al}(3p)^1$	115[a]
$\mathrm{Ga}(4p)^1$	296[a]
$\mathrm{Rb}^+(4p)^6$	252[a]
$\mathrm{In}(5p)^1$-$\mathrm{Sb}(5p)^3$	380 to 450[b]
$\mathrm{Pb}(6p)^2$-$\mathrm{Po}(6p)^4$	350 to 480[b]
$\mathrm{V}(3d)^5$	36[a]
$\mathrm{V}^{2+}(3d)^3$	16[a]
$\mathrm{Ni}^+(3d)^9$	22[a]
$\mathrm{Ni}^{3+}(3d)^7$	15[a]
$\mathrm{Zr}^{2+}(4d)^2$-$\mathrm{Ag}^{2+}(4d)^9$	~50[a]
$\mathrm{Y}^+(4d^2)$	66[a]
$\mathrm{Ag}^+(4d)^{10}$	55[a]
$\mathrm{La}(5d)^1$	~300[b]

[a] A. J. Freeman and R. E. Watson (unpublished).
[b] Relativistic and nonrelativistic Hartree results of J. Waber.

the limit

$$2e^2\eta(E_F)F^2\Omega\gg 1\,,$$

q' approaches a limiting, "saturated" value,

$$q'\to -q_{\rm latt}\frac{\langle r^2\rangle\langle r^{-3}\rangle}{F^2}\,. \tag{24}$$

In the limit of saturation, q' is independent of $\eta(E_F)$ and of Bloch orbital angular character. A list of $\langle r^2\rangle\langle r^{-3}\rangle/F^2$ values, for selected ions, appears in Table III. The ratios are large indicating that self-consistency limitations will seldom become severe. The ratios show a rough constancy as one scans ions of common valency and row in the periodic table. There is a tendency to decrease with increasing nuclear charge but this variation is slight when compared with the constituent integrals which vary strongly.

The p-conduction-electron ratios are particularly huge. This behavior is associated with the noded character of the radial wave functions, the greater ratios coming with the larger number of nodes. The innermost loop of a function is almost entirely responsible for $\langle r^{-3}\rangle$ (and the outermost for $\langle r^2\rangle$) but the $r_<^2/r_>^3$ operator in F^2 lets this loop contribute negligibly to that integral. The unnoded $3d$ (and $2p$) shells, and to a less extent the $4d$'s, have comparatively small ratios and even if saturation is not reached, one can expect self-consistency to visibly affect q'. Having one fewer nodes than p electrons of the same principal quantum number n, the d electrons penetrate less closely to the nucleus, and in turn tend to have the smaller ratios. Table IV gives results of having evaluated Eq. (22) for the angular distribution Case (a) of Table I. This involves a choice in the $\langle r^2\rangle\langle r^{-3}\rangle/F^2$ value and we have utilized monovalent ion values for the transition elements and neutral-atom values for the p-shell ions. As was to be expected, the d metals with their lower ratios and high $\eta(E_F)$ values have been most affected by self-consistency considerations (compare Table II).

TABLE IV. Self-consistent results for $q'/q_{\rm latt}$ as evaluated with Eq. (23) for case (a) for various metals.

Sc	−18
Ti	−7
Co	−10.5
Y	−28 to −30
Zr	~−10
Ru	−7
Nb in $\mathrm{Nb_3Sn}$	−42
V in $\mathrm{V_3Ga}$	−20
La	−220
Re	~−100
Os	−55
Ga	−16
In	−85 to −115
Sn	−100 to −125
Tl	−150 to −170
Bi	−8

The ratios of Table III have other implications.[18] Of interest to us here is that the V_2 perturbing potential was taken to be entirely associated with $q_{\rm latt}$. If q^0 is nonzero, there is, of course, a second potential term of the same P_2^0 symmetry which arises from the Bloch orbital character within the sphere at the onset of the calculation. To the extent that the full set of occupied Bloch conduction orbitals can be characterized by a single atomic l value and a single radial function, the Coulomb part of this new term is

$$V_2^{\rm loc}(\mathbf{r})\sim -(e^2/2)q^0r^2P_2^0(\cos\theta)[F^2/\langle r^2\rangle\langle r^{-3}\rangle]. \tag{25}$$

While yielding correct matrix elements, the spatial character of this expression is approximate, having been written so that it is of the same form as the V_2 of Eq. (6). Comparing equations, and making note of the inverse of the ratios appearing in Table III, we see that, unless q^0 is one or two orders of magnitude greater than $q_{\rm latt}$, the $V_2^{\rm loc}$ term may be neglected. Including it, Eq. (22) becomes

$$q'=-\frac{2e^2\eta(E_F)[q_{\rm latt}\langle r^2\rangle\langle r^{-3}\rangle+q^0F^2]\Omega}{1+2e^2\eta(E_F)F^2\Omega} \tag{26}$$

and in saturation

$$q'\to -[q_{\rm latt}\langle r^2\rangle\langle r^{-3}\rangle/F^2+q^0]\,. \tag{27}$$

Within the approximations giving Eq. (24) this term attempts to *exactly* shield q^0. Since full saturation will never occur, the cancellation will never be complete but we expect it to be significant when and if q_0 is.

