8

Super Conductivity

Q. 8.1. What is super-conductivity ? Give the main characteristic properties of a superconductor *(G.N.D.U. 1996, 1994, 1993; P.U. 1996, 1995; Bang.U. 1993)*

Ans. Super-conductivity. The electrical resistance of metals and alloys decreases as the temperature is lowered. If we study the variation of resistance of mercury with temperature it is found that at very low temperatures the resistance becomes immeasurable. At about 4.2 K the resistance falls sharply and below this temperature mercury shows no resistance at all.

This phenomenon in which the electrical resistivity suddenly drops to zero when the material is cooled to a sufficiently low temperature is called *super-conductivity*. The material is known as a *super-conductor*.

The temperature at which the resistance of a material suddenly falls to zero is known as *critical temperature* T_c. At this temperature the material undergoes a phase transition from a state of normal resistance to a state of super-conductivity. This temperature is, therefore, also known as *super-conducting transition temperature*.

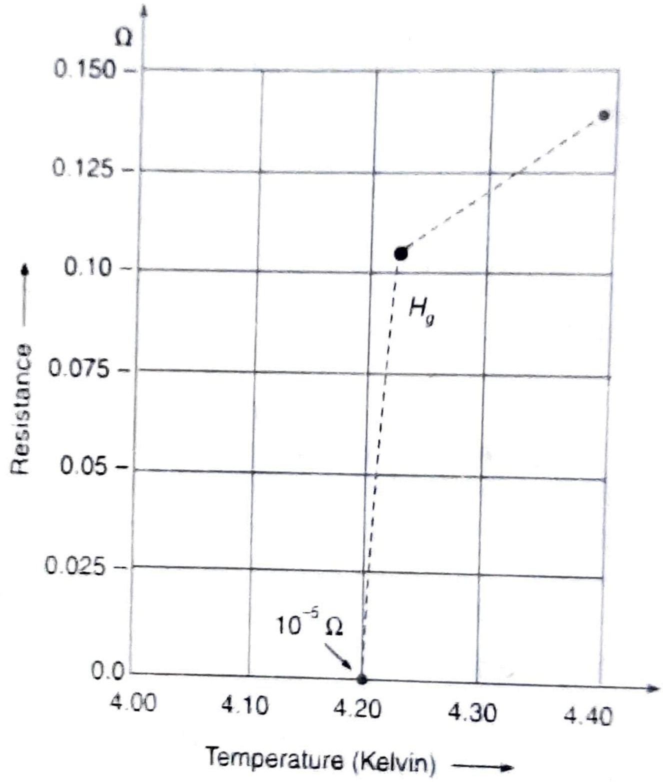

Fig. 8.1

Super-conductivity has been observed in many metals, alloys and compounds. It is superising that those metals which are the best conductors like silver, gold and copper are not super-condcutors. Some chemical compounds which are semiconductors at ordinary temperatures become super-conducting at low temperatures.

Till 1973 the highest critical temperature known was 23.2 K for Nb_3Ge alloy. In 1986 super-conductivity was abserved at 35K in a mixture of crystalline phase in *La-Ba-Cu-O* system. Recently many new super-conducting systems with T_c > 100 K have been reported to have been discovered.

Characteristic properties. We shall describe some characteristic properties of semi-conductors.

(i) **Effect of temperature.** If a ring of a super-conducting material is cooled in a magnetic field from a temperature above the transition temperature T_c to a value below T_c and then the magnetic field is switched off, an induced current is set up in the ring. The induced current is observed by the magnetic field it produces and it is found that the current continues undiminished for a very long time–say over two years. Since the current is very strong and decays according to the relation $i = I_0 e^{-\frac{R}{L}t}$, the decay time which is governed by the value of time constant $\frac{L}{R}$ becomes almost infinite as $R \to 0$.

Thus a current in a super-conducting ring flows almost indefinitely till the temperature and magnetic field remain unchanged. Such currents are called *persistent currents.*

The specific heat of a super-conductor shows an abrupt change at $T = T_c$ jumping to a large value for $T < T_c$

When the current through a super-conductor is increased beyond a critical value $I_c(T)$, the superconductor becomes a normal conductor. $I_c(T) = 0$ at $T = T_c$

(*ii*) **Effect of magnetic field.** If a magnetic field is applied parallel to the length of a super-conducting wire, the resistance of the wire is suddenly restored at a finite field strength depending upon the temperature and nature of super-conducting material. This magnetic field is called *critical field* (Also see **Q. 8.2**). It has been observed that the reappearance of resistance is abrupt only if there is no strain in the metal, it is pure and the current used to measure the resistance is small.

