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Phase diagram senses orbitals and prompts a fundamental constant

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Van der Waals' discovery of that the volumes of molecules and their intermolecular attraction between them cause the peculiarities of the phase diagrams of gases and liquids¹ gave the greatest impact on the progress of science and industry. Unfortunately, the phase charts of solids capable to advance scientific and technical progress remain uncomprehended mystery. Only the certain linear phase boundaries are understood by the struggle of magnetic field B against the thermal agitation^{2,3}. Here we show that the intersection volume of internal atomic orbitals determines the form of phase boundary and, furthermore, energy per unit volume of the intersection is a new fundamental constant $\nu = 8.941 \text{ eV/\AA}^3$. Together with the known struggle contribution^{2,3} to $T_C(B)$, we found a term proportional to the intersection volume of $3d_{eg}$ and $2p$ orbitals in the $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ manganite. Hysteresis of T_C is described by the avalanche-like widening of the intersection volume due to reducing the Coulomb distortion with double-exchange ferromagnetism. The pressure- T_C diagram⁴ of $(\text{Sm}_{1-x}\text{Nd}_x)_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ ($x=0, 0.2, 0.4, 0.5$) is approximated with the same parameters as the $T_C(B)$ diagram of $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$. Furthermore, the diamond's melting point 4157°C calculated from the intersection volume of sp^3 -orbitals is in excellent agreement with the real 4000°C . Tips explaining the puzzling pressure- T_N diagrams⁵⁻¹⁰ of NiS , $\text{Ni}_{1-x}\text{S}_{1-y}\text{Se}_y$, BaVS_3 , V_2O_3 , RNiO_3 and ferrites were given. Our discovery is the beginning of condensed-matter geometrodynamics and marks an era of studying phase diagrams to advance condensed-matter physics and tailor new materials with predicted properties necessary in sunrise industries. Moreover, internucleon, interquark and intergluon orbital intersections would be useful for understanding the properties of nuclei, nucleons and quarks.

Understanding the phase diagram of solid avails us the nature of interatomic interaction inducing the phase transition, but phase-transition lines often behave intriguing manner. It is especially interesting the phase chart of organic and cuprate superconductors where four different states meet at multicritical point¹¹. The phase diagram of iron, however, is no less attractive and puts up knotty issue about whether the number of solid phases should be raised to five¹².

Puzzling over phase diagrams of gases Van der Waals came to that the volume of a molecule of the gas had the matter and they interacted between them with the force named later in his honour¹. He also asked himself how the solid state behaved, however, was silent on this question. Atoms of inert gases have completely closed electron shells, and molecules of diatomic gases the closed valent shells at least, so Van der Waals'

liquid-gas equation state is in fact the consequence of dispersion forces between the closed shells very hard of Pauli principle. Emphasizing the great impact of Van der Waals' findings, H. Kamerlingh Onnes¹³ wrote in 1910 "that Van der Waals' studies have always been considered as a magic wand for carrying out experiments and that the Cryogenic Laboratory at Leyden has developed under the influence of his theories". Liquefying helium allowed H. Kamerlingh Onnes in 1911 discovered superconductivity, so unravelling the mystery of phase charts of liquefiable gases had moved forward physics not only gases and liquids, but also solids.

The aim of this article is to reveal the nature of the phase diagram of solid, that is, to answer the question been silent by Van der Waals. We have asked ourselves why the $T_C(B)$ diagram of $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$, the most-studied composition, behave straightly with different slopes along the BC and the DE lines and curvedly on the segment AC (Fig. 1).

Fig. 1. | The $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ $T_C(B)$ diagram. The ferromagnetism appears at downward and/or rightward crossing of the curve AC but disappears at upward and/or leftward crossing of the line BC . So if the bistable region has been reached from under AC (above BC) it is ferromagnetic (paramagnetic), that is, the nonvolatile memory effect driven both by temperature and by magnetic field takes place. AC , BC and DE are seen to excellently describe the Curie points (the red signs at heating and the blue at cooling) of polycrystallines^{24,25} and single crystal⁴.

