

of $1-10 \text{ cm}^{-1}$ which seems reasonable. More detailed studies of our mechanism⁸ and its application will be published elsewhere in the future.

Halley and Silvera's mechanism seems to us to be ineffective. If their first expression is correctly written, it is

$$Q = [\lambda \sum_m \langle \Gamma_1 | Q^{(\text{op})} | \Gamma_m \rangle \langle \Gamma_m | \tilde{L} | \Gamma_1 \rangle / (E_1 - E_m) + \lambda \sum_m \langle \Gamma_1 | \tilde{L} | \Gamma_m \rangle \langle \Gamma_m | Q^{(\text{op})} | \Gamma_1 \rangle / (E_1 - E_m)] \cdot \tilde{S}. \quad (6)$$

Considering the fact that the orbital functions appearing in Eq. (6) can be chosen to be real, we see that the matrix elements of \tilde{L} are pure imaginary while those of $Q^{(\text{op})}$ are real. This immediately leads to a vanishing Q because of the Hermitean nature of \tilde{L} . Putting it in a more sophisticated way, the quadrupole moment, which is Hermitean and invariant with respect to time reversal, cannot be represented by a Hermitean operator proportional to \tilde{S} which changes its sign upon time reversal.

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STRUCTURE OF THE ORDERED STATE OF ORTHO-HYDROGEN AT ABSOLUTE ZERO

Joshua Felsteiner

Department of Physics, University of Toronto, Toronto, Canada

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It is known that solid hydrogen has a specific-heat anomaly at about 1.6°K at high ortho-hydrogen concentrations ($>60\%$).¹⁻³ This anomaly is accompanied by a change in the nuclear magnetic resonance line shape.⁴⁻⁷ It has been shown that solid hydrogen undergoes an order-disorder transition at this temperature which could be caused by the quadrupole-quadrupole interaction between the ortho-molecules.⁸⁻¹⁰ Further, Nakamura⁸ has shown that this quadrupole-quadrupole interaction is the most important contribution to the energy of ordering. Below the transition temperature an ordered state is formed to give minimum interaction energy. Recently, the infrared-absorption spectrum of solid hydrogen has been measured by Clouter and Gush¹¹ near 1.5°K . They observed a change in the spectrum at the same tempera-

ture, which can only be explained if we assume that the crystal structure changes from one without inversion symmetry above the transition temperature to one with inversion symmetry below it.

The purpose of this note is to suggest a lowest energy configuration of pure ortho-hydrogen and to show that the minimum quadrupolar energy in the face-centered cubic lattice is lower than that in the hexagonal close-packed lattice, a result in accord with the measurements of Clouter and Gush.¹¹ This is done by the classical method of Luttinger and Tisza¹² for minimizing the dipole-dipole interaction energy which has been generalized by Nagai and Nakamura¹³ for quadrupole interaction.

The interaction energy between two quadrupoles, each of quadrupole moment Q , is given by

$$\frac{3}{4}e^2Q^2 \left\{ \frac{1 + 2(\tilde{S}_1 \cdot \tilde{S}_2)^2}{r^5} - 5 \frac{(\tilde{S}_1 \cdot \vec{r})^2 + (\tilde{S}_2 \cdot \vec{r})^2 + 4(\tilde{S}_1 \cdot \vec{r})(\tilde{S}_2 \cdot \vec{r})(\tilde{S}_1 \cdot \tilde{S}_2)}{r^7} + 35 \frac{(\tilde{S}_1 \cdot \vec{r})(\tilde{S}_2 \cdot \vec{r})^2}{r^9} \right\},$$

where \vec{r} is the vector joining the centers of the quadrupoles and \vec{S}_1 and \vec{S}_2 are unit vectors characterizing the directions of the quadrupole axes with respect to the axes of the lattice.

A quadrupole moment is a symmetrical rank-two Cartesian tensor. An alternative method of representing a quadrupole is by means of spherical tensors of spin 0 and 2. According to Nagai and Nakamura,¹³ only the spin-2 components enter into the interaction energy of two quadrupoles. We shall thus represent a quadrupole as a vector in a five-dimensional space, with components q_1, \dots, q_5 . These are related to the components of the axis of the quadrupole S_x, S_y, S_z , as follows:

$$q_1 = \frac{1}{2}\sqrt{3}(S_x^2 - S_y^2); \quad q_2 = \frac{1}{2}(2S_z^2 - S_x^2 - S_y^2);$$

$$q_3 = \sqrt{3}S_y S_z; \quad q_4 = \sqrt{3}S_x S_z; \quad q_5 = \sqrt{3}S_x S_y.$$

The condition $S_x^2 + S_y^2 + S_z^2 = 1$ implies

$$\sum_{i=1}^5 q_i^2 = 1,$$

but not every five-dimensional vector that satisfies the latter condition also satisfies the former one, and therefore is not a physical quadrupole.