Let us now consider how the inclusion of $k=2$ exchange terms modifies the self-consistent V_2 shielding. Exchange does not make coherent contributions in the sense seen for Coulomb terms in Eqs. (17)–(22) [in particular in the ratio in Eq. (20)] and one must make estimates assuming specific Bloch orbital angular dis-

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[18] Among these is the fact that self-consistency has visible but not catastrophic repercussions on the traditional perturbation estimates of γ_∞ [e.g., see R. E. Watson and A. J. Freeman, Phys. Rev. **131**, 250 (1963)].

tributions. This is most simply done if the set of orbitals may be defined in terms of two fractions, f_0 and $(1-f_0)$. Then, using Eq. (16), and ignoring V_2^{loc}, one immediately obtains expressions of the form

$$q' = -\frac{2\alpha\beta e^2 q_{\text{latt}} f_0(1-f_0)\eta(E_F)\langle r^2\rangle\langle r^{-3}\rangle(\langle P_2^2(\cos\theta)\rangle)^2}{1+2\beta e^2 f_0(1-f_0)\eta(E_F)F^2(\langle P_2^0(\cos\theta)\rangle)^2}, \tag{28}$$

where in saturation

$$q' = -\alpha q_{\text{latt}}(\langle r^2\rangle\langle r^{-3}\rangle/F^2). \tag{29}$$

The $\langle P_2^0(\cos\theta)\rangle$ matrix elements are for[19] either angular orbital type and the α and β are coefficients which follow from that choice after the insertion of Eq. (16), and a detailed evaluation of Eq. (13). In the absence of exchange terms, α equals one. The α and β values appropriate to cases (a) and (c) of Table I appear in Table V. Here, of course, the relative amounts of differing orbital angular character may vary, with $f_0=\frac{1}{3}$ corresponding exactly to the case (a) of table and $f_0=\frac{1}{2}$ to case (c). The α value of $+9$ corresponds to an order-of-magnitude enhancement of the saturation limits due to exchange. An additional example, case (d), is listed. It is an example of a negative α and, in turn, an *antishielding* saturation limit.

Predictions for these cases, plotted as a function of $2f_0(1-f_0)\eta(E_F)$ [or effectively[19] $2\eta(E_F)\Omega$] appear in Fig. 4. Cases involving Coulomb terms, without exchange, have also been plotted [and are indicated with the superscript c]. Vanadium radial integrals were used in the construction of the figure and the values of $2f_0(1-f_0)\eta(E_F)$ appropriate to V_3Ga, Ti, and Sc for case (a) of Table I are indicated on the figure. From the figure it is clear that we are seldom, if ever, near the saturation limit in a metal and that exchange, as well as Coulomb, self-consistent terms can appreciably affect q' well away from that limit.[20] The negative β associated with case (d) has led to an *enhancement*[21] of q' over what it would be if self-consistent effects were not considered.

TABLE V. The role of self-consistent exchange terms as manifested in the β and α appropriate to Eqs. (28) and (29) (see text).

		Fractions applying to			
Case	Band	f_0	$(1-f_0)$	β	α
a	d	xy	equal numbers of yz and zx orbitals	$+1/4$	$+9$
a	p	z	equal numbers of x and y orbitals	$+33/16$	$+4/11$
c	d	$3z^2\text{-}r^2$	$x^2\text{-}y^2$	$+17/4$	$16/7$
d	d	$3z^2\text{-}r^2$	equal numbers of yz and zx orbitals	$-7/16$	$-4/7$

Self-consistency effects are most severe for the $3d$ metals which we have just considered. Smaller $\eta(E_F)$ values and F^2 integrals cause the effects to be smaller for the $4d$, $5d$, and p-electron metals. The large q' values for the p metals in good part arise from the large $\langle r^2\rangle\langle r^{-3}\rangle$ factors and are relatively unaffected by self-consistency.

When one deals with d metals, $k=4$ terms occur. These will further perturb q' and saturation behavior. For example, the F^2 of Eqs. (28) and (29) would be replaced by $(F^2+\gamma F^4)$ where γ is yet another coefficient. We will not consider the effect of this here.

V. THE ROLE OF THE ELECTRON-PHONON INTERACTION

In the preceding sections we have relied on $\eta(E_F)$ values deduced from electronic-specific-heats data. It has been shown theoretically[22] that the electronic specific heat is modified by the electron-phonon interaction; other electronic properties, such as the magnetic susceptibility, are not affected.[23] We may then ask whether or not the density of states, $\eta(E_F)$, that was used to obtain the repopulation of states at the Fermi surface should be affected by the electron-phonon interaction and, if not, how this affects the results we have already seen. The existence or lack of an electron-phonon term also affects one's expectations concerning the temperature dependence of q_{loc} as one goes from low temperatures to well above the Debye temperature.

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[19] By convention we have taken $\langle P_2^0(\cos\theta)\rangle$ to be appropriate to the angular type designated by f_0 when β values are reported in Table V. The $f_0(1-f_0)$ product in Eq. (28) is associated, in part, with nonzero δE_F effects. This becomes quite obvious when f_0 equals zero or one for then the entire V_2 energy must go into δE_F with [see Eqs. (9)–(11)]

$$\langle P_2^0(\cos\theta)\rangle - \langle\langle P^0(\cos\theta)\rangle\rangle = 0.$$

This relation leads to a zero valued q' from expressions such as Eqs. (21) and (22) and it is the $f_0(1-f_0)$ product which serves the same purpose in (28).

