

emphasize that, although the present study gives interesting and additional information about the electron-phonon coupling at the defect responsible for the 355.7-nm zero-phonon line, it does not help resolve the question regarding its likely origin.

Finally, the lifetime of the excited F^+ center has been measured in these crystals. Contrary to measurements made on neutron-irradiated samples,¹² we find a measurable lifetime of 60 nsec. Compared with the radiative lifetimes of the F centers in the alkali halides,²² this value for CaO is very short. Presumably this reflects that both the ground- and relaxed excited-state wave functions of the F^+ center in CaO are compact relative to the alkali-halide F centers.

IV. CONCLUSIONS

The luminescence measurements discussed here give information on the nature of the electronic states of the F center in calcium oxide. It is shown that the results are consistent with the expected two-electron states of the F center. In particular, it is evident that in emission the $^1P \rightarrow ^1S$ transition occurs at 500 nm. That this

²² F. C. Brown, *The Physics of Solids* (W. A. Benjamin, Inc., New York, 1967).

allowed transition is weak, relative to the spin-forbidden $^3P \rightarrow ^1S$ transition (629-nm band), is thought to be due to a $^1P \rightarrow ^3P$ radiationless decay process, occurring with higher probability. The presence of structure in the zero-phonon line associated with the $^3P \rightarrow ^1S$ transition is explained as being due to spin-orbit interaction splitting the 3P configuration into 3P_2 , 3P_1 , and 3P_0 levels. The spin-orbit coupling constant λ is not more than 9 cm^{-1} . Studies of the $F \rightarrow F^+$ photoconversion demonstrate that the 3P and 1P levels of the F center are not more than 1.0 and 0.1 eV, respectively, below the bottom of the conduction band. Apparently, the electronic states couple mainly to the phonons in the optic branch for both the F and F^+ centers.

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Crystal Transformation for Hard Spheres*

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A proof is given that the ground-state energy of a hard-sphere particle in a hexagonal cell near close packing cannot be larger than it is in a face-centered cubic cell, and the energy difference is variationally evaluated. On the other hand, molecular-dynamics calculations suggest that in the classical region the fcc hard-sphere crystal is stabilized by an entropy which agrees well with that observed in the hcp to fcc phase transition in helium.

THE phase diagram of helium shows that the hexagonal phase is stable in the limit of low temperature and high pressure.¹ Since in this limit the zero-point energy can be made arbitrarily large compared to the depth of the potential well (i.e., the attractive part of the potential is unimportant), it must be concluded that one should be able to prove that hard spheres are stable in the hexagonal phase near close packing and at low temperature. The first part of this paper is devoted to such a proof in a one-particle approximation. Subsequently, the tiny energy dif-

ferences between the fcc and hcp ground and first excited states are numerically evaluated.

One would not expect this energy difference to agree closely with that observed in the helium transition for several reasons, although it is within an order of magnitude. The energy will be altered by many-body correlations, although the hard-sphere cell model has led to quite accurate classical results.² Furthermore, the experimentally observed energy difference might have a considerable contribution due to the difference in the lattice potential energies, though one which cannot be reliably estimated.³ Finally, the energy difference in a cell calculation using a more realistic potential, like

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¹ J. S. Dugdale and J. P. Franck, *Phil. Trans. Roy. Soc. London* **A257**, 1 (1964).

² B. J. Alder, W. G. Hoover, and D. A. Young, *J. Chem. Phys.* **49**, 3688 (1968).

³ B. J. Alder and P. H. Paulson, *J. Chem. Phys.* **43**, 4172 (1965).

the Lennard-Jones potential, will be shown to be an order of magnitude larger and in better agreement with experiment.⁴ On the other hand, the entropy of transition is less sensitive than the energy to the presence of a potential, since a perturbing potential on a hard core affects the entropy only to second order.⁵ Accordingly, entropies of melting could be accurately calculated for argon from the behavior of hard spheres.² The entropy of transition for helium which can be shown to result primarily from many-body contributions then suggests that one should be able to prove that classically hard spheres are stable in the fcc phase. This entropy of transition is evaluated for hard spheres via molecular dynamics with results to be found in the last part of this paper. The observed agreement reinforces the conclusion that hard spheres, like helium, should show a first-order phase transition between a low-temperature hcp phase and a high-temperature fcc phase.