(*iii*) **Current strength.** An important consequence of the existence of critical magnetic field is that there is also a critical strength of current flowing in the super-conductor. If the strength of the current is exceeded, there is a disturbance of super-conductivity. A striking result of disturbance of super-conductivity by a current, was observed in the melting of a lead wire, when immersed in liquefied helium. The reason is that when the critical current is exceeded the Joule heat could not be removed fast enough due to the formation of gas bubbles and the temperature rose to the melting point. Onnes attributed this restoration of resistance to the so called '*bad places*' in the wire. It has now been verified that the effect of current in restoring the resistance is due to the magnetic field which it produces.

(*iv*) **Stress.** With the application of stress there is a change in transition temperature. Generally a stress which increases the dimensions also increases the transition temperature. This increase in transition temperature per unit increase of stress is given by $\frac{dT_c}{dP}$ and is of the order of 10^{-10} dyne^{-1} cm^2. There is also a slight effect of stress on critical magnetic field.

(*v*) **Frequency.** At very high frequencies the zero resistance of super-conductors is affected. It is seen that the zero resistance remains the same upto a frequency of 10^7 Hz but when the frequency is still raised upto 10^9 Hz some resistance is shown by the super-conductor.

The transition temperature remains, unaffected by the frequency and at 0 K the resistance approaches a value which is less than 10^{-3} of R_0— the resistance in the normal stage.

(*vi*) **Isotope effect**. The critical temperature for a super-conductor varies with isotopic mass. The transition (critical) temperature is given by $T_c M^{1/2}$ = constant where M is the isotopic mass. Thus heavier isotopes have a lower critical temperature.

The Debye temperature θ_D of phonon spectrum is given by $\theta_D M^{1/2}$ = constant

$$\therefore \quad T_c \propto \theta_D \propto M^{-1/2}$$

The above relation shows that super-conducting transition depends upon the mass of the lattice ions or phonons. In other words *electron-phonon interaction* is an important factor for the super-conducting phenomenon.

This shows that super-conducting transition must depend in some way on the mass of the lattice ions (phonons). This led to the suggestion that electron-phonon interaction may be a cause of super-conductivity.

(vii) **Destruction of super conductivity by intense magnetic field.** It is possible to destroy the super-conductivity by the application of intence magnetic field.

The critical magnetic field is defined as the magnetic field where half the normal resistance has returned, using a small measuring current. It is denoted by H_c and found to be a function of temperature. If we plot a graph of critical magnetic field versus temperature, the curve is approximately parabolic, given roughly by the relation

$$H_c = H_0 \left[1 - \left(\frac{T}{T_c}\right)^2\right]$$

where H_o is the critical field at T_0 (absolute zero).

Q. 8.2. Explain and distinguish between type I and type II super-conductors.

(G.N.D.U. 1997, 1996; Pbi. U. 1997)

Ans. Types of super-conductors. There are two types of super-conductors depending upon their magnetic behaviour in an external magnetic field.

(i) Type I or *soft* *(ii) Type* II or *hard.*

Type I or soft super-conductors. These super-conductors are perfectly diamagnetic and exhibit Meissner effect completely.

A graph between the applied magnetic field $\vec{H}$ and corresponding values of diamagnetism $(-\mu_0 \vec{M})$ for a super-conducting material is shown in Fig. 8.2. It is seen from the graph that below a critical value of the applied magnetic field denoted by H_c, the specimen is super-conducting exhibiting complete Meissner effect *i.e.*, perfect diamagnetism. The material loses super conductivity abruptly at the critical value H_c and diamagnetism *suddenly* drops down to zero *i.e.*, the magnetic flux penetrates fully. Above the critical value H_c the material behaves as a normal conductor.