[20] This may seem surprising since direct Coulomb interactions are commonly an order of magnitude stronger than exchange. This is true here and is due to the spherical, $k=0$ term in the interaction. We have omitted this term and if it did enter, it would only do so through differencing due to varying Bloch orbital character [see the discussion between Eqs. (15) and (16)]. Considering terms with k equal to 2 or 4, exchange effects may be every bit as large as the direct interaction terms and it is the manifestation of this which we see in the examples above.

[21] For case (d) most of the V_0 potential energy goes into δE_F, hence the shallow initial slopes of its curves with and without exchange (the initial slope of any curve on the figure is what one obtains in the absence of self-consistent terms). The negative β, associated with this case, causes a singularity at $2f_0(1-f_0)\eta(E_F)$ $\sim$99 states per a. u. per atom with an antishielding region above the singularity. Being inside it, we have an enhancement over the result without self-consistent terms.

[22] M. J. Buckingham and M. R. Schafroth, Proc. Phys. Soc. (London) **A67**, 828 (1954); and D. Simkin, thesis, University of Illinois, 1963 (unpublished).

[23] J. J. Quinn, in *The Fermi Surface*, edited by W. A. Harrison and M. J. Webb (John Wiley, & Sons, Inc., New York, 1960).

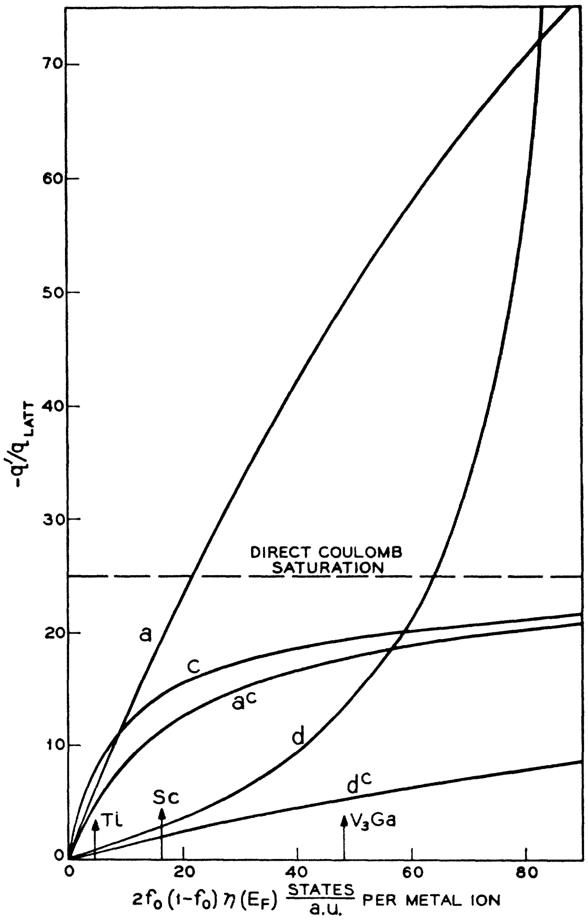

FIG. 4. The effect of self-consistency on the d band q'/q_{latt} with and without (superscript c) exchange as a function of $f_0(1-f_0)\eta(E_F)$ for the cases defined in Table V. Vanadium radial integrals have been used in evaluating Eq. (28).

To answer these questions we have considered the Hamiltonian

$$\mathcal{H}=\mathcal{H}_0+V_2(\mathbf{r})+\mathcal{H}', \tag{30}$$

where $\mathcal{H}_0$ is the Hamiltonian for a free electron, $V_2(\mathbf{r})$ is a periodic potential of lower symmetry (that of the lattice) and $\mathcal{H}'$ is the electron lattice interaction. We use the Frohlich Hamiltonian for $\mathcal{H}'$, which in second-quantized notation is given by

$$\mathcal{H}'=\sum_p\sum_k \alpha_k c_{p+k}{}^{\dagger}c_p(b_k+b_{-k}{}^{\dagger}), \tag{31}$$

where the constant α_k is equal to

$$\alpha_k=[(2\pi^2\hbar^2/Vmk_f)F\hbar\omega]^{1/2}.$$

Here k_f is the Fermi vector, F is the coupling constant, of order unity and for simplicity an Einstein spectrum with frequency ω has been assumed for the phonons.

We have calculated[24] (only to second order in $\mathcal{H}'$ which is sufficient for our purpose) the electron self-energy and used it to obtain the one-electron Green's function G for this Hamiltonian, retaining only the matrix elements of $V_2(\mathbf{r})$ which are diagonal in $\mathbf{k}$ since they alone are of interest to us. The imaginary part of G gives the density of occupied states as a function of $\mathbf{k}$ and energy,[25] and by integrating over E we obtained the expectation value $\langle n_{\mathbf{k}}\rangle$ of the one-particle state $\mathbf{k}$ in the ground state. We then let $V_2(\mathbf{r})=0$ and found $\langle n_{\mathbf{k}}\rangle_0$ for this case. The change in the electron population with a fixed direction of the wave vector that arises from the action of $V_2(\mathbf{r})$ is given by

$$\delta\langle n_{\mathbf{k}}\rangle=\int_0^{\infty}(\langle n_{\mathbf{k}}\rangle-\langle n_{\mathbf{k}}\rangle_0)d\mathbf{k} \tag{32}$$

where the integration is over all wave vectors with direction $\mathbf{k}$. This expression was found to differ from $\delta\langle n_{\mathbf{k}}\rangle$ found above (i.e., without electron-phonon interaction) only in order $\hbar\omega/E_f$, showing that the electron-phonon interaction has a negligible effect and that it is appropriate to use the "bare" density of states for $\eta(E_f)$.

