

rough grid to map the region 0.5–8.0 K in temperature and 0–15 kOe in field; note that the isotherm passing nearest the TCP is at $\epsilon \cong 0.03$. Unfortunately, there are considerable experimental difficulties associated with measuring magnetizations near the TCP and the first-order line; these are discussed in Refs. 1a, 1b.

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¹²A second possibility, though, is that the area around the TCP in which true asymptotic behavior could be observed is in fact quite small, so that the present data simply do not penetrate the actual "tricritical region." Of course, this interpretation is possible for all exponent data.

Pressure Variation of the Quadrupole Interaction in Cadmium Metal*

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A theoretical study, for the first time, of the electric field gradient in cadmium metal at two pressures yields a pressure variation in agreement with time-differential perturbed-angular-correlation data. The sign of the net electric field gradient determined by the electronic contribution, which is larger and of opposite sign to the ionic contribution, in conjunction with imminently expected experimental sign of the coupling constant, will provide the sign of the excited Cd¹¹¹ quadrupole moment.

The recent exploitation of the time-differential perturbed-angular-correlation (TDPAC) technique¹⁻⁴ to study nuclear quadrupole interactions in metals has provided a valuable opportunity to improve our understanding of the origin of the nuclear quadrupole effects in metals. This technique provides a means of studying quadrupole interactions in excited states of those nuclei which have zero quadrupole moment in the ground state and would therefore not have been suitable for study of field gradients at nuclear sites. One example which has been exploited most extensively in this respect is the excited state of Cd¹¹¹ which has a spin of $\frac{5}{2}$. In particular, both the quadrupole coupling constant in cadmium metal and its variation^{2,3} with pressure and temperature have been studied recently. In the present study, for the first time in a metal, a theoretical analysis is carried out for the pressure variation of the field gradient in cadmium, including both conduction electron and ionic contributions, for comparison with experiment. An equally important and timely result of the present study is the sign of the field gradient, since development of experimental procedures are currently⁵ under way to determine the sign of the coupling constant e^2qQ through the TDPAC technique. A combination of our theoretical sign for eq and the experimental sign for e^2qQ , when the latter is available, should provide the sign of Q for the excited state of Cd¹¹¹, which should be very useful for the testing of nuclear theories for Q .

The study of the conduction electron contribution⁶⁻⁸ to the field gradient eq requires a detailed scanning of the occupied Fermi volume, rather than just the Fermi surface as is the case for magnetic hyperfine properties. The band energy values and wave functions have to be calculated at each of the scanned \vec{k} points in the Brillouin zone (reduced zone scheme), the energy values being needed to decide which of the energy bands at the point lies below the Fermi energy. The occupied eigenstates are used^{7,8} to calculate the electronic contribution to the field gradient. In the present work, we have carried out two such calculations for two pressures, namely 1 atm (~ 1 bar) and 50 kbar.

In common with the earlier successful interpretations^{9,10} of Fermi-surface properties of cadmium, a pseudopotential approach is utilized here for obtaining the energy bands and band wave functions. However, in our present work, we require wave functions in the entire Fermi volume rather than the vicinity of the Fermi surface. The available nonlocal energy-dependent pseudopotential having been derived for the latter, it has to be modified to apply to all of \vec{k} space. The procedure for this shall be briefly described.

The general form of the energy-dependent pseudopotential is given by

$$V_p(E) = V_c + \sum_t (E - E_t) P_t, \quad (1)$$

where V_c is the real potential seen by the conduction electrons, and P_t is the projection operator

$|t\rangle\langle t|$ for the core state t . The potential V_c is split¹¹ into local and nonlocal parts in the following way, namely,

$$V_c = U + \sum_t \epsilon_t P_t, \quad (2)$$

where U is the local potential and the ϵ_t are non-local parameters for core states t that have to be determined. The pseudopotential of Stark and Falicov¹¹ at the Fermi surface has the following form¹²:

$$V_p(E_F) = U + \sum_t v(t) P_t. \quad (3)$$

On substituting for V_c from Eq. (2) in Eq. (1), and comparing the latter with Eq. (3) at $E = E_F$ (the Fermi energy) to eliminate ϵ_t , one obtains the pseudopotential applicable for a general \vec{k} point, namely,

$$V_p(E) = U + \sum_t [E - E_F + v(t)] P_t. \quad (4)$$

It would appear from Eq. (4) that one needs a knowledge of E itself in order to obtain pseudopotential $V_p(E)$. However, taking a linear combination of plane waves φ for the pseudofunction,

$$\Phi_{\vec{k}}^{\dagger}(\vec{r}) = \sum_{\vec{k}'} C_{\vec{k}+\vec{k}'}^{\dagger} \varphi_{\vec{k}+\vec{k}'}^{\dagger}(\vec{r}), \quad (5)$$

where \vec{k} represents reciprocal-lattice vectors; the variational equations for determining $C_{\vec{k}+\vec{k}'}$ can be written in the form

$$\sum_{\vec{k}'} C_{\vec{k}+\vec{k}'}^{\dagger} [(H_p)_{\vec{k}+\vec{k}', \vec{k}+\vec{k}'}^{\dagger} - ES_{\vec{k}+\vec{k}', \vec{k}+\vec{k}'}^{\dagger}] = 0, \quad (6)$$

