



RTS Workshop  
Loen, Norway, 17-23 June 2007

# High- $T_c$ superconducting elements under very high pressures

Katsuya SHIMIZU

KYOKUGEN, Center for Quantum Science and  
Technology under Extreme Conditions

Osaka University





## outline

Superconductivity on the table

How high can we push it up?

History

T<sub>c</sub> at Mbar pressure

Sc from insulator

Halogen, Chalcogen

Sc from metal

Alkaline, Heavy alkaline

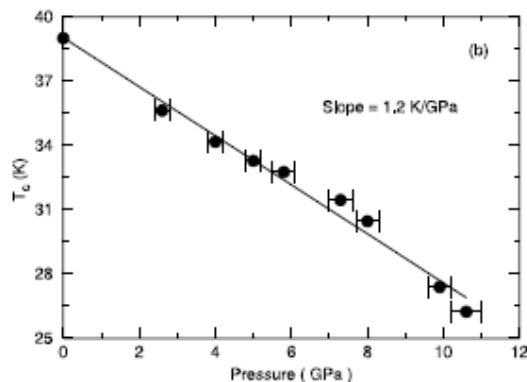
Summary and future challenge

# High- $T_c$ superconductors under pressure

- $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_y$   $\sim 138$  K  
 $\sim 164$  K (WR)

L. Gao et al., Phys. Rev. B 50, 4360 (1993).

- $\text{MgB}_2$  39 K



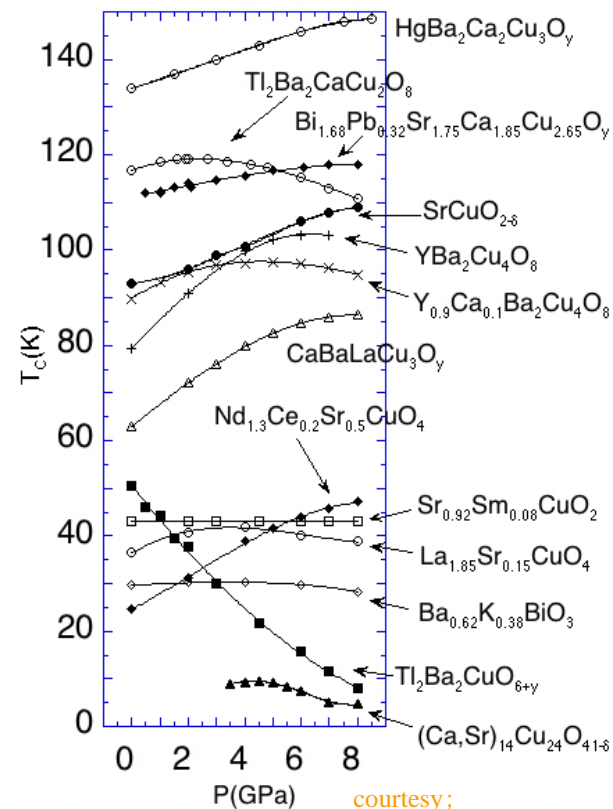
J. Nagamatsu et al., Nature 410 (2001) 63.

F. S. Razavi et al., Physica C 366 (2002) 73.

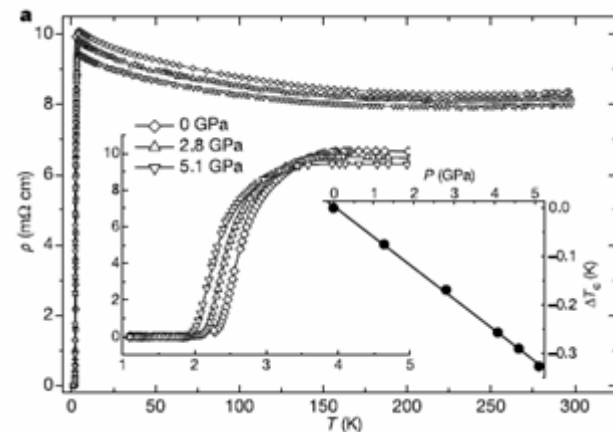
- B-doped diamond  $\sim 11$  K

- Li, Y, Ca  $\sim 20$  K (30~50 GPa)

