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Phase Transition in Superconductor

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Abstract : Phase transitions occur in a great variety of physical systems such as paramagnet-ferromagnet, fluid-superfluid, amorphous-crystalline, and normal-superconducting transitions. Temperature-induced phase transition has been observed in the phenomenon of superfluidity and superconductivity. In regard to superfluidity, extraordinary behavior is observed for liquid Helium below the transition temperature and even at normal state. Both the liquids ^{3}He and ^{4}He (Isotopes of He) do not have a triple point (solid-liquid-gas) and co-exist with a single point. According to the new classification, latent heat involvement in a system, phase transition can be named as 1st order or 2nd order. It is known that the entropy of material gives disorderliness to the system. A discontinuous change of free energy (Gibb's free energy) at a fixed temperature provides a change called 1st order, and continuous change is called as second-order phase change. The solid-liquid, liquid-gas transitions below the critical temperature are examples of 1st order phase transition. Similarly, metal-superconductor transition, and magnetic (ferromagnetic-paramagnetic) ordering transition show a 2nd order phase transition. The high pressure-induced in some materials exhibit the properties of room-temperature superconductors.

Keywords :phase transition; superconductivity; Bose-Einstein Condensate; order parameter; symmetry breaking; superfluid

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1. Introduction

Generally,the phase transition is driven by many parameters such as temperature, pressure, chemical composition, electric and magnetic field. Out of these, if the temperature is the driving parameter, the high-temperature state is more disordered than the low-temperature state. Phase transition is also associated with symmetry breaking. The system is in higher symmetry at high temperature. Matters generally exit in four states and have their phase transition in solid, liquid, gas, and plasma. We shall also discuss the 5^{th} state of matter that occurs at very low temperatures and is called as Bose-Einstein Condensate (BEC).

Phase transition is characterized by a minimum of free energy under specified thermodynamic variables. The system's free energy varies smoothly and continuously with the variation of temperature, pressure, or other variables such as an electric and magnetic field that act on the system. A phase transition occurs when free energy is associated with thermodynamic variables inducing a change in electronic or atomic configuration. A significant variation near transition is called anomalous change, which changes elastic coefficients, dielectric constant, thermal expansion coefficients, and specific heat. The loosely packed structure shows a higher response to pressure as compared to a highly packed structure. It has been observed that crystal structure with FCC (face-centered cubic) and HCP (hexagonal closed packed) exhibit phase transition under high pressure with small volume change. Pressure-induced phase transition has been observed in materials to give superconductivity even at room temperature. The phase transition can be reversible or irreversible depending on the response of the material to external pressure. On the release of pressure, if it returns back to its original phase, it is called a reversible phase transition. On the contrary, the transition can be called irreversible.

2. Symmetry breaking and Order parameter

A change in symmetry is accompanied by a phase transition without latent heat, has been proposed by L.D. Landau in 1937. In a magnetic material, permanent magnetization is observed below the transition temperature and no permanent magnetic moment above that. The material show ferromagnetic behavior below the transition temperature Tc and paramagnetic state above it. In this process, the symmetry was broken at the transition temperature. The material shows only invariant due to rotation around an axis and oriented in the direction of the magnetization. Landau has correlated the order parameter with braking of symmetry accompanying a phase transition. The process of crystallization of liquid shows more complex phenomenon involving symmetry breaking. A solid crystal is formed from the liquid on cooling, shows a symmetry like bcc, fcc, hexagonal etc. But an isotropic liquid shows invariant under translation. According to Noether theorem, “there exists a continuous symmetry for every conservation law and vice versa”. Conservation of angular momentum, linear momentum, and energy is related to space-time symmetries of rotation and translation in space and time.

Spontaneous symmetry breaking is observed as in ferromagnetism, electro-weak theory, superconductivity, and Bose-Einstein condensation. A simple example of symmetry breaking can be understood by

i. A ball located on top of a hill can roll down in any direction and configuration is not stable.
ii. In a round table dining party, the napkin can be used by a guest from his left or right side. The other person by his side has to follow the same way. He has no other choice of left or right. In this case, left-right symmetry is broken.