We can understand this result as follows: In the absence of $\mathcal{H}'$ the Fermi surfaces of $\mathcal{H}_0$ and $\mathcal{H}_0+V_2(\mathbf{r})$ are separated in $\mathbf{k}$ space by a distance

$$\delta\mathbf{k}_0=-[\langle V_2(\mathbf{k})\rangle-\langle\langle V_2(\mathbf{k})\rangle\rangle_F]/|V_{\mathbf{k}}(E)| \tag{33}$$

where $\langle\ \rangle_F$ indicates the average over the Fermi surface. We now turn on the electron-lattice interaction and ask for the difference in the self-energies $\Sigma(\mathbf{k}_f,E_f)$ of an electron, respectively, at the two Fermi surfaces, along a fixed direction $\mathbf{k}$. Clearly this change is of order $\delta\Sigma\sim(\delta k_0/k_f)\Sigma$ since δk_0 is the change in the $\mathbf{k}$ value at which it is being computed. $\Sigma(\mathbf{k}_f,E_F)$ is of order $F\hbar\omega$, and thus is small compared to the Fermi energy. The change Δk that would be needed to offset $\delta\Sigma$ is given by $(\partial E/\partial k)\Delta k=\delta\Sigma$, or $\delta\Delta\sim F(\hbar\omega/E_f)\delta k_0$. Thus $(\Delta k/\delta k_0)$ is of order $\hbar\omega/E_f$ which is negligible.

We might contrast this result with the fact that the electronic specific heat at low temperatures is strongly affected by the electron-lattice interaction. This effect is a consequence of the exclusion principle[22]; it would have been absent for a static electron-phonon interaction and it gives a significant contribution to Σ only when the energies of the electronic states connected by $\mathcal{H}'$ are separated by less than a phonon energy. This contribution is proportional to the number of electron states that are within an energy $\hbar\omega$ both of the Fermi surface and of the energy of the electron under consideration. The reason the specific heat is strongly affected is that this number decreases by half its value as the energy of an excited electron increases from E_f to $E_f+\hbar\omega$. In our problem of repopulation we are not concerned with the behavior of excited states but only with that of the ground state of the system.

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[24] A. B. Migdal, Zh. Eksperim. i Teor. Fiz. **34**, 1438 (1958) [English transl.: Soviet Phys.—JETP **7**, 996 (1958)].

[25] See for instance, T. D. Schultz, *Quantum Field Theory and the Many-Body Problem* (Gordon and Breach Science Publishers, Inc., New York, 1964).

In order to avoid the problem of evaluating the electron-phonon enhancement of the specific heat for the various metals, the uncorrected $\eta(E_F)$ were used in the preceding sections. As a crude rule of thumb, those values (and in turn the $q'/q_{\rm latt}$ of Table II) are too large by a factor of two. It is clear that the temperature-dependence of q' (and $q_{\rm loc}$) will be unaffected by the electron-phonon interaction. The other sources of temperature-dependent effects are considered in Appendix II and briefly in the section which follows.

VI. DISCUSSION

The division of $q_{\rm loc}$ into three terms may seem undesirable and unreasonably arbitrary. As a matter of practical computation, however, the division has considerable meaning. Any *a priori* estimate of $q_{\rm loc}$ starts with functions obtained in an energy-band calculation and by almost universal practice current energy-band methods utilize spherical potentials yielding functions appropriate to q^0 and not $q_{\rm loc}$. Equations (25)–(27) suggest that any accurate estimate of $q_{\rm loc}$, say to better than a factor two, requires going on and obtaining[26] q'. That this is necessary is borne out by the estimates of $q'/q_{\rm latt}$, which are sometimes as large as 100, even when calculated self-consistently.

We have avoided making estimates of q^0 since they require detailed knowledge of orbital character for *all* conduction-electron states below the Fermi surface.

