Broken symmetry phase transition in solid $p$-$H_2$, $o$-$D_2$ and HD: crystal field effects

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Abstract

We report the effect of the crystal field (CF) on the broken symmetry phase transition (BSP) in solid parahydrogen, orthodeuterium, and hydrogen deuteride. The CF was calculated taking into account a distortion from the ideal HCP structure. We find that, in addition to the molecular field generated by the coupling terms in the intermolecular potential, the Hamiltonian of the system contains a crystal-field term, originating from single-molecular terms in the intermolecular potential. Ignoring the CF is the main cause of the systematic underestimation of the transition pressure, characteristic of published theories of the BSP transition. The distortion of the lattice that gives rise to the negative CF in response to the applied pressure is in accord with the general Le Chatelier–Braun principle. © 1999 Published by Elsevier Science B.V. All rights reserved.

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Solid $p$-$H_2$, $o$-$D_2$ and HD display a unique pressure-driven phase transition, the so-called broken symmetry phase (BSP) transition, which results in change of both lattice and site symmetry (see Ref. [1] for a review). This transition was foretold by Raich and Etters [2] and found experimentally by Silvera’s group [3–5]. At low temperatures, molecular ordering was reported in $o$-$D_2$ at 28 GPa [3], in $p$-$H_2$ at 110 GPa [4] and in HD at 69 GPa [5]. The BSP transition line in HD turned out to be nonmonotonic; the minimum was located at $P_{\text{min}} \approx 53$ GPa and $T_{\text{min}} \approx 30$ K [5]. The nonmonotonicity of the phase transition line means that the disordered phase is reentrant; that is, for fixed pressure in the range between $P_{\text{min}}$ and $P_0$, as temperature is increased, the solid goes from a disordered to an ordered and then to a disordered phase again.

At low pressures the free rotor quantum numbers $J$, $M$ remain good quantum numbers for molecules in $H_2$ and $D_2$ solids. At low temperatures only the lowest states $J = 0$ in the even $J$ species are occupied, so at low pressures there is no orientational order in $p$-$H_2$, $o$-$D_2$ down to $T = 0$ K. With increasing pressure admixtures of higher rotational states into the ground-state wave function become more

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and more appreciable and eventually the transition into an ordered phase takes place.

The term “BSP transition” underlines the symmetry aspect of this phenomenon, but this transition is, first of all, a quantum phase transition such that the state of the system is controlled by the competition between the potential energy, which tends to order the system, and the kinetic energy, which tends to delocalize the system.

Well-known examples of the system where quantum melting is possible are $^3$He and $^4$He. The small atomic masses and the weak interatomic interaction lead to large-amplitude zero-point vibrations which do not permit the liquid to freeze into the crystalline state. Only if pressure of around 30 bar is applied will liquid He solidify. As has been shown in Refs. [6–9,18], a similar phenomenon, called quantum orientational melting (QOM), can be displayed by a system of quantum rotors.

In the case of QOM, the pressure, which makes orientational ordering possible, is more than four orders of magnitude higher. This pressure can be estimated crudely from the following considerations: at the transition point, when the orientational ordering takes place, the loss in kinetic energy, $\Delta E_{\text{kin}}$, is compensated by the gain in potential energy due to the ordering, $\Delta E_{\text{pot}}$. The former quantity can be estimated from the equation for the free rotors: $\Delta E_{\text{kin}} = B_{\text{rot}}(J + 1)$ assuming that the ordered molecules are in the $J = 2$ state in the case of even-$J$ species and $J = 1$ for HD ($B_{\text{rot}}$ is the rotational constant). To estimate $\Delta E_{\text{pot}}$ we will use the equation for the ordered phase of the Pa$3$ lattice. Then for the quadrupole–quadrupole interaction $\Delta E_{\text{pot}} = (5/12)951(V_0/V)^{5/3}$ where $\Gamma$ is the quadrupole interaction parameter, $V_0$ is the molar volume at zero pressure and $V$ is the molar volume at pressure $P$. From this, we predict the transition to take place at the reduced compressions $V_0/V$ of 4.8 for $p$-H$_2$ and 3.8 for $\alpha$-D$_2$. The transition pressure predicted from this model can be obtained from the reduced compression making use of the equation of state.

Two conclusions can be inferred from these estimates. First, that the transition pressure for QOM is very high compared with the solidification pressure in the case of helium (due to a large value of $B_{\text{rot}}$), and second, that these estimates are far below the experimental values. Even more sophisticated estimates that take into account a more realistic intermolecular potential and quantum effects leave these conclusions unchanged.

The underestimation of the transition pressure is characteristic for all published theories of the BSP transition (see Refs. [10–12]). As was shown in Refs. [8,9], the discrepancy between theory and experiment can be removed if CF effects are taken into account. The effect of the CF on a rotor model system was studied in Ref. [7] and it was shown that even very small CF can substantially change the behavior of the system of rotors. Negative CF shifts the phase transition line upward, to the range of higher pressures relative to the case of the zero CF.