The DE -line energy slope $\frac{k_B}{\mu} \Delta T_C / \Delta B = 0.99$ (according to Hund's rules $\mu = 6\mu_B$ both for Mn^{+3} and Mn^{+4}) means that magnetic field only suppresses the thermal agitation and so the Curie point is linear:

$$T_C = \frac{\mu}{k_B} B \cos \theta, \quad (1)$$

θ is an angle between the Mn magnetic moment and the magnetic field B or, at the same time, a tilting angle between the adjacent MnO_6 octahedrons. The DE -line energy slope

gives tilting angle $\theta_{DE} = \arccos 0.99 = 8.2^\circ$. The question, which could be answered by future studies, arises how long such linearity will remain above 15 T.

Our attempts to interpret the steep energetic pitch 2.37 of BC as easy as DE failed. It appeared to reveal the secret of BC was previously necessary to interpret AC and the zero-field hysteresis AB , which is a passway to BC . The insight has come with a lightning speed when we saw a spheric cap in a stereometry textbook, a portion of a sphere cut off by a plane, with the volume $V = \pi h^2(R - h/3)$, h is an intersection height and R a radius of the sphere. We supposed that the transition temperature T_{tr} is proportional to the volume $2V$ of the double spheric cap formed at the intersection of the orbitals (Fig. 2a) with the coefficient v being a volumetric energy density:

$$T_{tr} = \frac{2v}{k_B} \pi h^2 (R - h/3). \quad (2)$$

This formula is suited for different transitions because the subscript ‘ tr ’ means Curie, Neel or melting point for ferromagnetic, antiferromagnetic or melting transition, accordingly.

Fig. 2. | The biconvex-lens volume of the intersection of the orbitals $Mn^{3+(4+)}3deg$ and $O^{2-}2p$, and geometric calculation of its intersection height h_B . **a**, The tilting angle θ between MnO_6 octahedra and magnetic field B determines the magnetic energy $6\mu_B \cos \theta$ of the $Mn^{3+(4+)}$ cations. **b**, The blue letterings belonging to the point A yield the distance r from the site $Mn^{3+(4+)}$ or O^{2-} to the center of the curvature R of the spheric end of its e_g or $2p$ orbital, $r = (a - R + h_A)/\cos \theta_A$. The red letterings belonging to the point B give $h_B = r \cos \theta_B - a_B + R$, which with the r calculated from the blue lettering, transforms into Exp. (4).

Obviously, the intersection height $h = \varepsilon a$; a is half a distance between $Mn^{3+ \text{ or } 4+}$ and O^{2-} and ε a relative striction. If a solid shrinks in magnetic field, the magnetostatic energy of a transition-metal cation spends on to enhance the elastic energy a unit cell, that is, $\mu \cdot B = VE\varepsilon^2/2$; E is a Young's modulus and here V a unit-cell volume. Then $\varepsilon = \sqrt{2\mu \cdot B / VE}$ and so $h = a\sqrt{2\mu \cdot B / VE}$. On AC $h_{AC} = a\sqrt{2\mu \cdot B / VE} + h_A$, h_A is added on account of a zero-field intersection height inducing the zero-field Curie point at the point A . Inserting $h = h_{AC}$ into Exp. (2) gives

$$T_C = \frac{2\pi v}{k_B} \left(\frac{2a^2 \mu B}{VE} + 2h_A a \sqrt{\frac{2\mu B}{VE}} + h_A^2 \right) \left[R - \left(a \sqrt{\frac{2\mu B}{VE}} + h_A \right) / 3 \right]. \quad (3)$$

Magnetic field supports ferromagnetism along AC same as on DE , therefore, the best physical description of AC is the sum of Exps. (3) and (1) at $\cos\theta$ linearly turning down from θ_A at point A to θ_C at the point C (the linearization is quite reasonable as $\cos\theta$ also linearly depends on temperature¹⁴ and the radius¹⁵ of the rare-earth ion). The rotation $\theta_A - \theta_C$ also equals a sum of those at the zero-field hysteresis AB and along BC ; otherwise, AC and BC would not flow at the triple point C together. We found the best fit with the root-mean-square error 0.58 K at the corresponding parameters in the Table. So enigmatic behaviour of AC is de-facto a steric effect – the field-induced overlapping of the orbitals $3d_{eg}$ and $2p$.

