

HIGH TEMPERATURE SUPERCONDUCTIVITY

V. SARASWATI

Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India.

ABSTRACT

Unprecedented and record temperature for the superconducting transition (≥ 90 K), has been achieved this year. The factors favouring a high transition temperature are reviewed and recent results are discussed in this light.

INTRODUCTION

SUPERCONDUCTIVITY is a physical phenomenon of scientific and technological importance. It has been used for making compact magnets capable of yielding high magnetic fields and junction devices. From the commercial point of view, the most desirable features in the superconducting state of a material are that (i) it has zero resistance indicating dissipationless current flow, and (ii) it facilitates levitation owing to the Meissner effect. Transmission lines for communication and frictionless transportation systems have been on trial and Japan had run a train on a 8 km track based on the levitation principle. The chief impediment to its widespread application is the cost of the refrigeration required for achieving the low temperature at which the transition takes place. A search had been on for materials with higher transition temperatures. In the seventies and early eighties the temperature T_c had not gone above 23 K (table 1) but this year several groups¹⁻⁷ have announced T_c of 90 K. Apart from the savings in energy this superhike would make feasible smaller and cheaper magnets, accelerators and faster computers.

Table 1 Historical record temperatures^a

Year	T_c	Compound	Reference
1911	4.2	Hg	Kammerling Onnes
1930	10.3	NbC	Meisner & Franz
1941	15	NbN	Aschemann <i>et al</i>
1953	17.1	V ₃ Si	Hendy & Hulm
1954	18	Nb ₃ Sn	Mathias
1967	20.1	Nb ₃ Al _{0.75} Ge _{0.25}	Mathias
1973	23	Nb ₃ Ge	Gavaler
1986	36	La-Ba-Cu-O	Bednorz & Muller Chu <i>et al</i> , Cava <i>et al</i>
1987	90	Y-Ba-Cu-O	Wu <i>et al</i>

^a Data up to 1973 taken from Allen. P. B, *Dynamic properties of solids*, (eds) G. K. Horton and A. A. Maradudin, North-Holland, Amsterdam, 1980.

In this paper the earlier approaches on high temperature superconductivity (HTSC) are reviewed and the adequacy of the conventional wisdom in explaining the breakthrough is discussed.

THEORY

The basic theory of superconductivity was advanced by Bardeen, Cooper and Schreiffer⁸. The transition temperature according to the BCS theory could be written as

$$T_c(\text{BCS}) = 1.14 w \exp(-1/N(0)V), \quad (1)$$

where w is a characteristic phonon frequency, $N(0)$ the density of electron states at the Fermi surface and V the interaction potential. $N(0)V$ can be written as $\lambda - \mu$ where λ is a parameter measuring the strength of phonon-induced attractive electron interaction and μ is the Coulomb repulsion. For maximum T_c one expects $\lambda \rightarrow \infty$ and $\mu \rightarrow 0$ and thus $T_c(\text{BCS}) \sim w$. So from a simplified argument one arrives at the conclusion that for high T_c one should have resonant phonon frequencies as high as possible.

However, when λ is large, the above equation is not valid. For some typical values the calculated $T_{c \text{ max}}$ was only 10 K, which is not high. A strong coupling theory given by Eliashberg⁹ and modified by McMillan¹⁰ yields,

$$T_c \sim w \exp(-1 + \lambda/\lambda - \mu). \quad (2)$$

When the coupling is weak, this equation reduces to (1). Here μ contains both the electronic and ionic polarizabilities and is about 0.1 to 0.13. λ , which is influenced by the characteristics of the Fermi surface and distribution in the phonon frequency spectrum is given by

$$\lambda = N(0) \langle I^2 \rangle / M \langle w^2 \rangle, \quad (3)$$

where $\langle I^2 \rangle$ is the Fermi surface average of electron phonon matrix element of the interaction potential V and M is the average ionic mass. This expression is