K. S et al., Nature 419 (2002) 597.



courtesy;  
Prof. H. Takahashi



E. A. Ekimov et al., Nature 428(2004)542.

# RPS; room pressure superconductors

P = 1 bar (30)

<sup>1</sup>H

																<sup>2</sup> He	
<sup>3</sup> Li	<sup>4</sup> Be											<sup>5</sup> B	<sup>6</sup> C	<sup>7</sup> N	<sup>8</sup> O	<sup>9</sup> F	<sup>10</sup> Ne
<sup>11</sup> Na	<sup>12</sup> Mg											<sup>13</sup> Al	<sup>14</sup> Si	<sup>15</sup> P	<sup>16</sup> S	<sup>17</sup> Cl	<sup>18</sup> Ar
<sup>19</sup> K	<sup>20</sup> Ca	<sup>21</sup> Sc	<sup>22</sup> Ti	<sup>23</sup> V	<sup>24</sup> Cr	<sup>25</sup> Mn	<sup>26</sup> Fe	<sup>27</sup> Co	<sup>28</sup> Ni	<sup>29</sup> Cu	<sup>30</sup> Zn	<sup>31</sup> Ga	<sup>32</sup> Ge	<sup>33</sup> As	<sup>34</sup> Se	<sup>35</sup> Br	<sup>36</sup> Kr
<sup>37</sup> Rb	<sup>38</sup> Sr	<sup>39</sup> Y	<sup>40</sup> Zr	<sup>41</sup> Nb	<sup>42</sup> Mo	<sup>43</sup> Tc	<sup>44</sup> Ru	<sup>45</sup> Rh	<sup>46</sup> Pd	<sup>47</sup> Ag	<sup>48</sup> Cd	<sup>49</sup> In	<sup>50</sup> Sn	<sup>51</sup> Sb	<sup>52</sup> Te	<sup>53</sup> I	<sup>54</sup> Xe
<sup>55</sup> Cs	<sup>56</sup> Ba	<sup>57</sup> La	<sup>72</sup> Hf	<sup>73</sup> Ta	<sup>74</sup> W	<sup>75</sup> Re	<sup>76</sup> Os	<sup>77</sup> Ir	<sup>78</sup> Pt	<sup>79</sup> Au	<sup>80</sup> Hg	<sup>81</sup> Tl	<sup>82</sup> Pb	<sup>83</sup> Bi	<sup>84</sup> Po	<sup>85</sup> At	<sup>86</sup> Rn
<sup>87</sup> Fr	<sup>88</sup> Ra	<sup>89</sup> Ac															
			<sup>58</sup> Ce	<sup>59</sup> Pr	<sup>60</sup> Nd	<sup>61</sup> Pm	<sup>62</sup> Sm	<sup>63</sup> Eu	<sup>64</sup> Gd	<sup>65</sup> Tb	<sup>66</sup> Dy	<sup>67</sup> Ho	<sup>68</sup> Er	<sup>69</sup> Tm	<sup>70</sup> Yb	<sup>71</sup> Lu	
			<sup>90</sup> Th	<sup>91</sup> Pa	<sup>92</sup> U	<sup>93</sup> Np	<sup>94</sup> Pu	<sup>95</sup> Am	<sup>96</sup> Cm	<sup>97</sup> Bk	<sup>98</sup> Cf	<sup>99</sup> Es	<sup>100</sup> Fm	<sup>101</sup> Md	<sup>102</sup> No	<sup>103</sup> Lr	

# Superconducting Elements 2007

																		P = 1 bar (30)												
																		P > 1 bar (16)												
																		we found (6)												
1H																						2He								
3Li		4Be																5B	6C	7N	8O	9F	10Ne							
11Na		12Mg																13Al	14Si	15P	16S	17Cl	18Ar							
19K	20Ca	21Sc	22Ti	23V	24Cr	25Mn	26Fe	27Co	28Ni	29Cu	30Zn	31Ga	32Ge	33As	34Se	35Br	36Kr													
37Rb	38Sr	39Y	40Zr	41Nb	42Mo	43Tc	44Ru	45Rh	46Pd	47Ag	48Cd	49In	50Sn	51Sb	52Te	53I	54Xe													
55Cs	56Ba	57La	72Hf	73Ta	74W	75Re	76Os	77Ir	78Pt	79Au	80Hg	81Tl	82Pb	83Bi	84Po	85At	86Rn													
87Fr	88Ra	89Ac																												
58Ce	59Pr	60Nd	61Pm	62Sm	63Eu	64Gd	65Tb	66Dy	67Ho	68Er	69Tm	70Yb	71Lu																	
90Th	91Pa	92U	93Np	94Pu	95Am	96Cm	97Bk	98Cf	99Es	100Fm	101Md	102No	103Lr																	



