Negative Conduction-Electron Contribution to the Field Gradient in Beryllium*

N. C. Mohapatra, C. M. Singal, and T. P. Das
Department of Physics, State University of New York, Albany, New York 12203

and

P. Jena
Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada
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A first-principles calculation of the field gradient due to conduction electrons in Be leads to a contribution opposite in sign to that from ionic charges, in agreement with expectations from experiment. This result is of particular interest for the theory of nuclear quadrupole coupling constants in metals in view of recent experimental determinations of the sign of the latter.

Recently, there has been an upsurge of interest in the origin of nuclear quadrupole interaction in metals, as a consequence of a number of publications[1-7] of results of experiments where the sign[1,2,5-7] of the field gradient, and, in some instances, the variation of the field gradient with temperature[3] and pressure[4] have been measured. The net field gradient q at the nucleus is composed of a contribution q_{ion} from the positive ions in the lattice and a contribution q_{el} from the conduction electrons. Since q_{ion} can be obtained fairly accurately by various summation procedures,[8] one can extract the value of q_{el} from the experimental q. In those cases where the sign of q is determined, one can therefore get an unequivocal experimental prediction of the sign of q_{el}. Of five instances[1,2,5-7] where the sign of q is experimentally available, the sign of q has been predicted in this way to be the same as for q_{ion} in two cases[5,6] and opposite in three.[1,2,7] The theory should thus be able to explain both the sign and the magnitude of q_{el}.

There have been two mechanisms proposed[9,10] for q_{el}. One of these[9] involves the calculation of the field gradient from all the band electrons below the Fermi surface, and for antimony it gave the same sign as q_{ion}. The second mechanism,[10] important for transition metals and transition-metal compounds, involves the distortion of the Fermi surface by the $l=2$ component of the lattice potential and the resulting contribution from these Fermi surface electrons to q_{el}. This effect is always expected to be opposite in sign to q_{ion}, indicating a shielding effect due to the conduction electrons.

On the basis of these two results, an attempt has been made in a recent paper to decide on the relative importance of the two mechanisms[11] using the experimental sign of q_{el}. In addition, a recent theoretical calculation[12] of q_{el} in Mg gives the same sign as q_{ion} and close to the right magnitude, more than twice that of q_{ion}, leading to agreement of the total field gradient with the experimental q. In this metal, the Fermi-volume effect was found to give almost the entire q_{el}, the Fermi-surface effect being very small (about 2% of the Fermi-volume contribution) because of the relatively small density of states at the Fermi surface as compared to those for the transition metals. This result, taken together with that for Sb, may appear to reinforce the possibility of experimentally distinguishing between the two mechanisms. The purpose of the present work is to show that, in fact, q_{el} due to the volume mechanism can have either sign and we find it to be opposite in sign and about 21% of q_{ion} in Be, leading to essential agreement between the theoretical and experimental q's. Further, q_{el} is shown to be composed of mutually cancelling contributions from various bands, indicating that in any general metal q_{el} can have either sign.

The calculation will now be described briefly. What is needed for the electronic contribution to field gradient q_{el} is the evaluation of the expectation value integral

$$q_{\text{el}} = \int \rho_c(\vec{r}) r^{-3}(3\cos^2\theta - 1)\, d^3r. \tag{1}$$

In Eq. (1), $\rho_c(\vec{r})$ is the total conduction-electron charge density at the point $\vec{r}$, given by

$$\rho_c(\vec{r}) = 2\sum_{n\vec{k}} |\Psi_{n\vec{k}}(\vec{r})|^2 \tag{2}$$

with the sum on $n\vec{k}$ being taken over the occupied states only, n being the band index, and the factor 2 coming from the summation over the spin states. The origin of $\vec{r}$ is taken at the nucleus whose quadrupole interaction is under study. The orthogonalized plane-wave (OPW) procedure[13] was utilized for obtaining the wave functions $\Psi_{n\vec{k}}(\vec{r})$. For this purpose, the conduction-electron potential and the 1s core states were taken from the work of Loucks and Cutler.[14] In evaluating q_{el} through Eqs. (1) and (2) a summation has to be carried out over the various occupied states in the first Brillouin zone. By symmetry, in carrying out this summation, one can separate the Brillouin zone into 24 parts which contribute equally. In our calculation, we chose 189 $\vec{k}$ points in $\frac{1}{24}$th of the Brillouin zone in summing over $\vec{k}$, ascribing appropriate fractional volumes in $\vec{k}$ space to each of these points. These 189 points consisted of sets of 21 points over nine planes equally spaced along the c axis. Through a detailed examination for a few points in k space a linear combination of 23 OPW's was found to be an optimal choice for expanding the conduction-electron wave function, considering both convergence and the computational time involved. To allow additional flexibility in the variational aspect of the OPW calculation, a tight-binding function built out of a localized p-like orbital was added to the OPW basis set.

In obtaining the electronic contribution, the field gradient was divided into local and distant components by expressing the charge density in the following form:

$$\rho(\vec{r}) = \bar{\rho} + \sum_l \rho_l(\vec{r}) + \sum_l \sum_{N\neq 0} \rho_l(\vec{r} - \vec{r}_N). \tag{3}$$

In Eq. (3), the first term represents a uniform density which is slightly larger than the value 2/Ω (Ω being the volume of the Wigner-Seitz cell) from free electrons, due to the normalization factor $(1 - b_k^2)^{-1}$ associated with the OPW functions.[13] This uniform density, of course, does not contribute to the field gradient. The second term is a nonuniform density in the Wigner-Seitz cell centered around the nucleus in question and expanded in terms of l components, l being as usual the azimuthal quantum number. The local contribution arises only from the $l = 2$ component of this term. The third term gives rise to the distant contribution, the summation over N referring to the various Wigner-Seitz cells other than the central one under consideration. We would like first to discuss the distant contribution.