the most used equation for explaining high T_c . T_c is maximum when $\lambda = 2$ and is a characteristic for a given class of compounds with similar electronic and lattice structure. The recipe for high T_c was to increase $N(0)$, $\langle I^2 \rangle$ or decrease $M\langle w^2 \rangle$. According to BCS it looked as if $N(0)$ was the controlling factor for high T_c but another opinion that λ is more important was also not supported by experiments. Varma and Dynes¹¹ showed empirically that $\lambda/N(0)$ was nearly constant but as $N(0)$, $M\langle w^2 \rangle$, and $\langle I^2 \rangle$ are intimately related it may not be easy to pinpoint the controlling parameter for high T_c . There has been some difficulty¹² in using (3) when λ is greater than 1.5. For determining experimentally certain empirical correlations were sought for. Allen and Dynes¹² found that T_c/w_{avg} was a linear function of λ in the range $0.75 < \lambda < 2.6$ and could be determined from tunnelling experiments. A similar correlation with θ_D , the Debye temperature was observed by Rowell¹³ in the above range of λ ,

$$T_c = \theta_D/20 (\lambda - 0.25). \quad (4)$$

But the theoretical and experimental values for λ from various measurements such as tunnelling, specific heat and optics do not compare¹⁴ well. λ is also called the enhancement coefficient because the effective density of states and cyclotron mass of electron are enhanced. In the ultrastrong coupling limit λ attains an asymptotic value¹²

$$T_c = 0.18 (\lambda \langle w^2 \rangle)^{1/2} \quad (5)$$

A strong coupling between the electron and the lattice should lead to instabilities as discussed in the next section.

INSTABILITIES

Philips¹⁵ and Mathias¹⁶ independently suggested that lattice instability was related to HTSC. The instability which leads to structural transformation is usually signalled by the softening of the lattice moduli and short wavelength acoustic phonons. It is also exhibited as the coexistence of several structural phases near a composition. Anomalies in phonon spectra, resistivity and susceptibility data act as indicators to instability.

In several high T_c compounds a structural transition from cubic to tetragonal occurs at temperatures higher than T_c . Some examples are given in table 2. The main characteristics of the transformation were that they were diffusionless, reversible and from a higher symmetry to a lower symmetry. The dominant role of micro structure in structural transforma-

Table 2 Superconducting and structural transition temperatures in some materials

Compound	Initial struc.	Struc. after transformation	$T_m(K)$	$T_c(K)$
V ₃ Si	A15	Tetragonal	21–23	17
Nb ₃ Sn	A15	Tetragonal	43–45	18
HfV ₂	C15	Body centre orthorhombic	120	8.7
LaRu ₂	C15	Tetragonal	30	4.4
VRu	B2	Tetragonal	110–360	5
La ₃ S ₄	Th ₃ P ₄	Tetragonal	90	8.2

tion was explicitly shown¹⁷ in ZrV₂. From a study of perfect, twinned and grained crystals it was inferred that although all samples exhibited an electron instability ~ 100 K, actual structural transformation took place only in imperfect crystals. The perfect crystal did not transform down to 10 K indicating clearly that structural transformation is driven by the electronic instability when coupled to the localized lattice stress.

Those which have structural transition also exhibit anomalies in the elastic properties. Anomalous decrease in velocity of sound indicates the softening of shear modes¹⁸. Acoustic attenuation with decreasing temperatures was observed in A15 structure (V₃Si, Nb₃Sn, Nb₃Al), C15 (ZrV₂, HfV₂) and B2 structures indicating softening of the lattice moduli referring to the instability of acoustic long wavelength phonons. The temperature region in which the maximum softening occurs is close to the region at which structural transitions occur in these compounds.

A correlation between lattice constant instability and T_c was found¹⁹ in some binary carbides and nitrides (NbC, NbN, TaC). Dispersion curves for acoustic phonons had anomalies in the short wavelength region. By surveying macroscopic thermochemical data, such as the heat of formation and microscopic lattice constant together with phonon anomalies, Philips¹⁹ concluded that lattice instabilities especially at short wavelengths make the largest contribution to $\langle w \rangle$ softening and the instability is large for high T_c compounds.