The order parameter is a physical quantity of extrinsic character. It is zero in the most symmetric (most disorder) phase and non-zero in the least symmetry (ordered) phase. When the temperature decreases, the order of the system increases. While cooling a liquid by passing through the point of solidification, the crystalline solid is said to be more ordered than the liquid. Similarly, a ferromagnetic material when cooled below the Curie point, the magnetic ordering in turn the magnetization increases. For the superfluid case wave function is the order parameter and the super-electron wave function (energy gap) is the order parameter for the superconductor. Hence, we distinguish two types of transitions involving order parameters.

i. First-order transition is associated with latent heat. Potentials such as G (Gibb's free energy) are continuous in the transition, but its first derivative and associated quantites (V, the Volume and S, the entropy) are discontinuous.
ii. The symmetry group of the least symmetry phase is a sub-group of the most symmetry phase. Suppose the order parameter is discontinuous at the phase transition. In that case, it is called 1st order transition in Ehrenfest criteria [1], or if continuous at the phase transition, it is called second-order phase transition (without latent heat).

3. Phase transition for material at low Temperature: Superfluidity and superconductivity

Temperature-induce phase transition has been observed in the phenomenon of superfluidity and superconductivity. Extraordinary behavior is observed for liquid Helium at normal state. Both the liquids ^{3}He and ^{4}He (Isotope of He) do not have triple point (solid-liquid-gas) and co-exist with a single point. Generally cooling the material, liquids turn into solids. But these two liquids refuse to form solid (freeze down to 0 K) unless very high pressure (more than 25 atm.) is applied. Another surprise has been observed for ^{3}He liquid that below 300 mK one has to heat it instead cool it to form a solid which suggests, a negative melting curve below 300 mK. Another mystery is that if you want to pour liquid ^{4}He at a temperature below 2.17 K into a container, the liquid comes out of the container instead of filling up. The hydrodynamic of this liquid is quite different from other liquids.^{4}He becomes superfluid at 2.17 K and ^{3}He at 2.7 mK. These two superfluids lose their total viscosity and can flow past very fine pores showing fountain effect (which are impervious to normal liquid) without developing a pressure head. Hence, classical fluid changes to quantum fluid below T□□□□ point□□

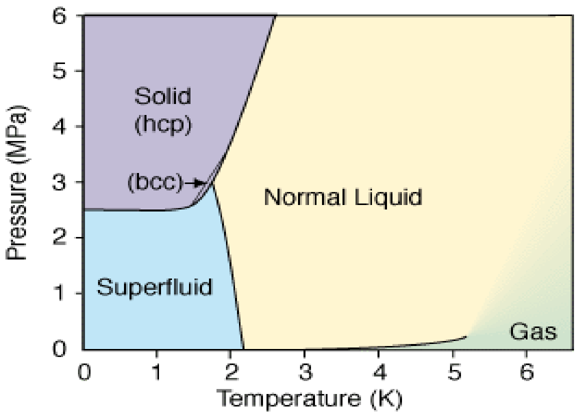

Fig. 1. The phase diagram of ^{4}He at low temperatures

Materials show superconducting behavior when cooled sufficiently low. As cooled from room temperature, the material lose its resistance at a certain temperature (R =0) and show diamagnetic behavior (susceptibility is negative) and B = 0 (Meissner effect). Superconducting material undergoes a phase transformation from the superconducting state to the normal state by applying temperature, electric field, and magnetic field. The critical behavior has been depicted as below.

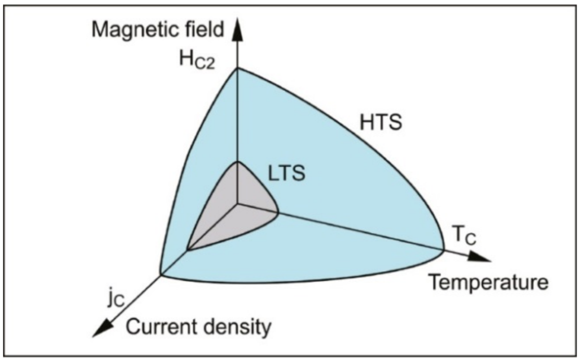

Fig.2. Variation of current density, Critical temperature and critical field in low temperature (LTC) and high temperature superconductors (HTSC)

