RMP Colloquia

Local fields in solids: microscopic aspects for dieletrics

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The authors offer a historical and pedagogical introduction to the local-field problem in dielectrics. They then discuss a microscopic approach to the problem and introduce momentum dependence. Finally they apply these results to electron-phonon coupling in quasi-two-dimensional systems, in particular the high-T_c superconductors.

The local-field problem is almost 150 years old. The earliest treatments are due to Mossotti (1850), Clausius (1879), Lorenz (1880), and Lorentz (1952, and references therein). These treatments studied metallic particles embedded in a dielectric. Clausius and Mossotti studied the effective dielectric constant of the resulting system, while Lorentz and Lorenz considered the resulting index of refraction. In spite of the fact that these early treatments suffered from a lack of knowledge of the molecular nature of matter, many of the results are surprisingly accurate.

The most familiar treatment of the local-field problem is due to Lorentz. Consider a dielectric in an applied electric field $\mathbf{E}_{mac}$, which induces a polarization field $\mathbf{P}$. Now imagine a fictitious spherical cavity within the sample and examine the field at a point near the center of the sphere. The radius of the cavity must be large compared with the nearest-neighbor spacing. The total field at this point can then be expressed

$$\mathbf{E}_{loc} = \mathbf{E}_{mac} + \mathbf{E}_{in} + \frac{4\pi}{3}\mathbf{P} \; ,$$

where E_{in} is the field due to the dipole moments induced on the molecules within the cavity. Lorentz showed that this contribution is zero for cubic or random structures. Using $\mathbf{P} = n\alpha\mathbf{E}_{loc}$, where n is the molecular density and α the molecular polarizability, leads to the Clausius-Mossotti (CM) or Lorentz-Lorenz result:

$$\frac{E_{loc}}{E_{mac}} = \frac{1}{1 - \frac{4\pi}{3}n\alpha} \; . \tag{1}$$

The result is more commonly expressed in terms of the

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dielectric constant:

$$\varepsilon = 1 + \frac{4\pi n\alpha}{1 - \frac{4\pi}{3}n\alpha} \; . \tag{2}$$

The CM relation has been shown to be accurate in gases (Lorentz, 1952 and references therein), where $n\alpha \approx 10^{-5}$. More recently precise measurements on the rare-gas solids proved its applicability in solids (Sinnock and Smith, 1969), where the value of the denominator in Eq. (1) or (2) can be as small as 0.7. The accuracy of Eq. (2) for a solid may come as somewhat of a surprise considering the obvious simplifications in the derivation. The most gross simplification is the assumption that the molecules are point dipoles. For spherical molecules at zero wave vector, the external field is indistinguishable from that of a point dipole. However, the field of an ellipsoidal or cigar-shaped molecule differs from that of a point dipole. Since the molecules making up cubic solids must be of high symmetry, the point-dipole approximation should be accurate outside the molecular volume. A more subtle simplification has been noted by Landauer (1978), who points out that the removed cavity cannot be spherical in shape, since whole molecules must either be taken out or left in. This results in a somewhat irregular shape for the surface of the cavity. However, since the dipole field falls off as $1/r^3$, the surface area grows as only r^2, and the cavity must be large to begin with, these contributions should be small.

The cavity approach is pedagogically useful, but not necessary. In effect the Lorentz method consists of averaging the contributions of all of the dipoles on the lattice of the system, then solving for the field. Aspnes (1982) has shown that the same result can be obtained by first solving for the field, then averaging over the sample. In addition, a number of treatments have appeared involving sums over the dipole moments of the lattice without removing nearby atoms (Cohen and Keffer, 1955; Nijboer and DeWitte, 1958; Fano, 1960). All of these

treatments have obtained the CM result for cubic structures at zero wave vector, indicating the accuracy of the Lorentz model despite the simplifications.