For the proof of the greater stability of the hexagonal phase at low temperature, a representative sphere in the limit of high density is considered as a free particle confined to a twelve-faced cell formed by the planes perpendicular to the nearest-neighbor directions at which the wave function ψ vanishes. The fcc and hcp cells have identical volumes and identical shapes both above and below a close-packed plane of atoms, but the difference is that in the hcp phase the two halves are reflected about the close-packed xy plane, while in the fcc case one of the two halves is rotated by 60° about the z axis. This difference in symmetry is sufficient to show that the energy of a particle in its ground state in the hcp cell cannot be larger than that of a particle in the fcc cell. The intuitive basis for this deduction is that the lack of symmetry about the xy plane in the fcc case puts an extra constraint on the variational calculation and hence raises its energy. For a rigorous proof, a trial function $F_{\text{hcp}}(x,y,z)$ is adopted for the hcp cell, which is related to the true ground-state wave function $\psi_{\text{fcc}}(x,y,z)$ of the fcc cell by

$$F_{\text{hcp}}(x,y,z) = \psi_{\text{fcc}}(x,y,|z|).$$

F is an admissible trial function since it satisfies the hcp boundary conditions. Since F is piecewise C^1 (that is, it is continuous, but has a piecewise-continuous gradient), the expectation value of the Hamiltonian must be written in a form⁶ equivalent to the customary one,

$$H[F] = \int \nabla F \cdot \nabla F dv / \int F^2 dv,$$

with the integration being over the hexagonal cell. Since, as is well known, the lowest value of $H[F]$ is the energy eigenvalue E_{hcp} of the hexagonal lattice,

$$E_{\text{hcp}} \leq H[F_{\text{hcp}}] = H[\psi_{\text{fcc}}] = E_{\text{fcc}}.$$

⁴ A. Luntz and B. J. Alder (to be published).

⁵ E. B. Smith and B. J. Alder, *J. Chem. Phys.* **33**, 1439 (1960).

⁶ R. Courant and D. Hilbert, *Methoden Der Mathematischen Physik* (Springer-Verlag, Berlin, 1931), Vol. 1, p. 398.

TABLE I. Energy levels (in units of $\hbar^2/8\pi^2m$).

fcc ground state	0.860923 ± 0.000001
fcc triplet excited	1.75261 ± 0.00001
hcp ground state	0.860908 ± 0.000007
hcp singlet excited	1.75276 ± 0.00001
hcp doublet excited	1.75218 ± 0.00014

The desired inequality has been proven except for the identity $H[F] = H[\psi]$, which is readily provable by virtue of the symmetry involved.

Unfortunately, an analogous proof for the relative energies of the first excited state cannot be made. The particle in the cubically symmetric fcc cell has a triply degenerate excited level. In the hcp cell, the degeneracy is split into a singlet whose wave function has a node on the xy plane and a doublet with nodes on the other reflection-symmetry planes which contain the z axis. The excited energy levels can be calculated by the same methods as for the ground state by considering only either half of the cell sectioned off by the nodal planes. However, only for those nodal planes which contain the z axis is it possible to apply the above inequality, so that it is possible to prove only that the fcc triplet level is an upper bound for the hcp doublet level.

It is most economical, in fact, to compute any of the energy levels in the smallest possible subregion of the cell which by reflections through symmetry planes can generate the entire cell. Thus a solution for the fcc ground state was sought in one of the 48 congruent tetrahedra in which one vertex was at the center of the cell, one at the center of a face of the cell, and the remaining two on the adjacent vertices of that face. In general, subregions have faces where the wave function must vanish because that face is either part of the face of the cell or a region which lies on a nodal plane. It proves most convenient to choose as basis functions in a variational calculation polynomials in xyz such that each polynomial vanishes on the appropriate face. On the remaining faces of the subregion, no boundary conditions need be imposed, since the variational principle ensures that the normal derivative of the solution is zero there.⁶ In general, advantage has been taken of this fact, although it was found that imposing the normal derivative condition helped convergence a little.

The basis function F hence is a sum of products of polynomials of the form $ax+by+cz+d$ (which ensure that $F=0$ wherever required) and of $x'^l y'^m z'^n$, where the primed and unprimed coordinates are linearly related. The sum is ordered in $l+m+n$, which determined the number of basis functions. Sometimes the choice of only either even or odd values of l, m, n helped convergence. For these basis functions the matrix elements of the free-particle Hamiltonian can be evaluated analytically, and the matrix eigenvalue must then be computed.

The results of these calculations are given in Table I. The scale of energy is chosen so that $\hbar^2/8\pi^2m$ is unity,

which corresponds to the ground-state energy of a free particle in a sphere of radius π inscribed in either the hcp or fcc cell. In the slightly larger sphere, whose volume equals that of the cells, the ground-state energy is $(\pi^2/18)^{1/3}=0.82$. The ground-state energy of a particle in the actual cell must lie between 0.82 and unity, because the spherical shape leads to the lowest-energy value for any given volume. The lowest excited level in a sphere is triply degenerate and 2.04 times as high as the ground state; therefore, the values given in Table I for the ground state and excited states (also 2.04 times as high as the ground states) are of reasonable magnitude.