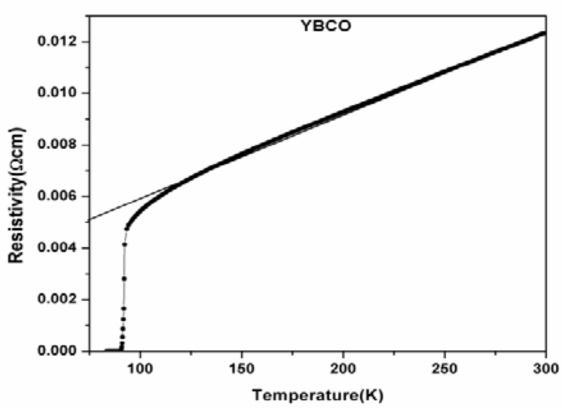

Fig.3. Temperature-dependent resistivity in YBCO, a high-temperature superconductor [2].Ph.D thesis, Arpna Kujur e-thesis d-space NIT Rourkela

As the temperature is lowered, the phase transition from a normal state to a superconducting state is reached. Temperature-dependent resistivity of YBCO superconductor with Tc = 92 K is depicted in the figure 3.

4. Phase transition on doping

The discovery of high-temperature superconductors has given us the information that varying the hole concentration, the insulator can be transformed to a superconductor. La_2CuO_4 a Mott-insulator, becomes a superconductor for $La_{2-x}Sr_xCuO_4$ having Tc ~ 35 K as shown in figure 4. This doping has given birth to high-temperature superconductivity, for which Bednorz and Muller got the Noble Prize in Physics in 1987. In a similar fashion La doped at Sr site in $Bi_2Sr_2CuO_{6+d}$ gives superconducting dome.

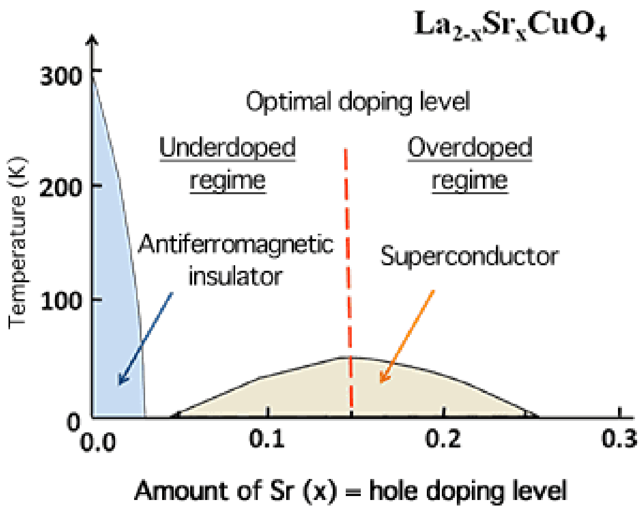

Fig..4. Variation of Sr in $La_{2-x}Sr_xCuO_4$ the process of creating hole doping.

5. Size driven Phase transition

It has been reported that high temperature superconductor, $YBa_2Cu_3O_{7-d}$ (YBCO) shows ferromagnetic MH loop behavior at room temperature (300 K) when the bulk material is reduced to nanomterial. This well-defined ferromagnetic property is reported due to the presence of oxygen vacancies (defects) at the surface of nanoparticles of YBCO [3-6]. In YBCO nanoparticles at 300 K and even at 91 K (above the transition temperature), ferromagnetic behavior is preserved. Hysteresis starts opening up as transition approaches, as shown in figure 5. Hence, a phase transition occurs for the YBCO sample as particles are of nano-order from ferromagnetic to diamagnetic as the temperature is reduced below the superconducting transition. With the decrease in particle size, the hysteresis loop becomes larger with increase in coercivity and remnant magnetization. For nanoparticles and nanostructured materials cohesive energy decreases with a decrease in particle size [3]. Size-driven Phase transition has been observed to induce (Metal-insulator) MI transition. As has been reported [7], MI transition is observed in Nb nanoparticles due to opening of energy gap at the grain boundaries. The critical size of the particle is 8 nm with the corresponding grain boundary width ~ 1.2 nm.

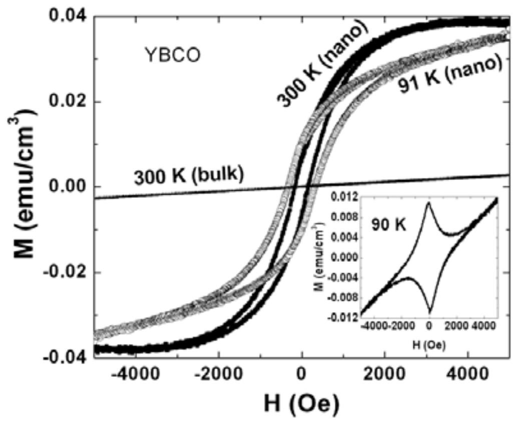

Fig.5. M(H) data of YBCO nanoparticles at 300 K and 91 K show the ferromagnetic

behavior. Inset shows the hysteresis at 90 K for the superconductor (reference 3)