# forgetting about "pressure"

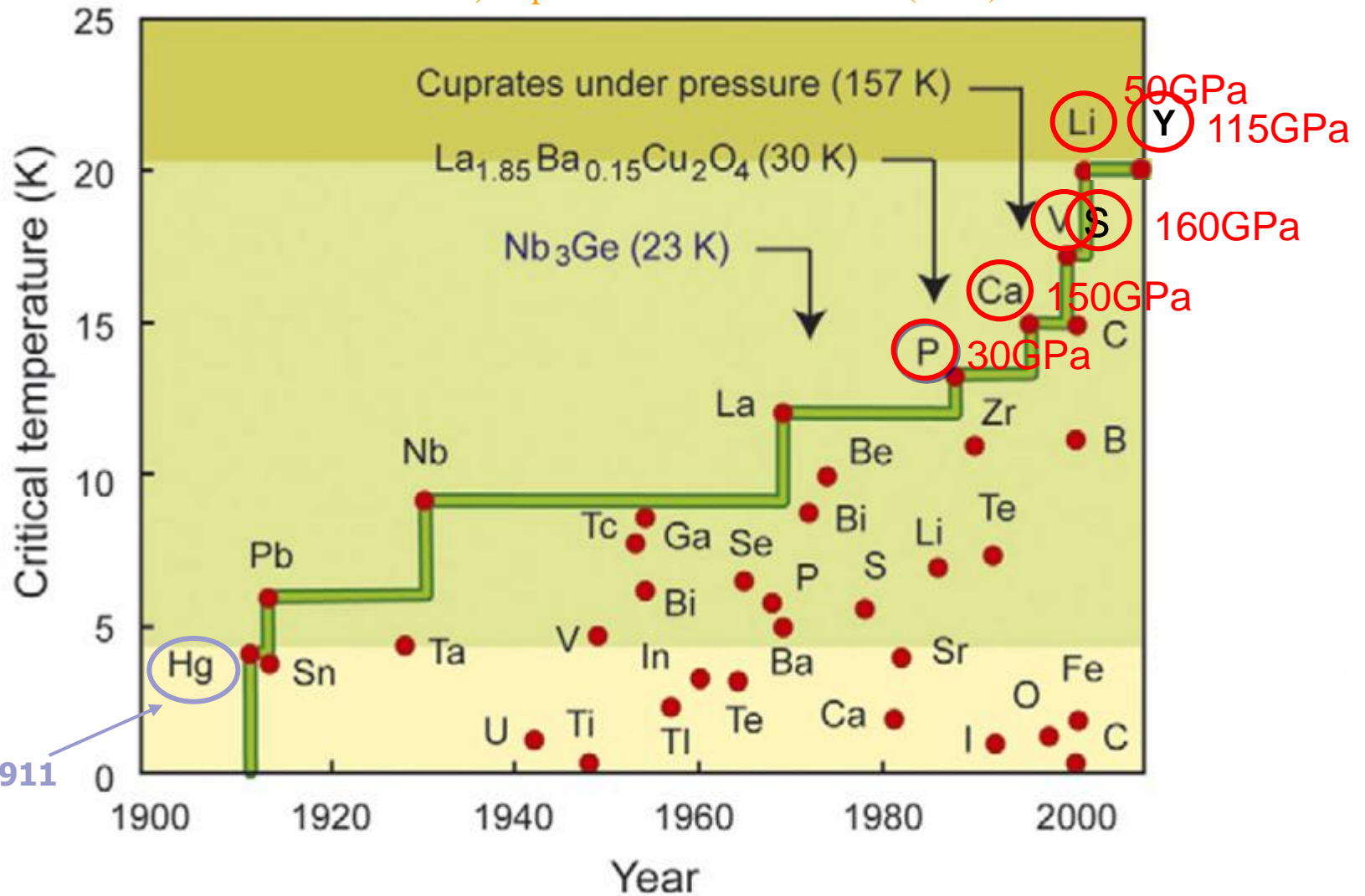
52 elements get Sc

<sup>1</sup>H

																<sup>2</sup> He													
<sup>3</sup> Li		<sup>4</sup> Be												<sup>5</sup> B	<sup>6</sup> C	<sup>7</sup> N	<sup>8</sup> O	<sup>9</sup> F	<sup>10</sup> Ne										
<sup>11</sup> Na		<sup>12</sup> Mg												<sup>13</sup> Al	<sup>14</sup> Si	<sup>15</sup> P	<sup>16</sup> S	<sup>17</sup> Cl	<sup>18</sup> Ar										
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<sup>55</sup> Cs	<sup>56</sup> Ba	<sup>57</sup> La	<sup>72</sup> Hf	<sup>73</sup> Ta	<sup>74</sup> W	<sup>75</sup> Re	<sup>76</sup> Os	<sup>77</sup> Ir	<sup>78</sup> Pt	