Nb_3Ga, and the crystal transformations resulting from instabilities are not the important limiting factor on T_c in this family of materials.

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Calculation of Electric Field Gradients in Crystals Using Molecular Wave Functions*

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The electric field gradient in stressed NaCl is calculated using a simple cluster approach. The assumption of independent bonding allows the contribution of cluster electrons to be calculated directly from their wave functions, without the use of shielding factors. Molecular rather than atomic wave functions are employed. Good agreement with experiment is obtained.

Although electric field gradients at nuclear sites in crystals have been routinely measured for a number of years by a variety of techniques, theoretical studies of the origin of the electric field gradient (EFG) have had only limited success. Most theories of solids assume inert and spherical atomic cores, a fatal approximation since the EFG interaction goes as R^{-3} from the nucleus and, hence, small perturbations of the inner electrons are likely to be important. This point has been recognized in recent years, and it has been shown in detail[1] that an EFG arises from the fact that core orbitals lose their spherical symmetry due to overlap with neighboring ions. The most complete calculation of this kind was done by Sharma[2] for Al_2O_3, using free-ion wave functions and including all the metal-ligand matrix elements. In spite of the good agreement achieved in this case there remain two major difficulties with this approach: (1) The use of free-ion wave functions restricts its validity to the most ionic solids, and (2) there is no consistent way of taking account of shielding and antishielding effects; for example, if ions A and B overlap, the EFG due to the charges on A and B may be calculated with the use of appropriate Sternheimer shielding factors,[3] but to the charge distributed in the "overlap region" no such shielding factor obtains. This is a serious problem since these shielding corrections are typically large.

This Letter proposes a new theoretical approach which largely overcomes these difficulties. First, consider a cluster of ions, with the ion of interest at the center. The EFG could be calculated very well in principle by finding the cluster wave functions in a reasonably good approximation, for example, Hartree-Fock, and computing the cluster EFG from these states. The EFG from the remainder of the lattice will be small and can be adequately calculated by the usual point-charge model with shielding corrections. For most solids the cluster could be limited to nearest neighbors. Such calculations may soon be undertaken but are unfortunately far too lengthy for routine applications. However, the method is greatly simplified if the assumption of completely localized and independent bonds[4] is made. The cluster EFG may then be found by computing wave functions for each bonded pair, then summing the EFG due to each pair in turn. The assumption of independent bonds may seem nearly as drastic as that of purely ionic bonding. The important point, however, is that for EFG calculations the independent-bonding approximation will probably be very good, since the R^{-3} EFG interaction emphasizes the contributions of inner electrons, which interact weakly and hence nearly independently with neighboring ions.

Thus, for ion A surrounded by ions B, C, etc., we proceed as follows: Consider each of the pairs $AB, AC, \ldots$, in turn, compute approximate Hartree-Fock wave functions for each pair or "molecule" for the appropriate interatomic separation, and then evaluate the A-site EFG by

$$q_A = \frac{2eZ}{R^3} - 2e\sum_i \langle \varphi_i | \frac{3\cos^2\theta_A - 1}{r_A^3} | \varphi_i \rangle, \qquad (1)$$

where φ_i are one-electron states, Z the B-ion nuclear charge, and R the nuclear separation. r_A and θ_A are polar coordinates measured from nucleus A with respect to the pair axis. The sum of these contributions and the EFG from the remainder of the lattice yields the total A-site EFG.

As an example, the EFG at the Na site in axially stressed NaCl was calculated. This system is ideal in several respects: There is no uncertainty in the lattice parameters, there are no ionic dipole moments, and the independent-bonding model is known to be very good. We are interested in the EFG per unit strain, a tensor with two components, S_{11} and S_{44}, corresponding to strains along ⟨100⟩ and ⟨111⟩ directions.

Let $q(R)$ be the (smoothly varying) Na EFG for a Na-Cl pair with separation R. By considering small ⟨100⟩ and ⟨111⟩ crystal strains, it can be shown that the EFG/strain due to the cluster is respectively $S_{11} = 2R\,dq/dR$ and $S_{44} = 3q$. For this crystal it happens that the point-charge EFG due to other than nearest neighbors is negligible (about 1% of the total EFG). To calculate $q(R)$ we have used wave functions computed by Matcha, McLean, and Yoshimine[5,6] for the NaCl molecule with internuclear separation $R = 4.30$, 4.485, 4.60, 4.75, and 5.00 a.u. As an indication of the accuracy of these wave functions, we note that Matcha's calculation[5] of the Na EFG in the NaCl molecule and other EFG calculations in alkali-halide molecules[5] are generally consistent with experimental determinations to within 5%. The matrix elements in Eq. (1) were computed for $R = 4.75$ and $R = 5.00$ using a Gauss-Legendre quadrature program written for the Burroughs B6700 computer at the Queen's University Computing Centre. The remaining values of $q(R)$ are those of Matcha.[5] To obtain q and dq/dR at $R = 5.329$ a.u., the Na-Cl separation in solid NaCl, we have had to extrapolate these data as shown in Fig. 1. This was done by a least-squares fit to $q(R)$.