In many HTSCs with A15 and B1 structures it has been found²⁰ that different structural phases exist in the vicinity of stoichiometric composition e.g. Nb₃Si, MoC, NbN. The compounds, Nb₃X (X = Ge, Ga, Al) are metastable and come in mixed phases. The high transition temperature could be due to any of the phases. Thus it is probable that the proximity

of a given composition to phase equilibrium boundaries may characterize one type of instability leading to high T_c .

BINARIES AND A15 COMPOUNDS

It is now known that most metallic elements are superconductors with notable exceptions, metals with unfilled d and f shells, alkalis, and noble metals. The binary intermetallics and compounds were found to have T_c higher than their constituent elements which may not even be superconducting¹⁴ (table 3). Semiconductors and even polymers have been found to be superconducting.

The earlier contention that cubic lattice is favourable to HTSC is no longer true. $T_c > 10$ K had been observed in several structural systems. However a good number belong to the A15 structure. Nearly 50 superconducting intermetallics and compounds have this structure including several record T_c of the past (table 1). A15 structure is also known as β -W, Cr_3Si and Cr_3O structure. The ideal composition is A_3B . The unit cell has the spacegroup $\text{O}_h\text{-Pm}3\text{n}$ and has 8 atoms. A atoms occur in pairs on each of the faces of a cubic cell and form 3 orthogonal chains with the smallest distance between A atoms being in the chain. The B atoms are arranged in body-centred cubic configuration. To form this phase the ratio of the radii of the A and B atoms should be near unity (0.84–1.12). The condition for crystallochemical stability of A15 lattice when B atom simultaneously contacts all the twelve atoms surrounding it is $r_A/r_B = 1.23$. None of the superconducting compounds with A15 structure satisfy this condition as the ratio is less than 1.23 implying that they are crystallochemically unstable. T_c tends to increase

with this instability in the A15 structure. In the linear chain A15 compounds there is an inherent degree of instability against shear distortion.

T_c is highly sensitive to deviation from stoichiometry. The highest T_c are reached in stoichiometric compounds in A15 structure (Nb_3Ge 23.2 K), B1 structure (NbN , 17.3 K) and in palladium hydrides¹⁴. Quenching is often adopted to get a stoichiometric phase. In general T_c tends to be high in those structures in which the energy bands are flat and the Fermi surface is nested, which results in high density of states. It is true for A15 structures.

THE CHEMICAL BOND

The influence of chemical parameters such as the relative strengths of chemical bonds coordination numbers etc is usually discussed in terms of heat of formation lattice constants and charge transfer¹⁹. In carbides and nitrides a correlation between T_c and heat of formation was found. Nonlinear variation of bond length as a function of valency was high in high T_c compounds (NbN). In high T_c A15 compounds metallic conductivity goes hand in hand with considerable brittleness inherent in covalent crystals. An indication of covalent bond is the low coordination numbers in the atoms of metal with A15 structure. High covalency is also inferred from hardness measurements. Brittleness and high melting point characterize the covalent bonding force. Hanke *et al*²¹ have shown that covalent bond as in V_3Si , due to hybridization of relatively localized metal d and extended nonmetal p states near E_F , lead to a resonance like increase in nonlocal dielectric function. This anomalous increase of the screening produces phonon softening with increase of $\langle I^2 \rangle$, thus increasing λ and T_c . In the B1 structure (NaCl) charge transfer from metallic to nonmetallic atoms has been established indicating the presence of an ionic component. C15 compounds (HfV_2) possess metallic conductivity but other metallic characteristics were not clearly marked¹⁴. In sesquicarbides metallic and ionic contribution to bonding has been observed. Thus the nature of the bond is varied in high T_c systems. Another parameter of importance is the valence electron per atom ratio, e/a . Most favourable values for superconductivity were 4.75 and 6.5. This appears universal for transition metal compounds. In A15 structures, high T_c compounds group around the two intervals 4.50–4.75, and 6.25–6.60 e/a . It holds also for other structures except sesquicarbides which favour $e/a \sim 3.6$. It must be mentioned that e/a becomes an