<sup>79</sup> Au	<sup>80</sup> Hg	<sup>81</sup> Tl	<sup>82</sup> Pb	<sup>83</sup> Bi	<sup>84</sup> Po	<sup>85</sup> At	<sup>86</sup> Rn												
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																<sup>90</sup> Th	<sup>91</sup> Pa	<sup>92</sup> U	<sup>93</sup> Np	<sup>94</sup> Pu	<sup>95</sup> Am	<sup>96</sup> Cm	<sup>97</sup> Bk	<sup>98</sup> Cf	<sup>99</sup> Es	<sup>100</sup> Fm	<sup>101</sup> Md	<sup>102</sup> No	<sup>103</sup> Lr

# The history in elements...

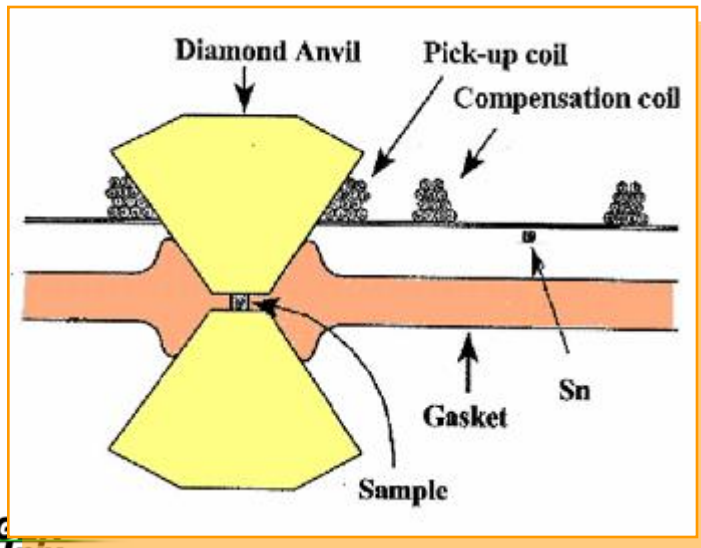
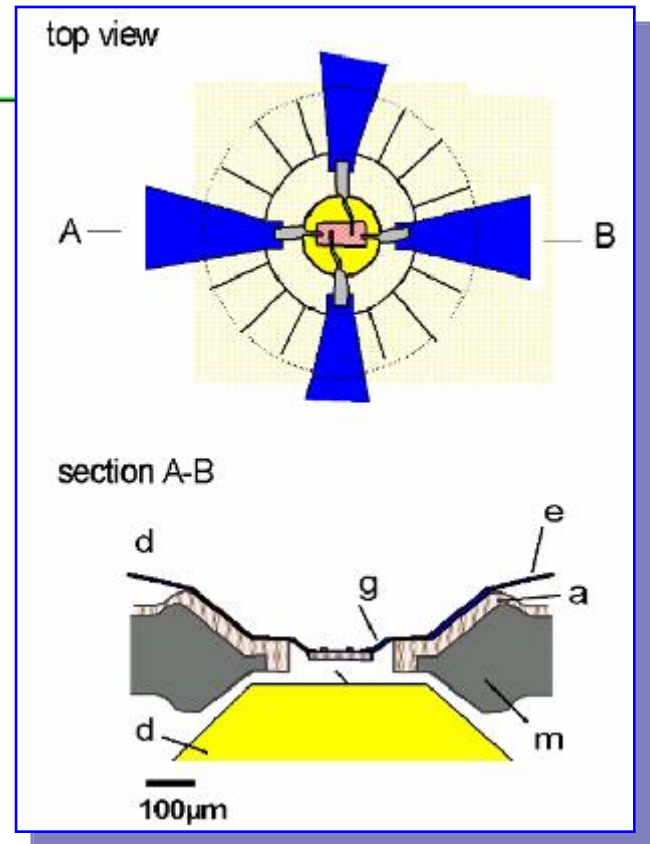
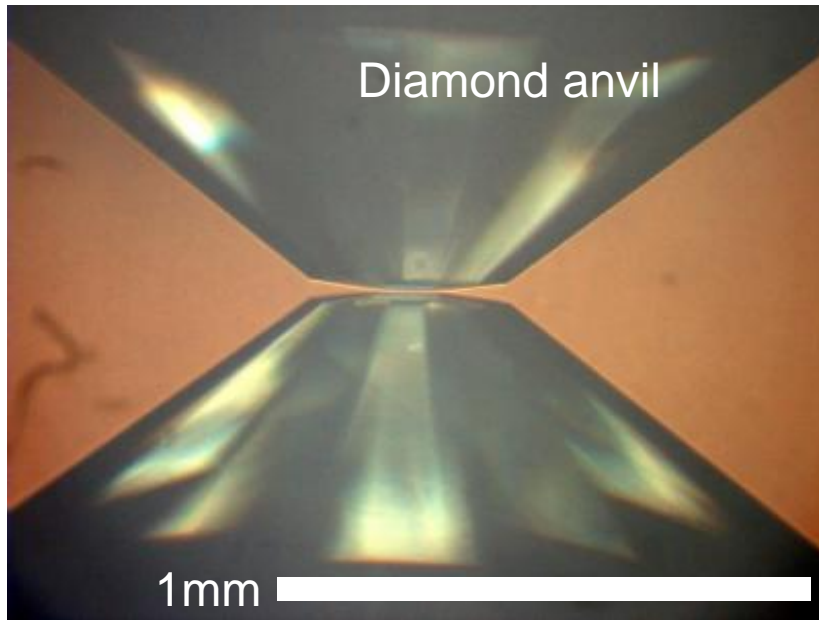
C. Buzea & K. Robbie, *Supercond. Sci. Technol.* **18** (2005) R1–R8