The superconducting critical temperature shows a variation with the grain size of Nb [4] as

i. Size > 28 nm the sample behaves as bulk metal with Tc of 9.4 K (grains with strong inter-granular coupling)

ii. grain size in the range 8-28 nm, the sample shows metallic behavior with the decrease of Tc to 4.7 K (decrease of inter-granular coupling)

iii. grain size < 8 nm the sample shows no superconducting behavior but shows a MI transition.

6. Pressure-Induced Phase transition and room temperature superconductor

Pressure-induced phase transition is significant in material that constitutes with loosely packed with molecules, ions and atoms. Due to the compression of these entities, there will be overlapping of the electrons that leads to changes in optical, electrical and other physical properties. Application of pressure affects the kinematics and induces phase transition. Hence, pressure induced phase transitions is associated with new atomic arrangement, structural instabilities. The loosely packed structure shows a higher response as compared to a densely packed structure. Liquid ^{4}He (superfluid) under the pressure of 25 atm. Changes to solid, and this liquid refuses to form solid with normal pressure even of temperature tends to zero (figure 6).

Pressure-induced phase transition has been observed in superconductors producing room temperature superconductors. It has been reported [8] that lanthanum hydride (LaHx) was synthesized by laser heating of lanthanum in hydrogen atmosphere at a pressure of P = 170 GPa. The sample shows a superconducting step at 209 K at pressure 170 GPa. By releasing the pressure to 150 GPa, the Tc increases to 215 K - the record breaking Tc during the year 2017. The three best known superconductors in LaH_{10}, YH_9, and YH_6 with Tc of 250-260 K, 243 K and 224-227 K, respectively have been reported. In Ca doped yttrium hydrides i.e. $CaYH_{12}$ the Tc of 258 K at pressure 200 GPa has also been reported [9]. Even the system Li_2MgH_{16} with Tc 473 K at 250 GPa shows the light for the new expectation [10]. This finding supports a way of achieving Tc higher than the one in H_3S (203 K) in hydrides.

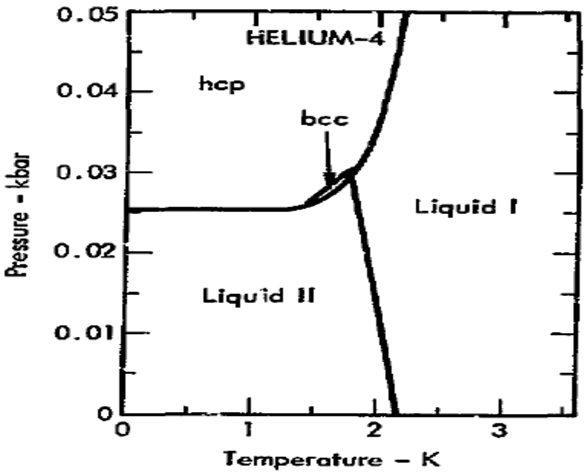

Fig.6. Phase change due to pressure in ^{4}He. The liquid phase changes to the solid phase at 0.025 kbar (25 atm.)

7. Phase transition by Irradiation

Irradiation-induced phase transition has been observed in metals, oxides, calcites, sulphides etc. High-temperature superconductor (YBCO) shows a structural phase transition from orthorhombic to tetragonal by oxygen disorder in the CuO basal plane when irradiated. This change has been reported from in situ resistivity measurement and XRD analysis [11]. It has been reported that swift heavy ion (SHI) irradiation with 120 MeV Ag ion, the monoclinic CuO phase changes to cubic Cu_2O phase [12,13]. Not only SHI irradiation, but even low energy ion irradiation has also been reported effecting phase transformation as

350 keVAr ion, and 340 keV Xe ion show transition from monoclinic to tetragonal phase in YBCO superconductor.

8. Conclusion

This manuscript discusses the different phase transitions and associated changes of properties in superconducting materials. High pressure induced in some materials give rise to room temperature superconductor. A magnetic phase transition is observed as the particles are reduced to nanosize. Attempts have been made to obtain room temperature superconductors at ambient pressure to have a revolutionary change in the material science and application to modern society.

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