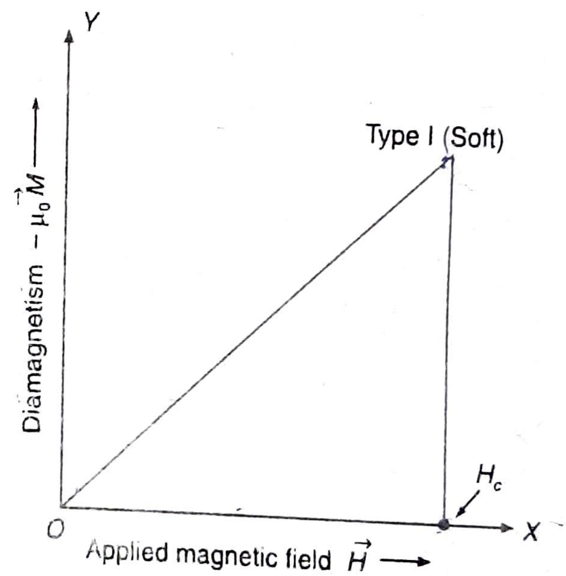

Fig. 8.2

Such materials known as type-I super-conductors are classified as SOFT because of their tendency to give away to low magnetic fields. The value of H_c is too small for SOFT super-conductors and hence these do not have any useful technical application. This behaviour is generally shown by pure specimens of some materials.

Type II or hard super-conductors. A graph between applied magnetic field $\vec{H}$ and corresponding value of diamagnetism $-\mu_0 \vec{M}$ is shown in Fig. 8.3.

It is seen from the graph that the magnetic flux starts penetrating the material at a value H_{c_1}. This value is less than the thermodynamic critical field H_c. The specimen is said to be in a vortex state between H_{c_1} and upper critical value H_{c_2}. The flux density $B \neq 0$ and the Meissner effect is said to be incomplete. The value of H_{c_2} may be 100 times or more higher than the value of the critical field H_c calculated from thermodynamics of the transition phenomenon. In the region between H_{c_1} and H_{c_2} the super-conductivity is partially destroyed or we can say that it is a mixture of normal and super-conducting states. A close examination of the specimen shows the presence of small circular regions in the normal state called *vortices* or *flexiods* surrounded by large regions in the super-conducting state. The presence of both the states gives rise to partial penetration of the field. The material is threaded by flux lines and is said to be in a vortex or

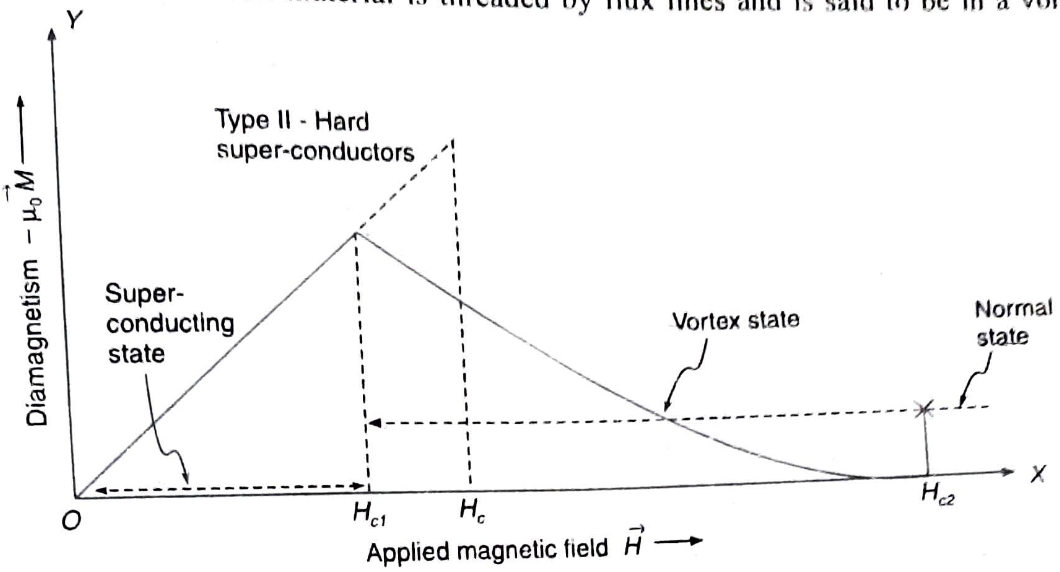

Fig. 8.3

intermediate state between H_{c_1} and H_{c_2}. Examples of such materials are alloys or transition metals with high value of electrical resistivity in the normal state.