K. J. Dunn and F. P. Bundy: *Phys. Rev. B* **25** (1982) 194.

S. Okada *et al.*, *J. Phys. Soc. Jpn.* **65** (1996) 1924.

# Experimental tools





# Halogen, Chalcogen, Nitrogen,..., Hydrogen,...

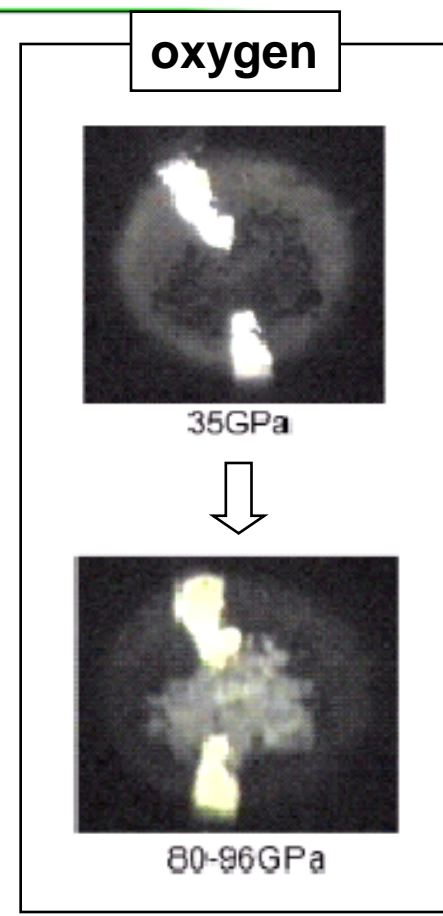
VOLUME 78, NUMBER 1      PHYSICAL REVIEW LETTERS      1 JANUARY 1997