Table 3 Comparison of T_c in different structures¹⁴

Compound	Type	Symmetry	Max T_c (K)	T_c of constit. K
Nb_3Ge	A15	Cubic	23.2	Nb:9.2
$\text{Mo}_{0.38}\text{Re}_{0.62}$	Phase	Tetrag.	14.6	Mo:0.92, Re: 1.7
NbN	B1	Cubic	17.3	Nb:9.2
Pd-AG-D	B1	Cubic	16	Pd < 0.01, Ag: < 0.01
$(\text{Y}_{0.7}\text{Th}_{0.3})_2\text{C}_{3.1}$	Pu_2C_3	Cubic	17	Th:1.38, Y < 0.03
$\text{Li}_{0.3}\text{Ti}_{1.1}\text{S}_2$	Ti_3S_4	Hexag.	13	Li 0.08, Ti:0.4
$\text{Pb}_{0.92}\text{Mo}_6\text{S}_{7.5}$	Mo_3Se_4	Rhombo	15.2	Pb:7.2, Mo:0.92

arbitrary variable when localized ionic or covalent orbitals mix with the conduction band and when there is structural disorder. The influence of atomic order has been well investigated. Amorphous or disordered state was achieved by sputtering or irradiation and a considerable drop in T_c observed²². The disordered Nb_3X ($X = Ge, Al, Sn$) have transition 3 K whereas the corresponding compositions with A15 structure have transitions above 18 K. The difference was attributed to the lowering in the coupling parameter. It was shown that $\langle I^2 \rangle$ changes by a factor 3 from crystalline to disordered. Similarly the influence of structural symmetry on T_c has also been demonstrated²³. By quick quench when V_3Au is changed from A15 to A2 structure, T_c fell from 11.1 to 1.2 K. Thus, a half-filled d orbital, covalent or mixed s,p,d band, stoichiometry and structural order appeared to be most favourable for high T_c from experimental observations.

TERNARY PHASE

Mathias¹⁹ felt that for instabilities and for high T_c one should go for ternary, quaternary and complex structures so that λ is high. Shelton's review summarizes²⁴ the status till 1982. A variety of borides, carbides, silicides, germanides, stannides, sulphides, oxides and selenides were investigated. Out of the three elements one is a transition metal, another a nonmetal and a third, Y, Sc, or rare earth was chosen essentially to tune in the electronic properties. The only exception to the rule was a nontransition metal compound, $Ba(Pb_{1-x}Bi_x)O_3$ with $T_c \sim 11.7$ K. Cheveral phase compounds are also in these. High critical fields favourable for technical applications were found in many of these compounds. An interesting feature was the superconducting nature of compounds with a high concentration of magnetic elements.

In $Lu_2Fe_3Si_5$ and $Sc_5Co_4Si_{10}$ a T_c of 5 K or greater was attained in spite of the presence of 30 at. % and 21 at. % magnetic $3d$ element²⁵. The complex crystallographic nature and the arrangement of the magnetic element in the structure are such that collective magnetic behaviour is inhibited. There was a strong correlation between high T_c and the presence of three-dimensional clusters. Superconductivity did not occur when magnetic ion separation fell below 4.5 Å in Sc compound or when the concentration of Co was higher. Special mention is made of Pd-Ag-D, Pd-Cu-H, Li-Ti-S exhibiting high $T_c > 10$ K when none of the constituents have T_c exceeding 0.5 K. Spin fluctuations of Pd are suppressed²⁶ by the introduction of H/D by ion

Table 4 Influence of structural order on T_c in A15 compounds¹⁴

Compound	T_c (K) cryst.	T_c (K) amorp.
Nb_3Sn	18	3
Nb_3Al	18.5	2
Nb_3Ge	22-23	3-4
V_3Si	17	< 1.5

implantation diminishing its paramagnetism. The noble metals serve the same purpose as H. But without H, T_c was very low for the alloys. High T_c was inferred as due to lattice instability by some phonon modes. The reverse isotope effect when D ions were implanted was explained as due to interaction of the electrons with optical phonons. Ternary hydrides showed a high T_c , 13 to 17 K and a proper isotope effect with respect to noble metals Cu, Ag, Au.