Hard superconductors (Type II) with large magnetic hysteresis are used in making electromagnets for producing high steady magnetic fields.

Q. 8.3. What is the effect of an external magnetic field on the super-conducting state of a material ? What do you mean by flux exclusion and what is Meissner effect?
(P.U. 1997, 1995, 1994, 1992)

Ans. Effect of external magnetic field on super-conducting material. If a long thin specimen of a super-conducting material is placed in a longitudinal magnetic field and then cooled through the transition temperature for super-conductivity (T_c) the magnetic effect originally present is ejected out of the specimen. This phenomenon is known as **flux exclusion.**

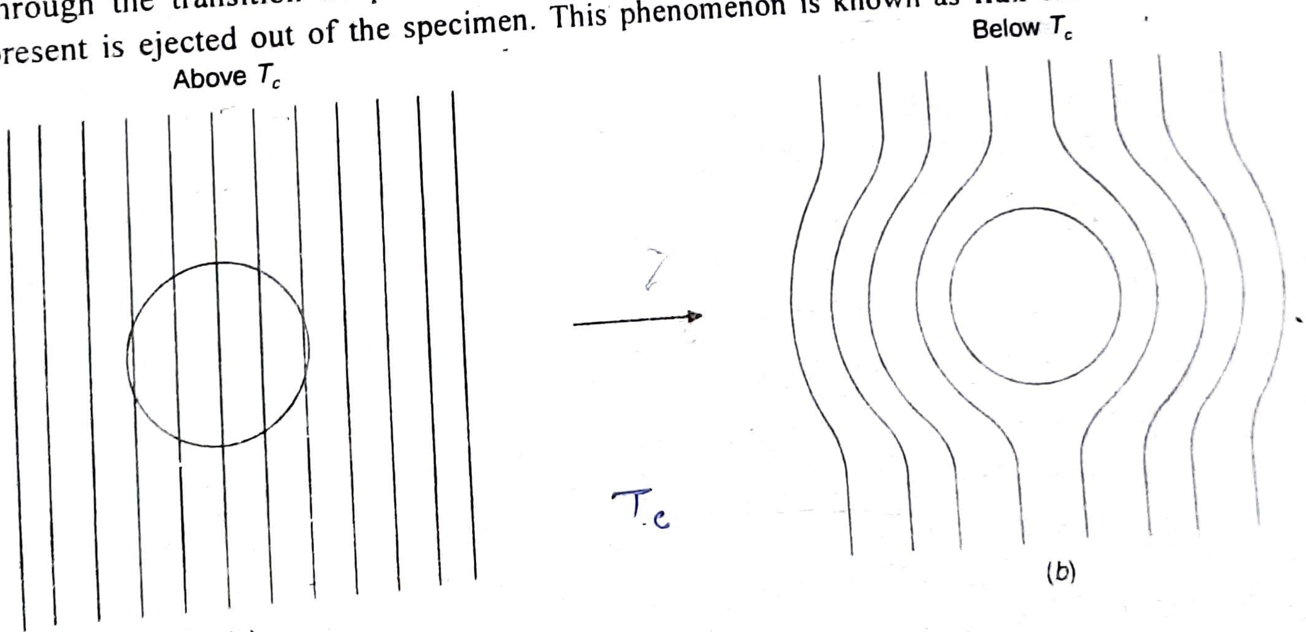

Fig. 8.4

This exclusion of flux from the bulk super-conductor is said to be complete only if the specimen is pure and free from strain.

Meissner effect. Meissner effect states that if a super-conductor is cooled in a magnetic field

H below the transition temperature T_c, then at the transition the lines of magnetic flux are pushed out of the specimen as shown in Fig. 8.4 (*b*).

Meissner effect shows that in an external applied magnetic field $\vec{H}$ the super-conductor behaves as if inside the material the value of $\vec{B} = 0$

Now (in S.I. units) $\vec{B} = \vec{H} + \mu_0 \vec{M}$

where $\vec{M}$ is the intensity of induced magnetism. At the critical temperature T_c, $\vec{B} = 0$

$$\therefore \quad \vec{H} = -\mu_0 \vec{M}$$

or

$$\frac{\vec{M}}{\vec{H}} = -\frac{1}{\mu_0} = \chi$$

i.e., the material has a negative susceptibility and behaves as perfect diamagnetic.