At $h = h_A$ Exps (2) and (3) give the zero-field cooling Curie point $T_C^A = 113.06$ K. A reason question suggests itself why the zero-field heating Curie point T_C^B is higher than T_C^A . The issue was qualitatively discussed elsewhere¹⁶. By resuming, we have come to the following quantitative explanation. The initial overlap h_A triggers double exchange which, in turn, due to extra removal of the Coulomb distortion¹⁶, inflates the orbital overlapping to h_B , the Curie point heightening to T_C^B . The geometric constructions for points A and B (Fig. 2b) gives

$$h_B = (a - R + h_A)\cos\theta_B / \cos\theta_A - a_B + R. \quad (4)$$

Exp (2) at $h = h_B$ yields $T_C^B = 129.99$ K (calculated from the entries for the point B in the Table) in excellent consistent with the experimental 128.60 K. Thus, at T_C^A the threshold intersection h_A avalanche-like widens till h_B generating T_C^B . It is natural to observe T_C^B may be at heating only. Such is the mystery of the hysteresis taking place at the first-order-like phase transition.

Now we can interpret BC , wherein magnetic field orientates the MnO_6 octahedrons and straightens θ from θ_B to θ_C , the intersection expanding. As θ does not change a spacing between the $\text{Mn}^{3+ \text{ or } 4+}$ and O^{2-} ions, for BC Exp. (4) transforms into

$$h_{BC} = (a_B - R + h_B)\cos\theta / \cos\theta_B - a_B + R, \quad (5)$$

where $\cos\theta \in [\cos\theta_B; \cos\theta_C]$ is linear of the field. Magnetic field supports magnetism on BC same as on AC and DE . And the best physical description of BC with the root-mean-square error 1.24 K is a sum of Exp. (2) with $h = h_{BC}$ and Exp (1) (see the Table for the fit parameters).

Our supposition confirmed on other cases. In the case of the $T_{tr}(P)$ diagram, the Hooke law $P = E(P)\varepsilon$ (the Young's modulus is supposed to depend on pressure as well as temperature¹⁷, magnetic order¹⁸ and even form¹⁹) gives $h = aP/E(P) + h_0$ (h_0 is an intersection height at the normal conditions) which turns Exp. (2) into

$$T_{tr} = \frac{2\pi v}{k_B} \left(\frac{a^2 P^2}{E(P)^2} + 2h_0 \frac{aP}{E(P)} + h_0^2 \right) \left[R - \left(\frac{aP}{E(P)} + h_0 \right) / 3 \right]. \quad (6)$$

This expression excellently describes The $T_C(P)$ diagram⁴ of $(\text{Sm}_{1-x}\text{Nd}_x)_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ ($x = 0, 0.2, 0.4, 0.5$) (see Fig. 3 and the Table).

In the case of superexchange, our discovery let us know the nature of the antiferromagnetism⁵⁻⁷ not clear for decades in NiS , V_2O_3 and RNiO_3 ($R = \text{Pr}, \text{Nd}, \text{Nd}_{0.7}\text{La}_{0.3}$). The pressure-induced shift of the transition-cation planes with respect to the anion planes causes the $3d_{eg}$ orbital to hold away from the $2p$ orbital and so their intersection narrows then T_N lowers and the e_g electrons, which contribute to the

antiferromagnetism and cannot migrate as current carriers, gradually delocalize that leads to metallization.

Fig. 3. | The $T_C(P)$ diagram reproduced of⁴ fitted by Exp. (6) at the nonlinear Young modulus $E(P) = 325P^{1/3} + E_0$ and $h_0 = h_B$ (the translucent purple curve).