Summarizing the salient features, the McMillans expression for T_c explains the experimental results in a qualitative way. HTSC is announced by precursors like phonon anomaly, softening of shear moduli and lattice instability. A strong e-ph interaction was conclusively established through several experiments. However it must be added that these precursors are not unique to the phenomena of superconductivity. Magnetic ordering and ferroelectricity also exhibit phonon mode softening and lattice instability because of strong e-ph interaction. Empirically for high T_c , the requisites were a high λ and high density of states assured by the half-filled d bands with mixed covalent character and structural order.

RESULTS 87

The values for high T_c this year surpass all records prior to 1986 (table 5). Following the first report by Bednorz and Muller¹ of a possible high T_c in La-Ba-Cu-O system intensive studies were carried out and a T_c of 36 K was observed. Substitution of La by Y brought in the substantial increase²⁷ to T_c 90 K. Presently several perovskite cuprates are said to have T_c close to this temperature. Non-superconducting La_2CuO_4 is a ternary phase semiconductor with tetragonal K_2NiF_4 structure²⁸ above 533 K. Below this it has an orthorhombic distortion. Addition of Ba or Sr stabilizes the tetragonal structure and metallizes the compound $La_{1-x}Ba_xCuO_4$, which becomes superconducting ~ 30 K. Structurally it meets the requirement of instability. r_{La}/r_{Cu} is 1.67 as against 1.7 to 2.4 for a

Table 5 T_c La-Cu-O systems*

No	Compound	T_c /K	Cu at. %	Ref 1987
1	La_2CuO_4	no	14.3	<i>Curr. Sci.</i> , 56, 47.
2	LaSrCuO_4	no	14.3	<i>Curr. Sci.</i> , 56, 47.
3	$\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$	30	14.3	<i>Phys. Rev. Lett.</i> , 58, 405.
4	$\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$	36	14.3	<i>Phys. Rev. Lett.</i> , 58, 408.
5	$(\text{La}_{1-x}\text{Pr}_x)_{2-y}\text{Sr}_y\text{CuO}_4$	20–30	14.3	<i>Curr. Sci.</i> , 56, 47.
6	$(\text{La}_{1.75}\text{Eu}_{0.25})_{1.8}\text{Sr}_{0.2}\text{CuO}_4$	20–30	14.3	<i>Curr. Sci.</i> , 56, 47.
7 ⁺	$\text{La}_4\text{BaCu}_5\text{O}_{13}$	no	21.7	<i>Curr. Sci.</i> , 56, 47.
8 ⁺	$\text{La}_{3.75}\text{Ba}_{1.25}\text{Cu}_5\text{O}_{13+\delta}$	20	21.7	<i>Pramana (J. Phys.)</i> , 28, L229.
9 ⁺	$\text{La}_4\text{BaCu}_5\text{O}_{13+\delta}$	no	21.7	<i>Pramana (J. Phys.)</i> , 28, L229.
10	$\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14}$	no	23	<i>Pramana (J. Phys.)</i> , 28, L229.
11	Y_2CuO_4	no	14.3	<i>Pramana (J. Phys.)</i> , 28, L229.
12	Y_2BaCuO_5	no	11	<i>Pramana (J. Phys.)</i> , 28, L229.
13	$(\text{Y}_{1-x}\text{Ba}_x)_2\text{CuO}_{4-\delta}$	80–90	14.3	<i>Curr. Sci.</i> , 56, 250.
14	$\text{Y}_{1.2}\text{Ba}_{0.81}\text{Sr}_{0.2}\text{CuO}_4$	110	14.3	<i>Curr. Sci.</i> , 56, 252.
15	$\text{Y}_{1.6}\text{Ba}_{0.4}\text{CuO}_4$	90	14.3	<i>Phys. Rev. Lett.</i> , 58, 1574.
16	$\text{Y}_{0.5}\text{Ba}_{0.5}\text{CuO}_3$	90	20	<i>Phys. Rev. Lett.</i> , 58, 1574.
17	$\text{Y}_{2.4}\text{Ba}_{3.6}\text{Cu}_6\text{O}_{14}$	115	23	<i>Pramana (J. Phys.)</i> , 28, L229.
18	$\text{Ba}_2\text{YCu}_3\text{O}_{9-\delta}$ $\delta \sim 2.1$	91	23	<i>Phys. Rev. Lett.</i> , 58, 1676.