The evaluation of q'' also formally requires knowledge of the orbital character of states below E_F, but, unlike q^0, a crude estimate of its behavior may be readily made for the case of a pure metal or an ordered intermetallic. Our perturbing V_2 potential is, after all, periodic for it occurs at all like atomic sites. As such, it has only off-diagonal matrix elements between conduction-electron states differing by reciprocal lattice vectors, i.e., between *different* bands in the conventional single-zone schemes. The gross behavior can be obtained as follows. Under the influence of the perturbing field V_2, any one given orbital will (1) distort radially keeping fixed angular character and (2) distort angularly, the two distortions moving the charge density into the region of lowest potential energy. Simple physical arguments [or our experience[5,27] with closed shell Sternheimer antishielding] indicate that the radial distortion antishields and the angular effect shields $q_{\rm latt}$. Both tendencies will occur for our Bloch orbitals within the sphere. Calculations for individual atomic orbitals or entire closed shells indicate that for p or d electrons, the radial antishielding effects dominate. We can use free ion antishielding results to obtain an upper limit for this antishielding. Given a $\gamma_\infty(l)$ computed for a closed shell of neutral-atom valence-shell orbitals,[28] of orbital momentum l, we have

$$\frac{q''}{q_{\rm latt}} < |\gamma_\infty(l)| \left[\frac{\text{number of conduction electrons per site}}{2(2l+1)}\right].$$

In principle this need not overestimate the $q''/q_{\rm latt}$ ratio but in practice it will almost inevitably do so (if only because s character in the Bloch orbitals will reduce the radial effect). We should note that this limit is large when the $\langle r^2\rangle\langle r^{-3}\rangle$ product is large, i.e., an antishielding q'' will tend to be largest for heavy p-electron metals. Assuming that there are no "resonant" effects associated with close lying bands just above E_F, the largest angular shielding which can occur (and hence the strongest tendency for q'' to shield) is but a few percent.

Our application of perturbation theory to the conduction-electron contributions to a field gradient may have reminded the reader of the important work of Kohn and Vosko.[29] In contrast with the present work appropriate to ordered or disordered systems, they dealt with the gradient arising from the response of an electron gas to an impurity charge. There, Fermi-surface repopulation does not contribute and the effect is entirely associated with the lowest order counterpart of q'', [i.e., their $\delta n^{(1)}(r)$ for $\mathbf{k}$ antiparallel to $\mathbf{k}'$]. Thus, the two cases are very different.

The investigations of the preceding sections have been appropriate to zero temperature. One might hope to sort out the respective roles of $q_{\rm latt}$ and $q_{\rm loc}$ by inspection of a gradient's temperature dependence. With electron-phonon terms unimportant, there are two leading sources of temperature variation. First, there are the changes associated with the thermal variation of the lattice constants. Secondly, there are thermal-repopulation effects across E_F associated with the Fermi-Dirac statistics of the system.

The role of lattice distortion can be independently investigated by pressure and stress experiments. The work[2] of O'Sullivan and Schirber on In suggests that q variation is not entirely associated with changes in the lattice constants, i.e., that a significant fraction remains to be explained by other sources. Unfortunately, lattice-constant changes cannot readily sort out the respective roles of $q_{\rm latt}$ and $q_{\rm loc}$ because both are affected. Repercussions on $q_{\rm loc}$ come in part from distortions of the Fermi surface which in turn arise from shifts in Brillioun-zone boundaries.

Providing that a significant shift in charge from one type of atomic site to another does not occur one can anticipate that thermal-repopulation effects will mainly affect $q_{\rm loc}$ (including, of course, q' with its dependence on the lattice field). The effects on $q_{\rm loc}$, and q' alone,

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[26] There are, of course, also terms similar to q' which are associated with the other nonspherical components of the potential. These are expected to be normally much less important because of the lack of coherence for such terms in the sense discussed at the end of Sec. III.

[27] See also, M. H. Cohen and F. Reif, Solid State Phys. **5**, 322 (1957).

[28] The neutral-atom valence shell will normally not be filled, but given the valence-shell radial orbital character we then want $\gamma_\infty(l)$ computed for a closed shell of such orbitals.

[29] W. Kohn and S. H. Vosko, Phys. Rev. **119**, 912 (1960).

are inspected in Appendix II. Their dependence on Fermi-surface behavior is much more detailed than that already considered in this paper since, for a given segment of Fermi surface, one samples orbital spatial character *and* other factors such as $[\partial\eta/\partial E]_{E_F}$. The increased detail of the samplings makes these terms less amenable to crude estimates. The estimates made in the Appendix suggest a substantially greater thermal variation of the V_3Ga gradient than the small change[30] which is seen. Almost nothing is known concerning the system's lattice constant variation and the small magnitude[30] of the q variation suggests, to us, an appreciable cancellation among terms. The estimates of the Appendix suggest that experimentally significant contributions to the temperature dependence of q can arise from thermal repopulation in high $\eta(E_F)$ metals.

VII. CONCLUSION

This treatment has concentrated on q', the electric-field-gradient contribution from conduction electrons within the atomic sphere, arising from the redistribution of occupied states about the Fermi surface in the presence of a noncubic crystalline potential (in the sphere). The other terms, arising when the noncubic potential is zero-valued within the sphere (q^0) and from orbital distortion (q''), may be important, but the most striking effects evidently come from q'. Large negative q'/q_{latt} ratios, i.e., overshielding, may occur, causing sign reversals in the total field gradient. The fact that an estimated q_{latt} differs in sign with experiment then need not imply that q_{latt} and its associated crystal field are not the essential source of the field gradient.

In the case of transition metals (or transition metal sites in intermetallics) a high density of states, $\eta(E_F)$, permits a substantial repopulation, i.e., a large Δn_i, and in turn a substantial ratio. The heavy p-electron metals, on the other hand, also have large ratios, in spite of their comparatively small $\eta(E_F)$. This is due to their large $\langle r^2\rangle\langle r^{-3}\rangle$ products. Self-consistency is most important when repopulation is substantial but q'/q_{latt} ratios as large as -100 occur, in spite of it, for *both* transition and p-band metals. We expect q' to tend to be most important, relative to the other terms of q_{loc}, for the transition metals.