The quadrupole interaction energy is an expression of fourth degree in the components of \vec{S} , but of only second degree in the components of \vec{q} . As thus expressed, the problem of finding the configuration of quadrupoles with minimum energy is mathematically the same as that of finding the configuration of minimum energy of dipoles, and the method of Luttinger and Tisza¹² for the latter problem may be used for the former. We assume that any two quadrupoles separated by two lattice spacings are always parallel. Thus, the fcc lattice is divided into 32 simple cubic sublattices and the hcp lattice is divided into 16 simple hexagonal sublattices, all the quadrupoles on the same sublattice being parallel to each other. Hence any state of a quadrupole array can be represented by a point in a 160-dimensional vector space for a fcc lattice, and an 80-dimensional vector space for a hcp lattice. The eigenvector is found corresponding to the lowest eigenvalue of the quadratic form which represents the interaction energy of the lattice. To find this eigenvector involves transformations in the configuration space which have no physical counterpart; if the eigenvector happens to rep-

resent a physically acceptable configuration, then this is the configuration of lowest energy – if it does not represent a physically acceptable configuration, then the configuration of lowest energy has an energy greater than the lowest eigenvalue.

Nagai and Nakamura¹³ have already done the calculations for the fcc lattice, and have found that the lowest eigenvalue has an eigenvector that corresponds to a physical quadrupole array and thus gives the lowest energy configuration. We have repeated these calculations using the IBM 7094 computer according to the way outlined previously,¹⁴ and have confirmed this result. Lattice sums were evaluated within a sphere of radius 300 Å. The lowest energy configuration for the fcc lattice is shown in Fig. 1. Although we assumed 32 sublattices, the calculations show that in the lowest state there are only four distinct sublattices. In each sublattice the quadrupoles are aligned along a different diagonal of the cubic unit cell. The nearest-neighbor distance in solid hydrogen is 3.75 Å, and the quadrupole moment of the ortho-hydrogen molecule is¹⁵ 0.110×10^{-16} cm². Using these values we obtain that the lowest energy per molecule in units of degrees Kelvin (i.e., divided by the Boltzmann constant)

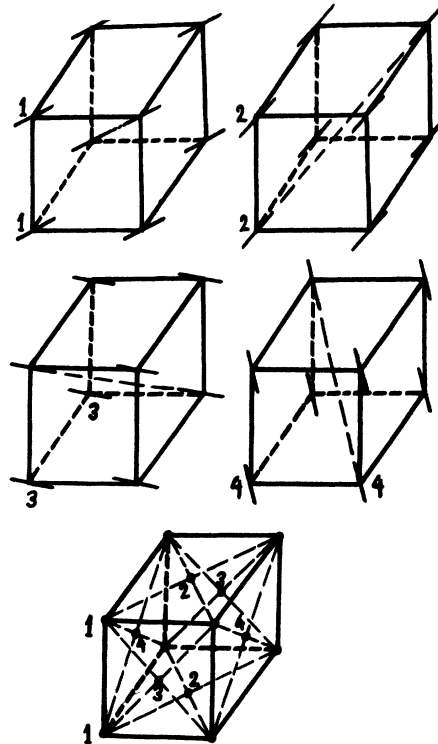


FIG. 1. The lowest energy configuration of quadrupoles in the fcc lattice.

is -28.9°K . We have performed the calculations for the hcp lattice, assuming 16 sublattices. The lowest eigenvalue was found to be -27.3°K . Unfortunately in this case the lowest eigenvalue does not have an eigenvector that corresponds to a physical quadrupole array. (We tried to guess some configurations and the lowest energy we could obtain is -16.5°K ; the corresponding configuration contains only two distinct sublattices with quadrupoles aligned along two different diagonals of the hexagonal unit cell.)

We have shown by classical calculations that the lowest energy of the fcc lattice is -28.9°K and that the lowest energy of the hcc lattice must be greater than -27.3°K . This shows that the molecules in pure ortho-hydrogen at 0°K will prefer to form a fcc lattice with orientations according to Fig. 1 rather than a hcp lattice, in accord with the infrared-absorption measurements of Clouter and Gush.¹¹

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EFFICIENT PHASE-MATCHED HARMONIC GENERATION IN TELLURIUM WITH A CO₂ LASER AT 10.6 μ

C. K. N. Patel

Bell Telephone Laboratories, Murray Hill, New Jersey

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Harmonic generation^{1,2} and optical parametric phenomena³ have been, heretofore, limited to near IR frequencies because of lack of suitable pump source at longer wavelengths and also because of lack of known efficient and phase-matchable⁴ optically nonlinear materials transparent in this region. In this paper we report extraordinarily large amounts of second-harmonic generation (SHG) in single-crystal tellurium using a focussed, 10.6 μ , continuous-wave, CO₂ laser⁵ as the fundamental. Thus, Te is the first elemental crystal in which phase-matched harmonic generation with an infrared source is achieved. (Earlier, reflected light harmonics from a Te surface have been reported using a Q-switched ruby-laser output as the fundamental.⁶) Under our experimental conditions, a second-harmonic power (at 5.3 μ) of 10 μW was obtained when a fundamental power of 0.17 W was phase matched over

a 9-mm length of the crystal. The measured nonlinear coefficient of Te is about 4000 times d_{36} of potassium dihydrogen phosphate. This optical nonlinear coefficient is the highest of any material reported to date and opens up the possibilities of extending other nonlinear optical effects such as parametric amplification/oscillation into the infrared with cw high-power CO₂ lasers.

Te is a member of Group VI B of the periodic table and is an elemental semiconductor. Crystals of tellurium have 32 (D_3) point-group symmetry and belong to the $P3_1,21$ space group (Hermann-Mauguin notation)⁷ assuring an absence of inversion symmetry necessary for SHG and other nonlinear optical phenomena. The crystal in its purest form (intrinsic, p type)⁸ is essentially transparent from about 5 μ (band gap at 4 μ) to wavelengths longer than about 25 μ .⁹ Single-crystal Te is uniax-