The $T_N(P)$ diagram¹⁰ of BaVS_3 become understandable if to take into account the increase of the orbital overlapping in the V-S chains, which favours to antiferromagnetism but forbids Mott's conductance. The linear $T_N(P)$ of the orthoferrites⁹ Gd, Pr and Tm means the fulfillment of Hooke law at the small rare-earth-ion radius. The more rare-earth-ion radius in the La orthoferrite⁹ shortens the Fe-O bond and so widens the intersection of the orbitals $\text{Fe}^{3+}3d$ and $\text{O}^{2-}2p$ that causes the lift and nonlinearity of the $T_N(P)$. Exp. (6) with the internal chemical pressure $P_i \sim 1 - y/y_p$ (y_p is a doping index of the paramagnetic composition) instead of P could fit the temperature-doping phase diagram of the antiferromagnet⁸ $\text{Ni}_{1-x}\text{S}_{1-y}\text{Se}_y$.

Finally, our calculation of diamond's melting-point is the brightest approbation of our condensed-matter geometrodynamics. The diamond's sp^3 -orbitals intersection is the carbon's p -orbital length minus the carbon's covalent radius²⁰ in diamond: $h = r_p - r_{\text{dia}}^{\text{cov}}$. The r_p is obtained as the carbon-hydrogen distance in methane plus the hydrogen covalent radius and minus Bohr radius: $r_p = r_{\text{CH}_4} + r_{\text{H}}^{\text{cov}} - r_B$. Then $h = 1.087 + 0.31 - 0.529177 - 0.772 = 0.095823 \text{ \AA}$. Exp. (2) with this h and $R=r_p/4$ multiplied by the four covalent bonds gives the diamond's melting point 4157°C in excellent agreement with the real 4000°C .

Thus, the phase diagram of the solid has been completely interpreted. It turned out that its certain phase boundaries sense the intersection of intra-atomic orbitals.

Intersection volume has geometric energy whose volumetric density is a new fundamental constant. Thus, the steric effect well-known in condensed-matter physics has at last received its quantitative explanation. The phase diagram of solid surprisingly appeared a bridge between the classic and the quantum physics, allowing us to get the precise picture of the orbital intersection unreachable even in the neutron microscopy.

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Competing financial interests

The author declares no competing financial interests.

Table I. | Initial data and fitted parameters in tracing the phase boundaries

	Point A	Point B	Curve AC	Line BC	Line DE	Curve $T_C(P)$
1. $a = 0.9775\text{\AA}$	✓	✓	✓	—	—	✓
2. $a_B = 0.9762\text{\AA}$	—	✓	—	✓	—	—
3. $\theta_A = 9.85^\circ$	✓	✓	✓	—	—	—
4. $\theta_B = 9.5^\circ$	—	✓	—	✓	—	—
5. $V = 226.301\text{\AA}^3$	—	—	✓	—	—	—
6. $R = 0.244375\text{\AA}$	✓	✓	✓	✓	—	✓
7. $h_A = 0.027147\text{\AA}$	✓	✓	✓	—	—	—
8. $E_0 = 25.31\text{GPa}$	—	—	✓	—	—	✓
9. $v = 8.941\text{eV/\AA}^3$	✓	✓	✓	✓	—	✓
10. $\mu = 6\mu_B$	—	—	✓	✓	✓	—
11. $\theta_C = 8.45^\circ$	—	—	✓	✓	—	—
12. $\theta_{DE} = 8.2^\circ$	—	—	—	—	✓	—
13. $h_B = 0.0289906\text{\AA}$	—	✓	—	✓	—	✓

The data in rows 1-5 are calculated from the neutron diffraction^{16,21}: a and a_B are half the Mn-O distances before and after the transition; θ_A and θ_B are calculated as $\theta = (180^\circ - \alpha)/2$ where the angle $\alpha = \text{Mn}^{3+}\text{O}^{2-}\text{Mn}^{4+}$; and V is a multiplication of the primitive-cell constants 5.424, 7.678 and 5.434 Å. R a fourth of the orbital length is standard for the d and p orbitals²². h_A , E_0 , and v are fitted parameters of curve AC (the normal-condition Young's modulus E_0 is in good agreement with values for manganites²³). θ_C and θ_{DE} are fitted parameters of AC and DE lines.

FIGURES LEGENDS