$$(H_p)_{\vec{k}+\vec{k}', \vec{k}+\vec{k}'}^{\dagger} \equiv \langle \varphi_{\vec{k}+\vec{k}'}^{\dagger}(\vec{r}) | -\nabla^2 + U + \sum_t [v(t) - E_F] P_t | \varphi_{\vec{k}+\vec{k}'}^{\dagger}(\vec{r}) \rangle, \quad (7)$$

$$S_{\vec{k}+\vec{k}', \vec{k}+\vec{k}'}^{\dagger} \equiv \langle \varphi_{\vec{k}+\vec{k}'}^{\dagger}(\vec{r}) | 1 - \sum_t P_t | \varphi_{\vec{k}+\vec{k}'}^{\dagger}(\vec{r}) \rangle. \quad (8)$$

Thus, the matrix elements involved in Eqs. (7) and (8) are cast in a form independent of E , with the matrix element $S_{\vec{k}+\vec{k}', \vec{k}+\vec{k}'}^{\dagger}$, replacing the Kronecker $\delta_{\vec{k}+\vec{k}', \vec{k}+\vec{k}'}$ in the usual counterpart of Eq. (6) in pseudopotential theory. The actual wave functions $\Psi_{\vec{k}}^{\dagger}$ were obtained as in earlier work on Knight shifts from the pseudofunctions^{9,10} by replacing the plane waves in Eq. (5) by the corresponding orthogonalized plane-wave functions.

For normal pressure, the ratio c/a is much larger than ideal (1.63299), namely,¹¹ 1.86164 at 0°K. We have carried out a scanning of $\frac{1}{24}$ th of the corresponding Brillouin zone by sampling nine equally spaced planes perpendicular to the c axis, each having 21 points. The electronic contribution to eq_{e1} is given by

$$eq_{e1} = -e \sum_{i, \vec{k}} \left\langle \psi_{\vec{k}, i}^{\dagger}(\vec{r}) \left| \frac{3 \cos^2 \theta - 1}{r^3} \right| \psi_{\vec{k}, i}(\vec{r}) \right\rangle \quad (9)$$

r and θ being referred to the nucleus in question as the origin and the c axis as the z direction, i referring to the band and the negative sign on the right being a consequence of the negative charge on the electron.

Our results for the electronic contribution to the electric field gradient (efg) at 1 atm are presented bandwise in Table I. We have made use of Hartree-Fock wave functions for the core electrons in evaluating the expectation value of the field gradient. For each band, we have listed the various types of contributions, namely sd , pp , dd , plane-wave-plane-wave (PW-PW), and distant⁷ contributions in the same notation as in earlier work.⁸ The sd and dd contributions are significant here in contrast to the earlier studies in the lighter hcp metals because cadmium does have filled d cores. The major contribution is seen to arise from the first band and from the pp -type term. This is understandable because the p orbitals are the nonspherical ones with lowest l having finite density near the nucleus. To the electronic contribution one has to add the ionic contribution given by

$$eq_{ion} = \sum_N' \zeta e [3 \cos^2 \theta_N - 1] (1 - \gamma_{\infty}) / r_N^3, \quad (10)$$

where the summation over N refers to the ionic sites in the crystal except for that belonging to the nucleus under question and ζ refers to the valence of the atom. γ_{∞} refers to the Sternheimer antishielding factor for the core electrons and has been used for the distant contribution in Table I. There are two values available in the literature for the antishielding factor for Cd^{+2} . One of these was calculated using Hartree-Fock-Slater wave functions.¹³ The other is an interpolated value¹⁴ obtained from Hartree-Fock results for other ions. In keeping with our use of Hartree-Fock wave functions for the atomic wave functions in the calculation of eq_{e1} , we have used the interpolated Hartree-Fock value for $\gamma_{\infty} = -15$. Using the results of lattice summation in Eq. (10)

TABLE I. Various contributions to the field gradient in cadmium metal at 1 atm. All field gradients are stated in units of 10^{13} esu/cm³.

Band no.	sd	pp	dd	PW-PW	Distant	Total
1	0.96	184.49	9.94	4.01	-5.08	194.32
2	2.08	11.24	2.74	4.56	-0.84	19.78
3	0.00	0.00	0.00	-0.81	0.00	-0.81
Total	3.04	195.73	12.68	7.76	-5.92	213.29

appropriate to the value of $c/a = 1.86164$,

$$eq_{\text{ion}} = -58.18 \times 10^{13} \text{ esu/cm}^3. \quad (11)$$

Combining this with the net electronic contribution in Table I, we obtained the total efg,