According to Ohm's law $\vec{E} = \rho \vec{j}$

where $\vec{E}$ is the applied electric field, ρ the resistivity of the material and $\vec{j}$ the current density.

For a super-conductor if the resistivity ρ becomes zero while the current density $\vec{j}$ has a finite value, then $\vec{E} = 0$. Further, according to Maxwell's equation

$$\vec{\nabla} \times \vec{E} = \frac{\partial \vec{B}}{\partial t}$$

If $\vec{E} = 0$ $\vec{\nabla} \times \vec{E} = 0$ and $\frac{\partial B}{\partial t} = 0$ or $\vec{B}$ = a constant

In other words, the magnetic flux density through the material for which $\vec{E} = 0$ is a constant *i.e., it cannot change on cooling* through the transition temperature. This result is contradicted by Meissner effect, according to which the phenomenon of flux exclusion ($\vec{B} = 0$) at the transition temperature *i.e.*, diamagnetism is an essential property of super-conducting state.

Hence for the super-conducting state perfect diamagnetism and zero resistivity are two independent properties. Thus

$$\vec{E} = 0 \quad \text{(zero resistivity)}$$
$$\vec{B} = 0 \quad \text{(Meissner effect / flux exclusion)}$$

both go side by side in a super-conductor.

Q. 8.4. Discuss the thermodynamic properties of the super-conducting state.

(G.N.D.U. 1993 1991)

Ans. Thermodynamic properties. We shall discuss the following thermodynamic properties of the super-conducting state. (*i*) Specific heat (*ii*) Latent heat of transition (*iii*) entropy and (*iv*) energy gap.

(*i*) Specific heat. The specific heat of a super-conductor at very low temperatures is found to be of the form

$$C_v = A\,(T/\theta)^3 + \alpha\, e^{-\Delta/kT}$$

The first term is the *lattice* specific heat, θ being the Debye temperature and A a constant $= \frac{12}{5}\pi^4 R$. The second term is the *electron contribution* to specific heat, Δ being the energy gap and α another constant. Thus the electron contribution to specific heat in a super-conducting state varies exponentially with temperature. For gallium $\Delta = 1.4\, k\, T_c$.

(*ii*) Latent heat of transition. When super conductivity is destroyed isothermally at constant temperature with the help of a magnetic field, the super-conductor absorbs heat. If the magnetic field is now reduced to regain super-conductivity heat is given out by the super-conductor. This heat is known as *latent heat of transition* L and is given by

$$L = \frac{-\rho T}{4\pi} \frac{H_c}{A} \frac{dH_c}{dT} \times 10^{-7}$$

where ρ is the density of the material, A the atomic weight, T the temperature in degree Kelvin and H_c the critical magnetic field. This is *first order phase transition* and is characterised by a latent heat as well as a discontinuity in energy gap. Since H_c is zero at T_c there is no latent heat of transition in the absence of the magnetic field. The transition in zero- magnetic field from the super-conducting state to the normal state is a *second order phase* transition so that there is no latent heat involved but only a discontinuity in the heat capacity. (Also see under entropy).

(*iii*) **Entropy.** The transition between the normal and super-conducting state is a reversible change in terms of thermodynamics. We can, therefore, apply the laws of thermodynamics to this change and thus obtain an expression for the change in entropy and increase in energy density when a super-conducting material undergoes transition from normal to super-conducting state. The super-conducting state is more ordered than the normal state and some or all the electrons thermally excited in the normal state are ordered in the super-conducting state. In type I super-conductors, the order extends to a distance of about 10^{-6} m. This distance (or range) is known as *coherent length.*

Entropy being a measure of the disorder of a system there is a marked decrease in entropy as a super-conducting material is cooled below the critical temperature.

If M is the magnetisation (magnetic moment per unit volume) induced in a specimen by a magnetising field H, and S is the entropy, then Gibb's free energy per unit volume in a magnetic field is given by

$$G = U - TS - HM \quad \text{... } (i)$$

The internal energy density in the presence of a magnetic field is given by

$$dU = T\,dS + HdM \quad \text{... } (ii)$$

For a gaseous system the expression is written as

$$dU = T\,dS - p\,dV \quad \text{... } (iii)$$

Comparing equation (*ii*) and (*iii*), we find that in our discussion H plays the role of p and M plays the role of V in the standard equation

$$G = U - TS + pV \quad \text{... } (iv)$$

Differentiating eq. (*i*), we get

$$dG = dU - TdS - SdT - MdH - HdM$$

$$dG = -S\,dT - M\,dH$$

or

as $dU - TdS - HdM = 0$

For a process at constant temperature (isothermal)

$$SdT = 0$$

∴

$$dG = -MdH \quad \text{... } (v)$$

We shall solve eq. (*v*) for *normal* as well as *super-conducting* state.