In closing, it is perhaps appropriate to return to the V_3X behavior seen in Fig. 1. The large q'/q_{latt} ratios obtained in Secs. III and IV, and the point-charge estimate[31] of q_{latt} reported in Appendix I, are all consistent with the idea that these experimental results are reflecting $\eta(E_F)$ behavior. Our inability to assess the relative role of q^0 makes any rigorous conclusion impossible but we do believe that q', with its dependence of q_{latt} and $\eta(E_F)$ is making a significant contribution to the gradient of the V_3X and other metals.

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APPENDIX I. THE STRUCTURE AND q_{latt} APPROPRIATE TO THE V_3X COMPOUNDS AND THE V^{51} NUCLEAR-QUADRUPOLE MOMENT

We would like to inspect the structure and q_{latt} associated with the V_3X compounds. These systems have the β-wolfram structure which is cubic with six V and two X atoms per unit cell as is indicated in Fig. 3. One-third of the V atoms lie in lines along the z axis, another third along the x and the remainder along the y. The nearest neighbors to a V atom in any particular line are the adjacent V atoms in the same line and in a nearest-neighbor tight-binding approximation one would thus expect the essential features of the V_3X compounds to be associated with one-dimensional chains of V atoms. The energy-band investigations of Mattheiss[4] show this approximation to be poor. The local symmetry at a V site is noncubic and a nonzero q_{latt} may occur. Limiting oneself to point charges Z_Ve and Z_Xe associated with the V and X lattice sites, lattice sums yield vanadium site values of

$$e^2q_{\mathrm{latt}}=\{3.2Z_{\mathrm{V}}-1.2Z_{\mathrm{Ga}}\}\times10^4\ \mathrm{esu}^2\ \mathrm{cm}^{-3}$$

and

$$e^2q_{\mathrm{latt}}=\{3.4Z_{\mathrm{V}}-1.3Z_{\mathrm{Si}}\}\times10^4\ \mathrm{esu}^2\ \mathrm{cm}^{-3}$$

for V_3Ga and V_3Si, respectively. Insofar as the ion cores of charge $+Z_ie$ are well localized and the conduction electrons are nonlocalized and uniformly distributed in space, this expression will hold. Assuming Z's of $+1$, one obtains $e^2q_{\mathrm{latt}}Q(1-\gamma_\infty)$ which is twice the observed V_3Ga interaction and proportionately greater than the observations appropriate to the other V_3X compounds. Limiting attention to point-charge terms and assuming Z's equal to one is admittedly unrealistic and has, we believe, overestimated q_{latt}.

Comparison of theory with experimental q behavior embroils one in estimates of Q, as was indicated in Sec. II. The V^{51} moment is a case in point. Murakawa obtained[32] a Q value of 0.28 ± 0.15 b from optical-atomic-hyperfine data. This involved a theoretical estimate of the atomic-field gradient. Using this Q value one obtains experimental V_3Ga and V_3Ge vanadium field gradients which are, respectively, 10 and 3% of what a single atomic V $3d$ electron (with $m_l=0$) will produce. This is consistent with one's general experience with field gradients in metals. We should perhaps note that there are other V_3X compounds, such as V_3As, which have still smaller gradients of the order of (using the Q of 0.28 b) one percent of the atomic $3d$ value. More

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[30] In V_3Ga, $e^2qQ(300°\mathrm{K})=3.17$ Mc/sec and $e^2qQ(20°\mathrm{K})=3.24$ Mc/sec.

[31] The important feature is the possibility of a significant q_{latt} for small point-charge values.

[32] K. Murakawa, J. Phys. Soc. Japan **11**, 422 (1956).

recently Nagasawa, Takeshita, and Tomono have obtained[33] an independent estimate of Q by observing the quadrupole interaction in V_2O_5. Assuming an ionic crystal, they performed a lattice sum for q, in turn obtaining a Q value 1/30th that of Murakawa. This implies a V_3Ga field gradient which is three times the atomic $3d$ value. While not impossible this seems rather improbable. We expect V_2O_5 to be highly covalent and a theoretical q, based on assuming it to be purely ionic, would be liable to severe potential errors. Comparing Murakawa's estimate of the atomic q with Hartree-Fock theory, and inspection of Hartree-Fock predictions[34] of fine and hyperfine structure suggest that his estimate of q is accurate to 10, or at worst 20%. If his Q is in more serious error, it is due to the optical hyperfine data. Earlier in the Appendix and elsewhere in this paper, stated experimental vanadium q values were based on a Q of 0.28 b.

