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CRYSTAL FIELD EFFECTS ON F CENTER WAVE FUNCTIONS IN KCl, CsF, AND MgO*

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Investigations are continuing of the interaction between an F-center electron and the core electrons of neighboring ions in the crystal. A pseudopotential is obtained for each ion from free ion wave functions, and the superposition of potentials is expanded around the vacancy in cubic harmonics.¹ Numerical wave functions are obtained for the spherical part of the expansion, and the crystal field effects of the first nonspherical terms are obtained by perturbation theory to first order in wave functions and third order in energy.

In all three crystals studied it is important to cut off pseudopotentials at about half the interionic spacing a_0 in order to obtain good stability of the solutions for the F electron; the effect is especially noticeable for negative ions, as expected. In KCl and MgO the calculated optical transition energy for the undistorted lattice is 20 to 30% smaller than the observed value, but agreement may be obtained by allowing inward displacements of nearest neighbors by 4 and 5%, respectively. The result for MgO corresponds to a minimum of the total energy for the ground state as calculated by Wood and Joy² and is opposite in direction to the estimate from the observed electric quadrupole splitting. For CsF the transition energy is 40% too large for the undistorted lattice, but an inward displacement of 2.5% is also needed in this case after inclusion of exchange.

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The general effect of using pseudopotentials is to make the potential well narrower than for the point ion case, and this causes an outward shift of the F wave function as seen in the figure. This shift means that the orbital radius is about $1.3 a_0$ in the unrelaxed excited state, compared to $0.5 a_0$ in the ground state, and indicates why treatment of the excited state is a difficult problem. When a Slater exchange term is included in the pseudopotentials, all potentials become more attractive, and the outward shifts of the wave function are even more pronounced. Since the excited state is lowered more than the ground state, the optical transition energy is decreased; the amount is perhaps several times the shifts produced by displacements of nearest neighbors.

Overlap integrals and matrix elements for g-shift, hyperfine constants, and spin-orbit interaction are calculated by Löwdin's α -function technique.³ Excellent agreement with experiment is obtained for the g-shift in KCl, and fair to good agreement is obtained for isotropic and anisotropic hfs constants for the first shell in MgO and the first two shells in KCl. The spin-orbit energy splitting for the excited state is more sensitive to the overlap integrals and is 4 times too small in KCl and too large in CsF. Thus it appears that the ground state wave function is rather good but that the excited state function is less reliable.

Electron-lattice interactions are treated phenomenologically. Reasonable values of 0.6 to 0.8 are obtained for oscillator strengths, but the calculated band widths are considerably too large. Fair agreement is also obtained for Faraday rotation constants.

Crystal field effects introduce nonspherical contributions to the wave functions of approximately 1% for the ground state in all three crystals and of 6%, 4%, and 11% for the excited state in KCl, CsF, and MgO. A number of

symmetry factors have been derived to express the effect of these nonspherical parts on various quantities; the form of the symmetry factors depends only on the crystal symmetry and should therefore be useful for other problems. For the F center in KCl the crystal field decreases the spin-orbit splitting by 12%, changes the vibrational energy by +40% for the breathing mode, +35% for the tetragonal mode, and - 8% for the trigonal mode, decreases the electric dipole matrix element by 6%, decreases the magnetic field splitting factor by 23%, and increases the optical absorption coefficient by 75%. The corresponding changes are somewhat smaller for CsF and larger for MgO. These changes are impressive when compared to the fairly small nonspherical wave function contributions from which they originate.

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The wave functions for the first excited state of the F-center