Normal state. Suppose that the normal state, is non-magnetic. It means it has zero susceptibility and hence there is no magnetisation *i.e.*, $M = 0$. Denoting Gibb's free energy for a normal state by G_N and putting $M = 0$, equation (*v*) becomes

$$dG_N = 0.$$

∴

$$G_N = \text{a constant and can be put in the form}$$

$$G_N(T, H) = G_N(T, 0) \quad \text{... } (vi)$$

Thus in the normal state G_N is not changed by the application of external magnetic field.

Super conducting state. If we consider the case of only Type I- super-conductor with complete Meissner effect so that $B = 0$ inside the super-conductor, then as $B = 0$ $$M = -\frac{H}{\mu_0}$$

Substituting this value of M in eq (v), we get

$$dG_s = -M\,dH = +\frac{H}{\mu_0}\,dH \quad \text{... } (vii)$$

Now, if $G_s\ (T, H)$ is the value of G at temperature T when the magnetic field H is applied and $G\ (T, 0)$ is the value of G when no magnetic field is applied (temperature remaining the same), then

$$d\,G_s = G_s\,(T, H) - G_s\,(T, 0) \quad \text{... } (viii)$$

From Eqs. (vii) and ($viii$), we get

$$G_s\,(T, H) - G_s\,(T, 0) = \int d\,G_s = \frac{1}{\mu_0}\int HdH = \frac{H^2}{2\mu_0} \quad \text{... } (ix)$$

This shows that Gibb's free energy of the specimen is increased on placing it in a magnetic field.

At critical field value H_c the energy of the normal (N) and super-conducting (S) states must be equal if they are to be in equilibrium

$\therefore$ $$G_N\,(T, H_c) = G_S\,(T, H_c)$$

But $$G_N\,(T, H_c) = G_N\,(T, 0) \qquad \therefore \quad G_s\,(T, H_c) = G_N\,(T, 0)$$

Substituting in Eq. (ix), we get

$$G_N\,(T, 0) - G_s\,(T, 0) = \frac{H_c^2}{2\mu_0}$$

Thus $\frac{H_c^2}{2\mu_0}$ gives the *stabilisation energy density* of a super-conductor. For aluminium, H_c at absolute zero is 10 5 Gauss which gives $\frac{H_c^2}{2\mu_0} = \frac{H_c^2}{8\pi}$ (in C.G.S. units) = 439 ergs cm^{-3}. This result is in excellent agreement with the result of thermal measurements, 430 ergs cm^{-3}

Difference of entropy between normal and super-conducting states. The difference of entropy between normal and super-conducting states is obtained by using the thermodynamic relation

$$S = -\left(\frac{\partial G}{\partial T}\right)_H$$

If S_N is the entropy in the normal state and S_s in the super-conducting state, then

$$S_N = -\left(\frac{\partial G_N}{\partial T}\right)_H \quad \text{and} \quad S_s = -\left(\frac{\partial G_s}{\partial T}\right)_H$$

$\therefore$ $$S_N - S_s = -\frac{\partial G_N(T,0)}{\partial T} + \frac{\partial G_s(T,0)}{\partial T}$$

$$= -\frac{1}{\mu_0}\left(\frac{\partial H_c^2}{2\partial T}\right) = \frac{-H_c}{\mu_0}\frac{\partial H_c}{\partial T}$$

$$= \frac{-H_c}{\mu_0}\frac{dH_c}{dT}$$

Since $\frac{dH_c}{dT}$ is always a negative quantity S_N is always greater than S_s. *This shows that the super-conducting state (having less entropy) is a more ordered state than normal state.*

Latent heat. As $\frac{dH_c}{dt}$ is never zero, there is a finite entropy change when the transition takes place in a magnetic field. *A finite entropy change, implies that there is a latent heat involved.*