**High Temperature Superconductivity in Metallic Hydrogen: Electron-Electron Enhancements**

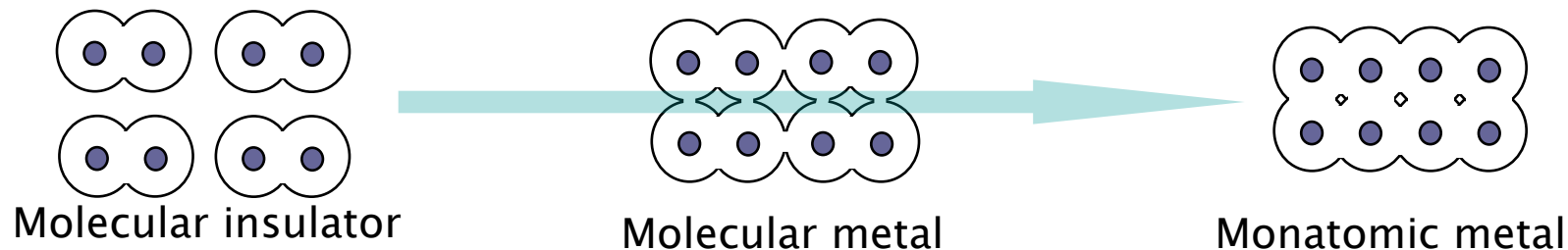
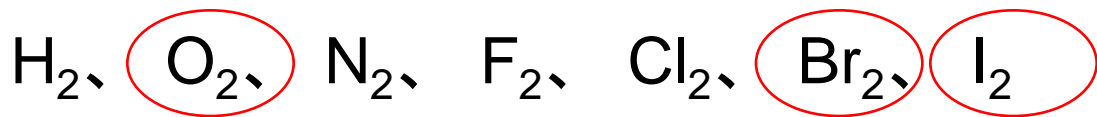
C. F. Richardson<sup>1</sup> and N. W. Ashcroft<sup>1,2</sup>

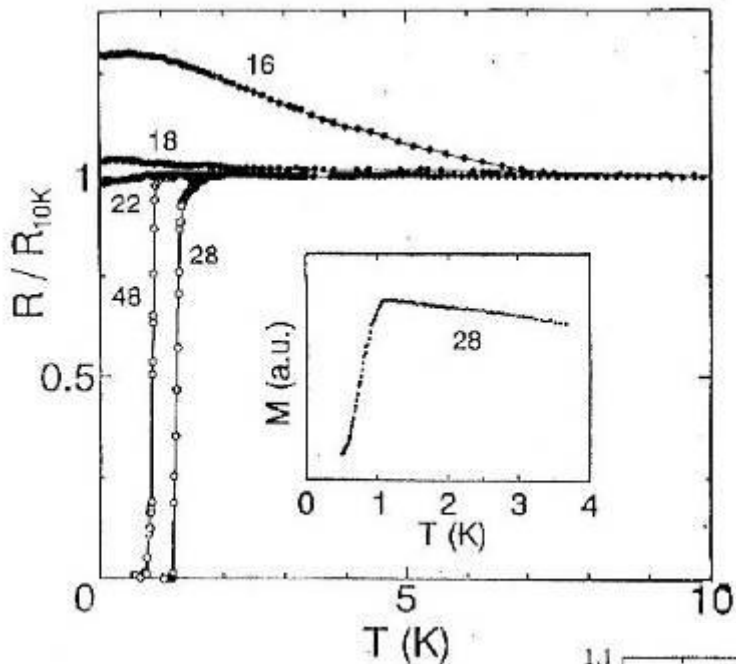
<sup>1</sup>Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853-2501  
<sup>2</sup>New Zealand Institute for Industrial Research, Lower Hutt, New Zealand  
(Received 28 August 1996)

We investigate the possibility of superconductivity in a dense phase of hydrogen which becomes metallic while retaining diatomic character. Correlated fluctuations between electrons and holes in the ensuing band-overlap state can lead to significant enhancements in the transition temperature (compared with monatomic phases) principally through a reduction in the associated Coulomb pseudopotential. The effective electron-electron interaction is determined by a method which treats electrons and phonons on an equivalent footing, an approach which confirms that monatomic phases also remain candidates for high temperature superconductivity. [S0031-9007(96)01982-5]