* Data compiled up to May 10, 1987. ⁺ change of oxygen content alone has not produced superconductivity, compare 7,8,9. – change of La:Ba ratio does 2, 4. – also Y:Ba change 11, 14.

stable K_2NiF_4 structure. The electronic properties of La_2CuO_4 are similar to the tungsten bronzes A_xWO_3 and $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ alloys where an interplay of superconductivity, structural changes and metal insulator transitions were reported²⁹. $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ is a bipolaronic semiconductor with metal-nonmetal transition caused by electronic instabilities³⁰. In such systems T_c can be expected to be high compared to intermetallics. $\text{Cu}^{2+}(\text{d}^9)$ is a Jahn–Teller ion in which polaron formation is likely. In LBCO system Cu is at the centre of a tetragonally distorted octahedron of O atoms. A high structural transition temperature (533 K), lattice instability, and current dependent resistance⁶ 160 K are indicators to high T_c . In spite of varied substitutions T_c remains 30–36 K in the La system. Mattheiss³¹ calculated the band structure and showed that a half-filled $\text{Cu}(3\text{d})-\text{O}(2\text{p})$ band with two-dimensional character and nearly square Fermi surface produces Peierls instability for La_2CuO_4 and makes it semiconducting. A slight addition of Ba or Sr spoils the nesting features and makes the material metallic and stable, while retaining the strong e–ph coupling. From the calculations of Weber³², strong $\lambda \geq 2$ and light oxygen mass which allows the phonon distribution to extend to high frequencies have raised T_c to 30 K. Peierls instability has been confirmed by Raman scattering. It appears that LBCO system can be explained within the BCS–McMillan framework. On replacing

La by Y, in the YBCO system T_c is 90 K. YBCO has perovskite structure whereas LBCO has K_2NiF_4 i.e. perovskite separated by La–O layers. T_c in BCS is said³⁴ to have a limit given as ~ 40 K. Hence for YBCO a new theory is sought for. Chu *et al* attribute the high value to the quasi 2D assembly of CuO_2 – Ba-CuO_{2+x} layers, T_c becoming higher as bigger assemblies of CuO_2 layers attach to Ba. High critical fields > 750 Koe and antiferromagnetism have also been observed in these. Some noncopper compounds showing high T_c are Nb–Ge–Al–O films³⁵ (44.5 K) and probably³⁶ $\text{Ba}_{1-x}\text{Pb}_x\text{BiO}_3$. In another Nb–Si film superconductivity like anomaly was observed³⁷ at 180 K but could not be repeated owing to the high sensitivity of T_c to preparatory conditions. As the films also contained oxides of Nb, Ge, and Al the excitonic mechanism of Allender *et al*³⁸ was proposed. A similar mechanism had been suggested for the anomalous³⁹ superconductivity like behaviour for CuCl under pressure. The local strain in the sample could generate a piezoelectric current which can make the defect infested part conducting. These conducting microdomains are imbedded in the semiconductor matrix. The metal electrons can penetrate the semi-conductor surface and are coupled by the excitons which may give rise to superconductivity. Since the LBCO and YBCO are also in mixed phases such an explanation is feasible. But, for exciton coupled pairing λ is not

large. The limit set by Bardeen⁴⁰ was 0.5. Another mechanism which had earlier successfully explained⁴¹ the influence of disorder and the differing T_c in Nb₃Ge and V₃Ge (23 and 6 K) though both have the same A15 structure is the electron pairing through acoustic plasmons considered by Frolich⁴². In a two-component electron system, acoustic plasmon arises as a collective branch of charge density oscillations similar to phonons in a system of ions and electrons. Lighter *s*-electrons screen the heavier *d*-electrons similar to the screening of ions by electrons. Acoustic and optical plasmon branches appear similar to the phonon branches. $\lambda = \lambda_{ph} + \lambda_{pis}$ is the full electron-boson coupling constant and this could explain the high T_c for materials with weak e-ph coupling (Nb₃Sn, 18 K).