In the following numerical work we have used a method that follows the Lorenz approach in spirit but that does not involve removing a cavity of molecules. We consider an applied polarizing field with arbitrary spatial variation. If we Fourier-analyze this field in both space and time, then the equations separate in such a way that we can treat each Fourier component separately. We choose a direction in space along which the phase of the plane-wave polarizing field will vary and evaluate the dipole sum for planes of equivalent molecules perpendicular to that direction. Near the origin the dipole fields are summed discretely, but beyond a certain distance, typically ten nearest-neighbor distances, the discrete sum becomes indistinguishable from the result for a dielectric slab, and the result for that plane can be extended to infinite distance analytically. This method reduces computer time and also has the advantage of removing the pathological behavior of the discrete dipole sum for momenta near reciprocal-lattice vectors (Cohen and Keffer, 1955).

The above discussion has indicated that the local field in primitive cubic lattices at zero wave vector is well understood, but many systems of physical interest are not in primitive cubic structures, and many quantities involve wave vectors throughout the Brillouin zone. In these cases the CM relation is not expected to be valid, and a microscopic approach is needed in which the dipole fields of the molecules are treated individually and a momentum-dependent phase factor must be included. Within the point-dipole approximation Nagel and Witten (1975) have generalized Eq. (1) as follows:

$$\frac{E_{\mathrm{loc}}(q)}{E_{\mathrm{mac}}(q)} = \frac{1}{1 - B(q)n\alpha} , \tag{3}$$

where q is the momentum and $B(q)$ the momentum-dependent local field factor, which is written in terms of the dipole sum:

$$B(q) = 4\pi + \sum_{i \neq j} \cos(\mathbf{q} \cdot \mathbf{r}_j) \frac{3[\hat{\mathbf{q}} \cdot (\mathbf{r}_i - \mathbf{r}_j)]^2 - (\mathbf{r}_i - \mathbf{r}_j)^2}{|\mathbf{r}_i - \mathbf{r}_j|^5} , \tag{4}$$

where $\mathbf{r}_i$ is the point in the solid at which the field is evaluated, $\mathbf{r}_j$ is another lattice point, $\hat{\mathbf{q}}$ is a unit vector parallel to $\mathbf{q}$, and the sum is over a sufficiently large cluster. $B(q)$ curves are shown in Fig. 1 for the three principal axes of the fcc structure. Some characteristics can be noted. Each of the curves approaches the CM value of $4\pi/3$ as $q \rightarrow 0$, although the behavior is obviously different for each of the directions. The behavior can be understood qualitatively by considering the nearest-neighbor spacing along the axis. The most closely packed direction, the 110 direction, shows the largest momentum dependence, nearly a factor of three, while the least closely packed direction, the 111 direction, shows very little momentum dependence. Each of the curves is periodic, with the periodicity proportional to
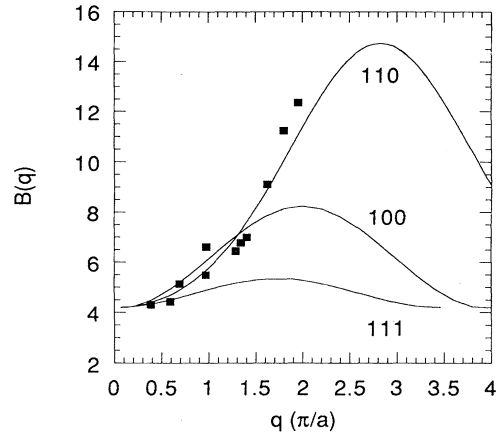

FIG. 1. Local-field factor $B(q)$ for the fcc structure: solid curves, point-dipole results for the three principal axes; ■, experimental results for solid N2.

the inverse lattice spacing.

$B(q)$ can be measured in certain cases by a direct comparison of the appropriate physical quantities in the gas phase and the solid state. N_2 provides a good example. The gas-phase and solid-state oscillator strengths, $f(q)$ and $N_{\mathrm{eff}}(q)$, of an excitation localized on a N_2 molecule, can both be measured using inelastic electron scattering. The ratio provides a direct measure of the square of the local-field enhancement:

$$\frac{N_{\mathrm{eff}}(q)}{f(q)} = \frac{E_{\mathrm{loc}}^2(q)}{E_{\mathrm{mac}}^2(q)} . \tag{5}$$

Included in Fig. 1 are results for $B(q)$ from the ratio of the oscillator strength in the solid state (Tarrio and Schnatterly, 1991a) and the gas phase (Skerbele and Lassettre, 1970). The results seem to indicate that our sample was an oriented crystal with momentum transferred along the 110 axis; however, diffraction patterns indicated a polycrystalline sample with small crystallites. Results for a polycrystalline sample can be approximated by calculating $B(q)$ for many random directions and averaging the measured quantity. Figure 2 shows our results for the square of the field enhancement for solid N_2 with averages in the three principal planes; our data are still better described by the 110-axis result, suggesting that a degree of alignment must have occurred under the growth conditions of the samples.