APPENDIX II. THERMAL-REPOPULATION EFFECTS AND THE FIELD GRADIENT

We are interested in the thermal-repopulation effects associated with the Fermi-Dirac distribution function

$$g(E)=1/[e^{(E-\epsilon)/kT}+1], \qquad \text{(A1)}$$

where ϵ equals E_F when $T=0$. Such contributions have generally been ignored and we will see suggestions that they play their largest role when the $\eta(E_F)$ is high. For the moment let us concentrate on the temperature dependence of q', as defined in Eqs. (10) and (11). Using standard procedures,[35] q' at $t>0$ becomes

$$q'(T)=2\sum_j\int_0^\infty \langle 2r^{-3}P_2{}^0(\cos\theta)\rangle_{j,E}\,\eta(E)_j \times[g(E+\langle V_2\rangle_j-\delta E_F)-g(E)]dE, \qquad \text{(A2)}$$

where the V_2 matrix elements and δE_F are defined at the original unperturbed Fermi surface as in Eq. (7). The j summation is essentially a sum[36] over segments, j, of the Fermi surface with associated density of state contributions $\eta(E_F)_j$. It is a more detailed sampling than the $f_i\eta(E_F)$ of Secs. III and IV for it involves more than just orbital spatial character. If $\langle 2r^{-3}P_2{}^0(\cos\theta)\rangle_{j,E}$ and $\eta(E)_j$ vary slowly in an interval E to $E+\langle V_2\rangle_j-\delta E_F$, we have

$$\begin{aligned} q'(T)&=2\sum_j\int_0^\infty \langle 2r^{-3}P_2{}^0(\cos\theta)\rangle_{j,E} \\ &\qquad\times\eta(E)_j\frac{dg(E)}{dE}[\langle V_2\rangle_j-\delta E_F]dE \\ &=2\sum_j \langle 2r^{-3}P_2{}^0(\cos\theta)\rangle_{j,E}\,[\langle V_2\rangle_j-\delta E_F] \\ &\qquad\times\left\{\eta(E_F)_j+\frac{\pi^2}{6}(kT)^2\left[\frac{\partial^2\eta(E)_j}{\partial E^2}\right]_{E_F}+\cdots\right\} \end{aligned} \qquad \text{(A3)}$$

or for the jth component

$$\begin{aligned} \frac{q'(T)_j-q'(0)_j}{q'(0)_j}&=\frac{\pi^2}{6}(kT)^2\frac{[\partial^2\eta(E)/\partial E^2]_{E_F,j}}{\eta(E_F)_j}+\cdots \\ &=\frac{-\eta(E_F)_j-\int_0^\infty \eta(E)_j(dg/dE)dE}{\eta(E_F)_j}. \end{aligned} \qquad \text{(A4)}$$

Without a detailed knowledge of the band structure and wave functions, an accurate determination of this temperature dependence is not possible. The magnitude may be estimated if we made the assumption that the right-hand side of Eq. (A4) is independent of j. Clogston[37] has estimated the temperature dependence of $\int_0^\infty \eta(E)(dg/dE)dE$ from available susceptibility and specific-heat data for V_3Ga. His results suggest that

$$[q'(300)-q'(0)]/q'(0)\cong-0.35$$

which is an order of magnitude greater than the 2.2% temperature dependence actually observed[30] in V_3Ga. There are, of course, many potential sources of such a discrepancy.

Let us now consider the Fermi redistribution effect appropriate to the entire $q_{\rm loc}$ and define $q_{\rm loc}(0)$ and a Fermi surface which are appropriate to the *exact crystal potential.* Again using the standard expansion techniques[35] one obtains

$$\begin{aligned} q_{\rm loc}(T)-q_{\rm loc}(0)=\frac{\pi^2}{3}(kT)^2\sum_j\Bigg\{&\langle 2r^{-3}P_2{}^0(\cos\theta)\rangle\Bigg\langle\left[\frac{\partial\eta(E)}{\partial E}\right]_{E_F,j}-f_j\Bigg\langle\left[\frac{\partial\eta(E)}{\partial E}\right]_{E_F}\Bigg\rangle\Bigg\rangle \\ &+\eta(E_F)_j\left[\frac{\partial\langle 2r^{-3}P_2{}^0(\cos\theta)\rangle_j}{\partial E}\right]_{E_F}\Bigg\}+O(T^4), \end{aligned} \qquad \text{(A5)}$$

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[33] H. Nagasawa, S. K. Takeshita, and Y. Tomono, J. Phys. Soc. Japan **19**, 764 (1964).

[34] For example, M. Blume, A. J. Freeman and R. E. Watson, Phys. Rev. **134**, A320 (1964) and M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **A271**, 565 (1963).

[35] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958), Chap. 6.

[36] In practice one would probably replace this sum by an appropriate integral over k-space surfaces of common energy (e.g., the Fermi surface proper) but for our purposes here, notation is simpler if we leave this as a sum.

[37] A. M. Clogston, Phys. Rev. **136**, A1417 (1964).

where the factor involving $\partial\eta/\partial E$ plays essentially the same role here as the $(\langle P_2^0(\cos\theta)\rangle_i - \langle\langle P_2^0(\cos\theta)\rangle\rangle)$ of Eqs. (11) and (19)–(23). We may rewrite this as

$$q_{\mathrm{loc}}(T)-q_{\mathrm{loc}}(0)$$
$$=\sum_j \left\{ \Delta n(T)_j \langle 2r^{-3}P_2^0(\cos\theta)\rangle_j + \frac{\pi^2}{3}(kT)^2\eta(E_F)_j \times\left[\frac{\partial\langle 2r^{-3}P_2^0(\cos\theta)\rangle_j}{\partial E}\right]_{E_F}\right\} + O(T^4). \quad \text{(A6)}$$