$$eq = +155.1 \text{ esu/cm}^3. \quad (12)$$

Using this value of eq and the extrapolated experimental value³ of $|e^2qQ/h| = 137.5$ MHz, one gets $|Q| = 1.2229$ b. This value is to be compared with $|Q| = 0.77 \pm 0.12$ b derived¹ from the combination of TDPAC data for Cd^{111} in cadmium compounds and for In^{117} in an In^{++} -ion substitutional impurity in the same compounds. Our theoretical result is in reasonable agreement with experiment considering the possible sources of correction in both the theoretical and experimental values. On the theoretical side, the use of the pseudopotential approximation and neglect of relativistic¹⁵ and many-body effects, and also Sternheimer antishielding¹⁶ effects of the atomic type on the field gradient due to conduction electrons, could produce corrections that might bridge the gap with experiment. On the experimental side, the value of $|Q|$ is derived from data in insulators assuming¹ that the value of q at the cadmium and an impurity indium site are the same (except for antishielding effects). While the trend of the data¹ in some of the compounds does provide some support for this assumption, nevertheless it could also introduce enough uncertainty to bridge the gap with our value of $|Q|$. In any case, the most important feature of our work is that the electronic contribution is opposite in sign and about a factor of 3.5 larger in magnitude than the ionic contribution. The latter alone would have led to a theoretical value of Q about 4 times as large as experiment and of opposite sign to that predicted by the present calculation.

A more critical comparison between theory and experiment, and one that is independent of the value of the quadrupole moment, is the variation

of the quadrupole coupling constant with pressure. We have carried out the entire calculation of the electronic contribution to the field gradient at the pressure 50 kbar following exactly the same procedure as at 1 atm. The value of c/a and a , 1.7857 and 5.56273 a.u., respectively, were obtained by interpolation¹⁷ from x-ray data at neighboring pressures at 25°C. In Table II our calculated electronic, ionic, and total efg are compared at 1 atm and 50 kbar. The corresponding theoretical values of $|e^2qQ/h|$ listed are obtained using the value of $|Q| = 1.2229$ b from the data at 1 atm. Also listed are the ratios of the coupling constants due to the ionic, electronic, and total field gradients at the two pressures. The last column gives the values of $|e^2qQ/h|$ from experiment at the two pressures. The magnitude of the ratio of e^2qQ/h at two pressures predicted from our calculated total field gradients is seen to be close to the experimental ratio.¹⁸ This good agreement is in contrast to the relatively poorer comparison² in the change due to the ionic contributions alone at the two pressures. The net change in eq is seen to be a combination of changes of opposite sign due to eq_{el} and eq_{ion} with the former being the dominant one and determining the sign of the net change. Unfortunately, the experimental sign of the change is not currently available to compare with the theoretical result. However, the agreement in the magnitude of the change in e^2qQ/h and the ratio at the two pressures between experiment and theory clearly demonstrates the importance of the calculated electronic contribution and its relative sign compared to ionic in explaining the pressure variation.

As stated in the beginning, our theoretical sign for eq can be used to advantage in the future when the sign of e^2qQ is measured to predict the sign of Q , which will be of interest from the standpoint of nuclear theory. From the point of view of testing the theory of the origin of the field

TABLE II. Pressure variation of efg and coupling constant. All field gradients and coupling constants are in units of 10^{13} esu/cm³ and MHz, respectively.

Pressure (kbar)	eq_{ion}	eq_{el}	eq	$\left \frac{e^2q_{\text{ion}}Q}{h} \right $	$\left \frac{e^2q_{\text{el}}Q}{h} \right $	$\left \frac{e^2qQ}{h} \right _{\text{theor}}$	$\left \frac{e^2qQ}{h} \right _{\text{exp}}$
10^{-3}	-58.18	+213.29	+155.11	51.57	189.07	137.50	137.50
50	-39.72	+155.71	+115.99	35.21	138.03	102.82	100.5
Ratio ^a	+1.46	+1.37	+1.34	1.46	1.37	1.34	1.37

^aThe ratio refers to the 1-atm value divided by the 50-kbar value.

gradient, it will be desirable to study⁵ the relative sign of the Cd¹¹¹ coupling constant in the metal as compared to that in an ionic crystal¹ so that the sign of Q itself will not be involved.

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Surface Structure of Electron-Hole Droplets

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We consider the surfaces of the condensed phase of excitons in semiconductors, the electron-hole liquid (EHL). By using the theory of the inhomogeneous electron gas and a variational technique we estimate the surface tension for the EHL in Ge to be 10^{-4} erg/cm²; the carrier density in the surface region varies on a scale of ≈ 50 Å. We suggest an experiment to measure the surface tension of the EHL.

The condensation of excitons in certain semiconductors at low temperatures has been the subject of much recent interest.¹⁻⁸ The metastable condensed phase which results has become known as the electron-hole liquid (EHL). A source of particular fascination in the study of this phase is its apparently unique microscopic structure: Most current investigations^{1-5,7,8} consider that the EHL consists of two interpenetrating plasmas (the electrons and holes) *both* of which have quantum dynamics, in strong contrast with an ordinary solid or liquid. The differences in microscopic

structure might be expected to affect, among other things, the nature and properties of the surface of the EHL.

In an ordinary metal the surface properties can be understood by assuming the ions give rise to a fixed potential in which the electrons move. One then calculates surface energies, dipole layers, etc.⁹ In the EHL the mass ratio of electrons and holes is near unity. We might anticipate unusual surface energies and surface structure; very likely both components will have slowly varying density near the surface, each density