As mentioned, the point-dipole approximation is a good one at zero momentum; however, as the momentum grows, higher multipole moments become important. The reduction in dipole strength with q can be included through a form factor similar to that used in x-ray diffraction. Figure 3 shows results for solid Kr, a large atom in which the form factor is expected to introduce a large effect (Tarrio and Schnatterly, 1991b). A Lorentzian form factor was used, which decreased the polarizability to 0.75 of its low-momentum value at $q = 1/r_{\mathrm{atomic}}$. The resulting comparison with measurement is favorable,
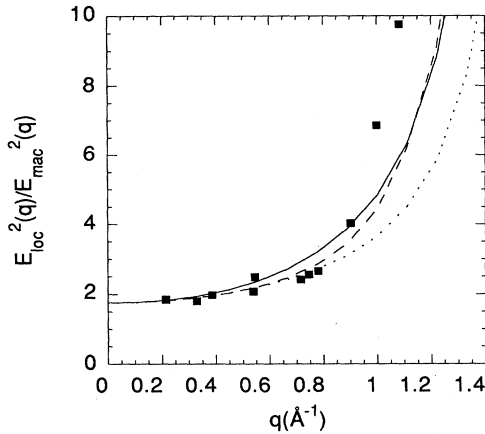
FIG. 2. Local-field enhancement ratio: ■, experimental results for solid N2; solid curve, point-dipole results averaged over the (100) plane; dotted curve, point-dipole results averaged over the (111) plane; dashed curve, point-dipole results averaged over the (110) plane.

although the scatter in the data is large.

If electrons are localized in one direction and extended in the other two directions, they will experience the macroscopic field within the plane but the local field perpendicular to the plane. Most of the high-T_c superconductors have conducting planes separated by insulating layers, and thus provide this sort of system. This becomes important when considering electron-phonon coupling, which includes contributions proportional to the square of the phonon-induced electric field. The BCS electron-phonon coupling parameter, λ_{BCS}, and the transport electron-phonon coupling parameter, λ_{tr}, are generally taken to be equal; however, in some cases they can be quite different. Using the McMillan (1968) equation, we find that the λ_{tr} of 0.3 measured in several of the high-T_c superconductors is much too small to account for transition temperatures of up to 125 K. However, conventional BCS theory may still be able to account for the high
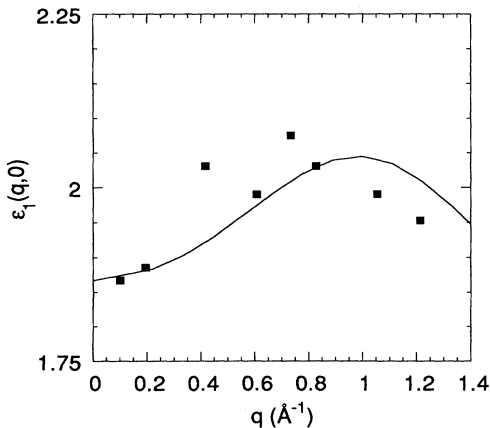

FIG. 3. Dielectric constant of solid Kr: ■, experimental results; solid curve, point-dipole results averaged over the (110) plane as described in the text.

temperatures if the superconducting electron-phonon coupling is enhanced sufficiently over that measured in normal transport.