When in addition to the MF generated by the coupling terms in the intermolecular potential, there is a CF originating from single-molecular terms in the intermolecular potential ($U_0$ and $U_1$ are MF and CF constants, respectively), the above estimate of the transition pressure changes. The new estimate can be easily obtained if one takes advantage of the close analogy that exists between orientationally and magnetically ordered systems, the MF constant being the analog of the exchange field and the CF the analog of the anisotropy constant (with positive and negative CF mirroring easy-axis and easy-plane anisotropy, respectively). With this analogy in mind, we can obtain the following estimate for the potential energy: $\Delta E_{\text{pot}} = (U_0|U_1|)^{1/2}$. At $|U_1|/U_0 \approx 0.1$ the estimate discussed above gives a value for the transition pressure that is in accord with experiment. In the previous approach (Refs. [8,9]) the CF was treated as a parameter of theory; it was shown that for the reduced CF (crystal to molecular field ratio) of $-0.13$, $-0.14$, the theory gives correct range of values for the transition pressure.

We have calculated the MF and CF constants $U_0$ and $U_1$ assuming the Pca$_2$$_1$ structure for the BSP phase [13,14]. The CF constant $U_1$ was calculated taking into account both the deviation of the $c/a$ ratio from the ideal HCP value of $\sqrt{(8/3)}$ [15] and a monoclinic distortion of the lattice [14]. The calculated value for the reduced crystal field of $-0.1$ is in accord with the range of values obtained from fits to experimental data [8,9].
The second-degree term of the crystal-field interaction in a rigid hcp lattice can be written in the form [16]
\[
V_{\text{CF}} = - (4\pi/5)Y_{20}(\Omega)\sum_{\rho} B(\rho)Y_{20}(\Omega_{\rho}).
\]
(1)

Here the sum extends over all molecules around a "central" molecule; its orientation \( \Omega = (\theta_0, \phi_0) \) is specified by a polar angle \( \theta_0 \) relative to the \( c \)-axis and an azimuthal angle \( \phi_0 \) relative to the \( a \)-axis, \( \Omega_{\rho} = (\theta_\rho, \phi_\rho) \) denotes the orientations of the nearest-neighbor molecules, \( B(\rho) \) is the radial function of the single-molecule term in the anisotropic pair potential, and \( R \) is the nearest-neighbor distance at the given pressure.

In the case of an ideal HCP lattice, the \( V_{c/a} \) component of the CF vanishes. Let us consider the CF to first order in \( \delta_c = c/a - \sqrt{3}/3 \). The resulting equation for the CF takes the form
\[
V_{c/a} = - (3/2)^{3/2}(4\pi/5)^{1/2}R(dB/dR)\delta_c Y_{20}(\theta_0).
\]
(2)

In addition to the deviation of the \( c/a \) ratio from the ideal HCP value, there could be another source of the CF, namely, a monoclinic distortion of the lattice, when the \( b/a \) ratio deviates from the ideal HCP value of \( \sqrt{3}/3 \). This distortion produces for the CF
\[
V_{b/a} = - (\sqrt{3}/2)(4\pi/5)^{1/2}R(dB/dR)\delta_m Y_{20}(\theta_0),
\]
(3)

where \( \delta_m = b/a - \sqrt{3}/3 \). The resulting crystal field is
\[
V_{\text{CF}} = V_{c/a} + V_{b/a} = - R(dB/dR)\delta^* Y_{20}(\theta_0)
\]
where \( \delta^* = (4\pi/5)^{1/2}(3/2)^{1/2}\delta_c + (1/\sqrt{3})\delta_m \). Thus, the CF interaction is defined by the product of two factors: \( R(dB/dR) \) and \( \delta^* \). The first one could be estimated using the leading term of the analytical model expression \( B(R) = \exp(\gamma_B R + \beta_B + \gamma_B R^{-1}) \) [16,17] where the coefficients are \( \gamma_B = -1.3252 \) bohr \(^{-1} \); \( \beta_B = -1.9292 \); \( \gamma_B = 3.8103 \) bohr. Taking into account the contribution from the multipole interactions for \( p-H_2 \) at the transition pressure (110 GPa), we obtained the following estimate: \( R dB/dR \approx -4.34 \times 10^3 \) K. To estimate \( \delta^* \) we used the experimental data of Loubeyre et al. [15] for the pressure dependence of the \( c/a \) ratio and data on \( b/a \) ratio from ab initio molecular dynamic simulations by Kohanoff et al. [14]. As can be deduced from Ref. [15], the deviation of the \( c/a \) ratio from the ideal HCP value is a linear function of pressure: \( \delta_c = -\gamma P \) where \( \gamma = 3.8 \times 10^{-4} \) GPa \(^{-1} \); the monoclinic deviation in this pressure range is pressure independent according to theory [14] (\( \delta_m = -0.017 \)).

As a result, we obtain for the reduced crystal field \( x = U_1/U_0 \approx -0.1 \) which is in an excellent agreement with the value estimated from a fit to the experimental data [8,9]. Though it is difficult to judge the accuracy of our result, the order of the magnitude and (most important) the sign of the crystal field are correct.

In summary, we find that the Hamiltonian of the system contains a negative crystal field term that originates from single-molecule components in the intermolecular potential, and we have calculated the magnitude of this term. Neglecting the CF is the main cause of the systematic underestimation of the transition pressure characteristic of all theories of the BSP transition. The deformation of the lattice giving rise to the negative CF is a response of the lattice to the applied pressure which is in accord with the general Le Chatelier–Braun principle.

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References