Since the net distant contribution was quite small and the dominant effect for this contribution arises from the $l = 0$ term in Eq. (3), only the latter term was retained. This term leads to a contribution to the field-gradient integral in Eq. (1) expressible as a lattice summation, similar to the contribution[8] from the charges on the ions, since the integrated effects of $\rho_0(\vec{r} - \vec{r}_N)$ in each cell end up as effective charges at the lattice points. These charges turned out to be positive in character as a result of charge-neutrality considerations and because the uniform density $\bar{\rho}$ in Eq. (3) was larger than the free-electron value. The distant contribution was evaluated to be 2.9% of the ionic contribution and of the same sign, the absolute values of the ionic[15] and distant contributions being

$$q_{\text{ion}} = 1.918 \times 10^{13} \text{ esu/cm}^3, \tag{4}$$

$$q_{\text{el,dist}} = +0.055 \times 10^{13} \text{ esu/cm}^3. \tag{5}$$

The experimental value of q in the metal, using the measured value[7] of the quadrupole coupling constant e^2qQ and the most recent value, 0.054×10^{-24} cm^2, of $Q(\text{Be}^9)$, is[16]

$$q_{\text{expt}} = 1.576 \times 10^{13} \text{ esu/cm}^3. \tag{6}$$

Thus, $q_{\text{el,dist}}$ is only a small fraction of q_{ion} and q_{expt} and adds to the difference between the two. As we shall see now, it is the local contribution which provides the bulk of the difference between q_{expt} and q_{ion}. The local contributions from the various bands were found to be[17,18]

$$q_{\text{I}} = +13.75 \times 10^{13} \text{ esu/cm}^3, \tag{7}$$

$$q_{\text{II}} = -21.35 \times 10^{13} \text{ esu/cm}^3, \tag{8}$$

$$q_{\text{III}} = +6.72 \times 10^{13} \text{ esu/cm}^3, \tag{9}$$

$$q_{\text{IV}} = +0.39 \times 10^{13} \text{ esu/cm}^3, \tag{10}$$

adding up to a total of

$$q_{\text{el,loc}} = -0.49 \times 10^{13} \text{ esu/cm}^3. \tag{11}$$

The field gradients q_{I}, q_{II}, etc., are composed of sd- and pp-type contributions as in the case of magnesium.[12] However, in contrast to magnesium, the pp contribution arises from only the plane-wave components of the OPW wave functions, since there are no p cores. The signs of the first- and second-band contributions are the same as in magnesium. This is understandable, because an examination of the symmetry of the first band indicates that the p character in most parts of the band is of p_x and p_y types, while for the second band, the dominant effect is due to p_z character, the z direction referring to c axis. The magnitudes for the two bands are sensitively dependent on the conduction-electron wave functions, which, in turn, are determined by the conduction-electron potential. It is interesting that, while the magnitudes are in general comparable to those in magnesium, the second-band result is larger than the first band in contrast to the magnesium situation. The third and fourth bands have very little occupancies and give very small contributions as of the same sign as for the first band. However, the magnitude of the second-band contribution is larger than the sum of the other three, and so one obtains the negative value for $q_{\mathrm{el,loc}}$ shown in Eq. (11), which agrees very well with the expected value of -0.397×10^{13} esu/cm^3 obtained from the difference between q_{expt} in Eq. (6) and the sum of q_{ion} and $q_{\mathrm{el,dist}}$ in Eqs. (4) and (5). Thus, the electronic contribution, in fact, provides near agreement (within 6%) of the total theoretical field gradient -1.483×10^{13} esu/cm^3 obtained from the sum of the numbers in Eqs. (4), (5), and (11) with the experimental value in Eq. (6).

From the present work and earlier calculations on antimony[9] and magnesium,[12] one can conclude, therefore, that the Fermi-volume contribution to q can, in fact, have either sign and is sufficient in nontransition metals to provide agreement with experiment when combined with the ionic contribution.

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[15] The value quoted in Eq. (4) is from the paper by Barnaal *et al.*, Ref. 7, and is very close to the value 1.93×10^{13} esu/cm^3 obtained earlier by Pomerantz and Das, Ref. 8.

[16] The value quoted for Q is obtained from the measured quadrupole coupling e^2qQ for a Be atom in the excited $(1s^2 2s 2p^3p)$ state and a recent many-body calculation of the field gradient q in this state by S. N. Ray, T. Lee, and T. P. Das, to be published.

[17] In Eqs. (7) to (10), q_i ($i = \mathrm{I, II, III, IV}$) denotes the local contribution to the electronic field gradient from the ith band.

[18] The numbers quoted for the various bands do not include any shielding effects due to the $1s^2$ core electrons of the Be^{++} ion. This type of shielding effect is expected to be quite small since the shielding factor for an external charge, which is expected to be much more important, is only -0.189 for Be^{++} ion [R. M. Sternheimer, Phys. Rev. 115, 1198 (1959)], close to the earlier value of -0.185 by T. P. Das and R. Bersohn, Phys. Rev. 102, 733 (1956). In any case, this type of shielding effect influences the individual contributions from various bands by the same factor since the part of the charge density producing the field gradient has predominantly $2p_x$, $2p_y$, or $2p_z$ characters for all the bands. In fact, recent calculations on the Be atom $(1s^2 2s 2p^3p)$ state (Ref. 16) indicate that the shielding factor for the $2p$ electrons due to the $1s^2$ core electrons is about 5%. Thus shielding effects are not expected to influence the sign of $q_{\mathrm{el,loc}}$ and change its magnitude very little, perhaps less than 5%.