The first term of either Eq. (A5) or (A6) represents the thermal repopulation, $\Delta n(T)_j$, into or out of the jth Fermi-surface region and the second term represents the change in q_{loc} due to thermal repopulation normal to the Fermi surface. Despite superficial dissimilarities, these equations include the $q'(T)-q'(0)$ term of Eqs. (A3) and (A4). Standard assumptions were made in deriving these equations, namely that $\eta(E)_j$ and $\langle 2r^{-3}P_2^0(\cos\theta)\rangle_j$ vary slowly with respect to $\partial g(E)/\partial E$ in the energy range $E_F \pm kT$. Normally such requirements are reasonably well met in a metal but this may be marginal for the V_3X compounds. If so, not only are the above equations suspect for these compounds but so are the existing analyses of the electronic specific heats and the temperature-dependent spin susceptibilities.

Estimates of $q_{\mathrm{loc}}(T)-q_{\mathrm{loc}}(0)$ are more formidable than any already made in this Appendix and elsewhere in this paper because we require knowledge of $\eta(E)_j$ and $\langle 2r^{-3}P_2^0(\cos\theta)\rangle_{j,E}$ as a function of both j and E (in the vicinity of E_F).

An effect which could decrease the expected temperature dependence of the field gradients is the self-consistency and associated saturation behavior discussed in Sec. IV. Limiting attention to direct Coulomb F^2 terms, one expects saturation to reduce the temperature dependence of $q_{\mathrm{loc}}(T)$. This becomes obvious if the orbitals in the vicinity of the Fermi surface have essentially common radial character because any thermal j repopulation [the first line of Eqs. (36)–(37)] causing q_{loc} to change will then also produce a repopulation potential term [e.g., see Eqs. (14)–(20)] which opposes the repopulation. This is due to the common angular character of the gradient and the F^2 potential operators. Both experimentally and in the observations of the preceding sections, there is the suggestion that saturation effects play a significant role in the V_3X compounds.

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Compressibility and Electrical Conductivity of Cadmium Sulfide at High Pressures

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The compressibility and electrical conductivity of CdS were investigated to over 60 kbar under nearly hydrostatic conditions. Volume change was measured by the inductive-coil technique. In single-crystal samples, the wurtzite → rocksalt phase transformation starts at 23±1 kbar at 25°C. At the transition a sudden volume change of 21% occurs, and the electrical resistivity decreases by several orders of magnitude. The average volume compressibilities are 18.2×10^{-4} kbar^{-1} for the wurtzite phase (0–23 kbar) and 9.5×10^{-4} kbar^{-1} for the rocksalt phase (40–60 kbar). Both phases exhibit semiconducting behavior. For the high-resistivity samples used ($\rho > 10^5$ Ω cm), an activation energy of 0.9 eV and a band gap of ≃2.3 eV were obtained for the wurtzite phase. Both increase with pressure. For the rocksalt phase an activation energy of 0.1–0.2 eV and a band gap of ≃1.3 eV were obtained. The progress of the forward and reverse transitions was followed visually under high magnification, and some observations are made concerning the mechanism of the transformation.

I. INTRODUCTION

CADMIUM sulfide (CdS) is a dimorphous compound crystallizing in both the hexagonal wurtzite and the related cubic zincblende structures. Both of these are loosely packed structures which transform to phases with closer packing at high pressure. Drickamer and co-workers,[1–3] using optical and electrical techniques, were the first to report a pressure-induced polymorphic transition in CdS. The transition, observed in the range 20–30 kbar, is accompanied by a large discontinuous red shift in the optical-absorption

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[1] A. L. Edwards, T. E. Slykhouse, and H. G. Drickamer, J. Phys. Chem. Solids 11, 140 (1959); A. L. Edwards and H. G. Drickamer, Phys. Rev. 122, 1149 (1961).

[2] G. A. Samara and H. G. Drickamer, J. Phys. Chem. Solids 23, 357 (1962).

[3] S. Minomura, G. A. Samara, and H. G. Drickamer, J. Appl. Phys. 33, 3196 (1962).

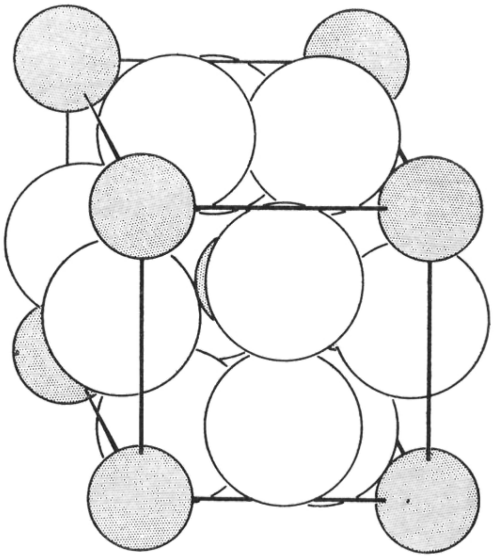

FIG. 3. The unit cell for the V_3X (X = Si, Ge, Ga, etc.) compounds having the β-wolfram structure, the X atoms being shaded. The V atoms form nearest-neighbor chains lying in the x, y, or z direction.