The present explanations for high T_c in LBCO and YBCO systems are based on the large tetragonal distortion of CuO₆ octahedra, which leads to a near planar, 2D bandstructure, Fermi surface etc. But the Eliashberg equation is not valid for a highly anisotropic Fermi surface. As pointed out by Baryakhtar *et al*⁴³ the topology of the Fermi surface might become important under the influence of a strong e-ph interaction. If the Fermi level lies in the vicinity of a critical energy value corresponding to a variation of topology of Fermi surfaces (formation of pockets or transition from a closed surface to an open one) then the density of states in the vicinity of Fermi energy should have a singularity which manifests itself in the variation of superconducting transition temperature if the position of Fermi level is varied by doping with impurities or by pressure. Seeing the high sensitivity of T_c response to material preparation, oxygen and stoichiometry as in NbSi films, large pressure dependence seen in CuCl and LBCO system, a singularity appears likely. Several questions in the past and present remain unanswered. The breakthrough in T_c can probably stimulate the answers now.

27 May 1987

1. Bednorz, J. G. and Muller K. A., *Z. Phys.*, 1986, **B64**, 189.
2. Uchida, S., Takagi, H., Kitazawa, K. and Tanaka, S., *Jpn. J. Appl. Phys.*, 1987, **26**, L1.
3. Chu, C. W., *et al.*, *Phys. Rev. Lett.*, 1987, **58**, 405.
4. Cava, R. J., *et al.*, *Phys. Rev. Lett.*, 1987, **58**, 408.
5. Rao, C. N. R. and Ganguly, P., *Curr. Sci.*, 1987, **56**, 47.
6. Ganguli, P., Raychaudhuri, A., Sreedhar, K. and Rao, C. N. R., *Pramana (J. Phys.)*, 1987, **28**, L229.
7. Sampathkumaran, E. V., Paulose, P. L., Grover, A. K., Nagarajan, V. and Dhar, S. K., *Curr. Sci.*, 1987, **56**, 252.
8. Bardeen, J., Cooper, L. N. and Schrieffer, J. R., *Phys. Rev.*, 1957, **106**, 162.
9. Eliashberg, G. M., *JETP*, 1960, **38**, 966.
10. McMillan, W. L., *Phys. Rev.*, 1968, **167**, 331.
11. Varma, C. M., Dynes, R. C., In: *Superconductivity in d-and f-band metals*, (ed.) D. H. Douglas, Plenum, New York, 1976, p. 507.
12. Allen, P. B. and Dynes, R. C., *Phys. Rev.*, 1975, **B12**, 905.
13. Rowell, J. M., *Solid State Commun.*, 1976, **19**, 1131.
14. Vonsovsky, S. V., Izyumov, Yu. A. and Kurmaev, E. Z., *Superconductivity of transition metals, alloys and compounds*, Springer Verlag, Berlin, Heidelberg, New York, 1982.
15. Philips, J. P., *Phys. Rev. Lett.*, 1971, **26**, 543.
16. Mathias, B. T., *Comm. Solid State Phys.*, 1970, **3**, 93.
17. Inoue, K. and Tachikawa, K., *J. Jpn. Inst. Metals*, 1975, **39**, 1266.
18. Testardi, L. R., Bateman, T. B., Reed, W. A. and Chirba, V. G., *Phys. Rev. Lett.*, 1965, **15**, 250.
19. Philips, J. C., In: *Superconductivity of d-and f-band metals*, (ed.) D. H. Douglas, American Institute of Physics, New York, 1972.
20. *Superconductivity in d-and f-band metals*, Academic Press, New York, 1980.
21. Shen, I. J. *et al.*, *Appl. Phys. Lett.*, 1978, **33**, 103.
22. ref 20, Tsuei C. C., 133.
23. Stewart, G. R. and Giorgi, A. L., *Solid State Commun.*, 1978, **26**, 669.
24. Shelton, R. N., In: *Novel materials and techniques in condensed matter*, (eds) G. W. Crabtree, and P. Vasista, 1981, North-Holland, New York.
25. Braun, H. F., *Phys. Lett.*, 1980, **A75**, 386.
26. Stritzker, B., *Z. Phys.*, 1974, **A268**, 261.
27. Wu, M. K., *et al.*, *Phys. Rev. Lett.*, 1987, **58**, 908.
28. Ganguli, P. and Rao, C. N. R., *Mater. Res. Bull.*, 1973, **8**, 408.
29. Mattheiss, L. F. and Hamann, D. R., *Phys. Rev.*, 1983, **B28**, 4227.
30. Hiramoto, A., *J. Phys. Soc. Jpn.*, 1985, **54**, 245.
31. Mattheiss, L. F., *Phys. Rev. Lett.*, 1987, **58**,