In normal transport the electrons scatter from phonons with momenta in the conducting plane. Thus the phonon momentum component perpendicular to the plane does not contribute to the normal-state resistivity. However, the superconducting electron-phonon coupling involves a sum over all the phonons, including those with momenta perpendicular to the conducting plane. Since the macroscopic field is experienced in the conducting plane, but the local field is experienced perpendicular to the plane, the electron-phonon coupling is enhanced by a factor of

$$\lambda_{\perp}^{p} \approx \lambda_{\parallel}^{p} S^2 L^2 \tag{6}$$

for LO phonons with momenta perpendicular to the conducting plane. In this expression the subscript $\perp$ ($\parallel$) indicates perpendicular to (parallel to) the conducting plane, the superscript p indicates the contribution due to polar phonons, S is the screening factor by which the in-plane coupling is reduced, and L^2 is an average over momentum of the local-field enhancement, i.e., the square of the ratio of the local field to the macroscopic field. Thus we can estimate the enhancement in λ due to the two-dimensional nature of these compounds by evaluating the electric-field enhancement through $B(q)$.

The induced dipole moment on an atom depends on its local environment as well as its polarizability. This increases the number of dipole sums that must be evaluated in complex crystal structures that have several inequivalent ions and sublattices. $B(q)$ then becomes a matrix, and the electric field at a point in the solid is obtained by solving the simultaneous equations

$$E^i_{loc} = E_{mac} + \sum_j B_{ij}(q) E^j_{loc} , \tag{7}$$

where E^i_{loc} is the local field at sublattice i and B_{ij} is the element of B arising from the field at sublattice i due to sublattice j. B_{ij} is diagonally symmetric.

Since B_{ij} is simply a geometric quantity, we can calculate it directly from crystal structures (Yvon and François, 1989). Figure 4 shows our results for $B(q)$ for q in the z direction for the highly polarizable sublattices in $La_{1.85}Sr_{0.15}CuO_4$ (Tarrio, Benitez, and Schnatterly, 1991). As in the cubic cases, the sublattices with the closest nearest-neighbor spacing in the z direction have the largest momentum dependence for $B(q)$. However, since these are not cubic structures, the curves generally do not approach $4\pi/3$ as $q \rightarrow 0$. The low-momentum behavior can be visualized by considering the shape of the dipole field. For a sublattice with close neighbors in the x-y plane but distant spacing in the z direction, such as the O2 sublattice in $La_{1.85}Sr_{0.15}CuO_4$, the dominant contribution is negative, and, as shown in Fig. 3, $B(q)$ is negative. However, for sublattices with smaller spacing in the z direction, such as La and O1, the nearest-neighbor contributions are large and positive, and $B(q)$ is positive.
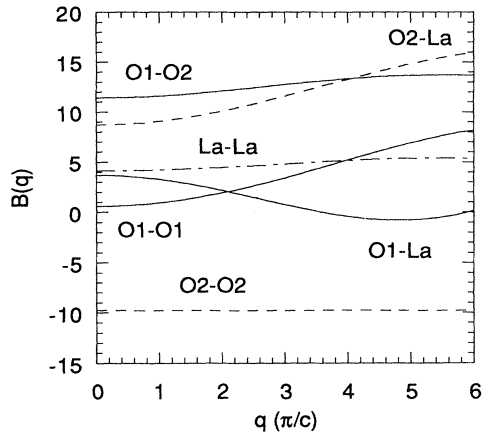
FIG. 4. Calculated $B(q)$ for three sublattices in $La_{1.85}Sr_{0.15}CuO_4$.

The momentum dependence in $B(q)$ is also larger for more closely spaced planes.

We have calculated the local field at the O2 (conducting) sites for momenta out to $4\pi/a$, where a is the lattice constant in the x-y plane, and averaged the square of the field enhancement for several of the high-T_c compounds. Form factors similar to that found for Kr were used to reduce $E(q)$ at very large momentum.

We find values of L^2 of 4 ± 1 for the Tl family and smaller values for the other families of high-T_c superconductors. Recently $KBaBiO_3$, which is cubic and has an isotropic conductivity, has been shown to be a weak-coupling BCS superconductor (Loong et al., 1991). Its T_c value is 30 K, and its phonon spectrum is similar to that of the other high-T_c materials. Therefore coupling electrons to these relatively-high-frequency phonons can yield $T_c = 30$ K with no local-field enhancement. It appears possible, then, that the enhancement factors we find for these materials, which are largest for the family with the highest T_c values, may contribute significantly to the observed superconductivity.

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