The results of the calculation of S_{11} and S_{44} are given in Table I along with experimental data of Marsh and Casabella.[7] The agreement is good considering the experimental uncertainty and the possible error in the extrapolation of $q(R)$.

In summary, the EFG in stressed NaCl has been derived using molecular[8] rather than free-

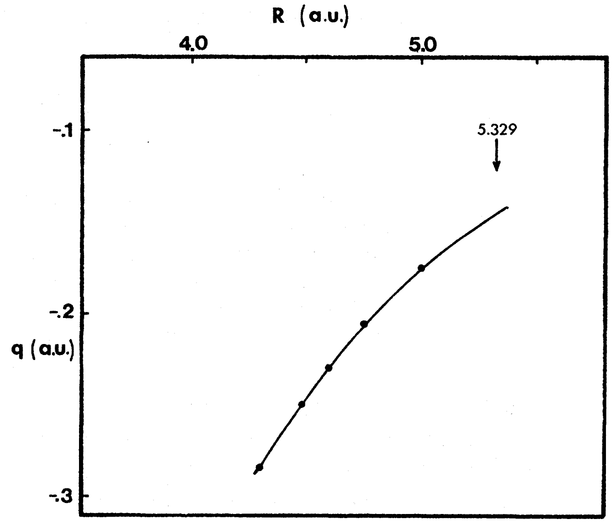

FIG. 1. EFG at the Na nucleus in the NaCl molecule as a function of internuclear separation. Computed values of the EFG are shown as points. The solid line represents the least-squares fit $q(R) = -0.254 + 3.626/R - 16.143/R^2$.

TABLE I. The EFG/strain tensor for NaCl.

	S_{11} (a.u.)	S_{44} (a.u.)
Calculated	+0.85	−0.43
Experiment[a,b]	0.82 ± 0.12	0.34 ± 0.03

[a] See Ref. 7.

[b] The signs of S_{11} and S_{44} were not determined experimentally, but were assumed to be opposite.

ion wave functions. This is probably the first calculation of an EFG in any solid that has not required the use of any Sternheimer shielding factors. The method can be applied to other solids and complex molecules and to other hyperfine interactions. Further studies are needed to determine the limits of validity of the model and to consider possible refinements in the case of more covalent solids.

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[8] Confusion may arise in regard to the meaning of the term "molecular wave functions." In this Letter it refers to solutions of the Schrödinger equation for a diatomic molecule. In the literature this term as well as "molecular orbitals" may often refer to wave functions for a molecule or cluster obtained by assigning free-ion wave functions to each electron, the only modification being to require orthogonality between one-electron states.

X-Ray Photoemission Spectra of Crystalline and Amorphous Si and Ge Valence Bands*

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High-resolution x-ray photoelectron spectra of the total valence bands of crystalline and amorphous silicon and germanium are reported. For the crystals, the spectra yield results that are strikingly similar to current theoretical calculations of the electron density of states, $\rho(E)$. Amorphous Si and Ge exhibit definite band structures that are similar to one another but markedly different from the crystalline results. They agree very well with the theoretical model of Joannopoulos and Cohen.

Although several density-of-states calculations have been carried out on silicon[1] and germanium,[2] relatively little experimental information is as yet available concerning the densities of states $\rho(E)$ of the more tightly bound valence electrons of these semiconductors. The valence-band densities of states of the crystalline modifications of Si and Ge are of current and continuing interest. In addition, a considerable amount of recent activity has been directed toward elucidating the electronic structure in the amorphous forms.[3] Thorpe and Weaire[4] have discussed three alternative models for the densities of states of amorphous Si and Ge, and Joannopoulos and Cohen[5] have recently given quantitative predictions for $\rho(E)$. In this Letter we present the first high-resolution x-ray photoelectron (XPS) spectra for the densities of states of crystalline and amor-