- 1028.
32. Weber, W., *Phys. Rev. Lett.*, 1987, **58**, 1371.
 33. Cava, R. J., *et al.*, *Phys. Rev. Lett.*, 1987, **58**, 1676.
 34. Ginzberg, V. L. and Kirzhnits, D. A., *High temperature superconductivity*, Consultants Bureau, New York, 1982, p. 12.
 35. Ogushi, T and Osono, Y., *Appl. Phys. Lett.*, 1986, **48**, 1167.
 36. Varma, C. M., as reported in the 5th ICVF, Jan. 87 at Bangalore.
 37. Ogushi, T., Obara, K and Anayama, T. J., *Jpn. Appl. Phys.*, 1983, **22**, L523.
 38. Allender, D., Bray, J. and Bardeen, J., *Phys. Rev.*, 1973, **137**, 1020.
 39. Chu, C. W. and Wu, M. K., In: *High pressure in science and technology*, North-Holland, Amsterdam, 1989, Vol. 1.
 40. Bardeen, J., in ref. 11.
 41. Tutto, I. and Ruvalds, J., *Phys. Rev.*, 1979, **B19**, 5641.
 42. Frolich, H., *J. Phys. (Paris)*, 1968, **C1**, 544.
 43. Baryakhtar, V. G., Gann, V. V. and Makarov, V. I., *JETP*, 1972, **62**, 1118.

NEWS

BACTERIA COME TO THE AID OF WOUNDED PLANTS

British botanists have developed a novel way to protect plants from attack by pests. Rather than breeding resistant strains of crop plants, the researchers, based at the University of Durham, have pressed into service a bacterium that produces a biological pesticide.

The bacteria live in close association with plants and produce their own pesticide only when stimulated by a plant at risk of attack. The bacteria produce the pesticide in small, controlled amounts, while in intimate contact with the plant. This form of protection will be cheap and eliminate the environ-

mental damage caused by conventional pesticides.

Protecting plants from pests and diseases, particularly insects and fungi, is a big part of agrobusiness worth an estimated \$5000million a year. Unfortunately, wastage is high, the chemicals break down or are leached away before they have a chance to act. Moreover, some pesticides have caused severe environmental problems. (New Scientist 2 April 1987) *News Monitor*, Vol. 2, No. 3, July 1987, p. 5 (Published by: Centre for Advancement of Biotechnology—Prof. K. S. Gopalakrishnan, 1276 32 G Cross, IV Block (T) Jayanagar, Bangalore 560 011)

CANCER FROM PESTICIDES

As many as 20,000 cases of cancer may result from pesticides that contaminate common foods, says a report issued on May 20 by the National Academy of Sciences (NAS). Foods posing the greatest risk include tomatoes, beef, potatoes, oranges, and lettuce. In its study the NAS made "worst-risk" assessments of 28 pesticides and assumed a daily consumption over 70 years of foods containing the maximum amount of pesticide residue. The risk is considered to be nearly equal to that of exposure to

asbestos and radon but far smaller than the risk from cigarette smoking. Pesticides evaluated by NAS include captan, chlordime-form, permethrin, and zineb. NAS panel members and EPA officials emphasized that because the worst-case estimates were used, the actual risks to consumers are much lower. (*Environment Science and Technology*, Vol.21, No.7, p. 616, 1987; American Chemical Society, 1155, 16th Street, N. W. Washington, D. C. 20036, USA.)