The energy eigenvalues given in Table I confirm the greater stability of hcp, but, as suspected, by an exceedingly small amount. In order to get that difference reliably, it was necessary to go to a large basis set and, amazingly enough, to triple-precision arithmetic—approximately 42 decimal places—in order to eliminate difficulties connected with roundoff errors. The larger 300×300 matrices in triple precision could no longer be contained in the fast core so that it was necessary to deal in succession with blocks of the partitioned matrix. Table II illustrates the convergence of the energy eigenvalue for one of the levels with increasingly larger basis sets.

The weighted mean value of the excited energy levels of hcp as given in Table I, 1.75237, is also lower than that of the triplet fcc state, so that this model fails to show a phase transition to fcc at moderate temperatures. In the high-temperature or classical limit, the one-particle model leads to indistinguishable properties between the two lattices inasmuch as the free volumes are identical. Hence the question as to which phase is more stable classically depends on an accurate solution of the many-body problem.

By means of the numerical method of molecular dynamics, it has not been possible to detect any difference which is statistically reliable. However, in the solid near the melting point, a difference in pressure, a difference in the collision rate involving second nearest neighbors, as well as a difference in location of the tie line seem to be indicated, which all favor stability of the fcc lattice. The pressure of the fcc phase appears to be about 0.01 lower in PV/NkT (or 0.1%) in a system of 216 particles with identical boundary conditions for each phase. If it is assumed that this absolute difference decreases linearly as the density increases, the difference in entropy between fcc and hcp at close packing is about $0.002Nk$.

This difference is comparable to the one found between fcc and hcp in the nearest-neighbor harmonic-oscillator model⁷ ($0.0015Nk$). One would, in fact, expect the difference to be slightly larger for hard spheres than for harmonic oscillators, based on the larger value of the mean-square displacements of a particle from its lattice site. This displacement is a measure of the free

TABLE II. Convergence of hcp singlet excited state.

N^a	E	$10^5 \Delta E^b$	R^c	E_{ex}^d
70	1.752938630	7.5512	2.023	1.752789
95	1.752863118	3.7327	1.679	1.752771
125	1.752825791	2.2236	1.492	1.752758
161	1.752803555	1.4900	1.495	1.752759
203	1.752788655	0.9964	1.569	1.752761
252	1.752778691	0.6352		
308	1.752772339			
Result ^e	1.75276 \pm 0.00001			

^a The number of terms in the variational function as ordered by the value of $l+m+n$.

^b The difference between successive energies.

^c The ratio of successive differences.

^d The extrapolated energy based on geometric series with quoted ratio.

^e The error estimate is based on the difference between the extrapolated value and the most accurate computed value.

volume accessible to a particle, and hence its logarithm is a measure of the entropy. For harmonic oscillators the ratio of the mean-square displacement for the fcc crystal to that of the hcp crystal was calculated to be 1.0065 from the inverse second moment of the frequency distribution.⁸ For hard spheres this ratio was found to be 1.02 ± 0.01 from molecular dynamics. These mean-square-displacement values at least confirm the greater stability of the classical hard-sphere fcc crystal.

The experimental difference in entropy for helium, $0.0019Nk$, falls gratifyingly in between those for hard spheres and harmonic oscillators. It can be readily shown that the first excited state contributes negligibly to that entropy difference. Furthermore, the correction for the change of entropy at constant pressure, as experimentally observed, to that at constant volume, as calculated, is unimportant.

The above results disagree, however, with the finding of the classical cell cluster theory,⁹ which predicts greater stability of the hcp phase in the close-packed limit by $0.0008Nk$. Although the cell cluster theory shows that the corrections to the single-particle cell theory are quite small, the ability to calculate these corrections reliably has previously been questioned.² In this regard the only exactly known quantum-mechanical result is for hard rods where the ground-state energy of the one-particle model is $\frac{3}{4}$ that of the exact solution. In three dimensions an estimate of the many-body effects in the ground-state energy of helium has been made from an analysis of experimental data.¹⁰ Unfortunately, the calculation of the exact ground-state energy of the sphere system represents a formidable problem, and the best hope of proving the existence of the crystal transformation resides in generalizing the proof of the inequality given earlier and in improving the accuracy of the results from molecular dynamics.

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⁸ W. G. Hoover (private communication).

⁹ F. H. Stillinger and Z. W. Salsburg, *J. Chem. Phys.* **46**, 3962 (1967), and later private communications.

¹⁰ R. K. Cole, *Phys. Rev.* **155**, 114 (1967).

⁷ W. G. Hoover, *J. Chem. Phys.* **49**, 1981 (1968).