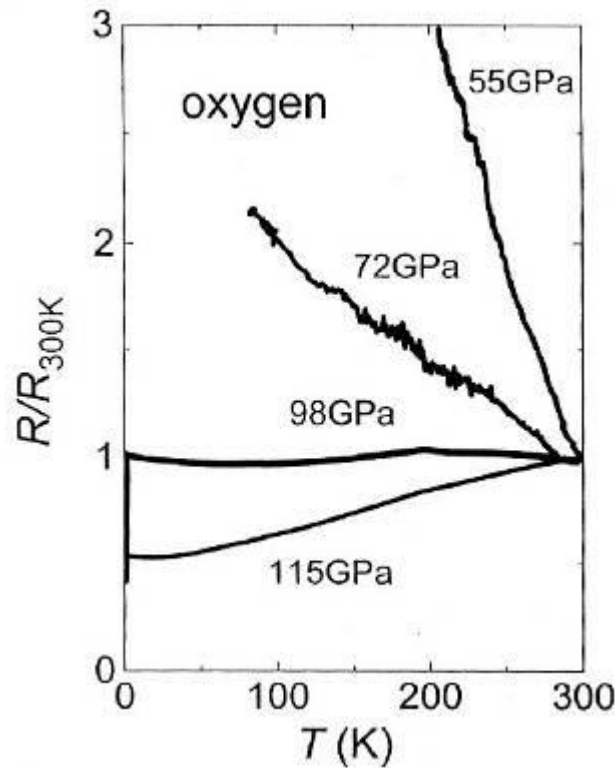


X<sub>2</sub> molecule

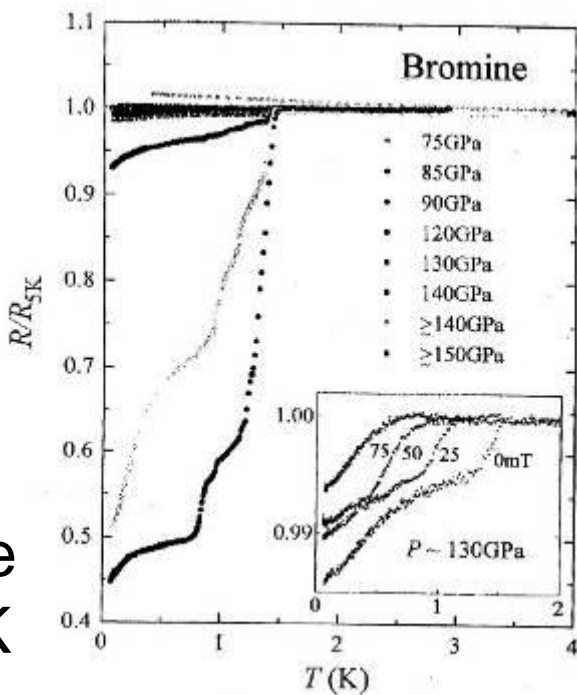




Iodine  
Tc~1.5K

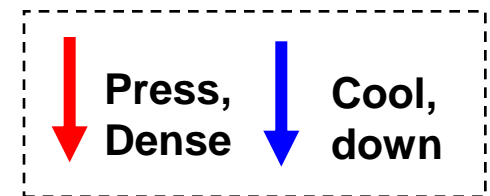
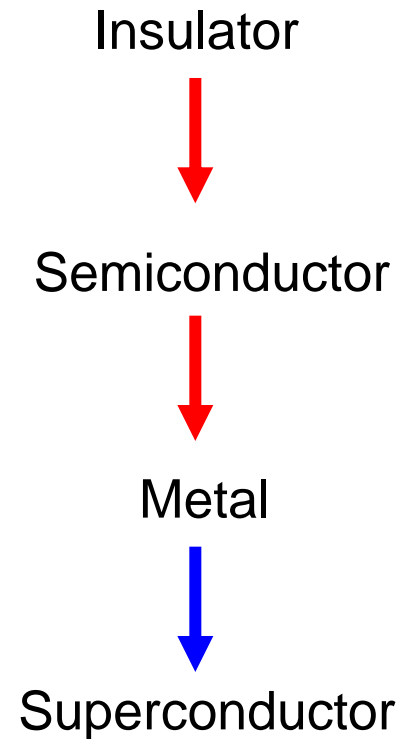
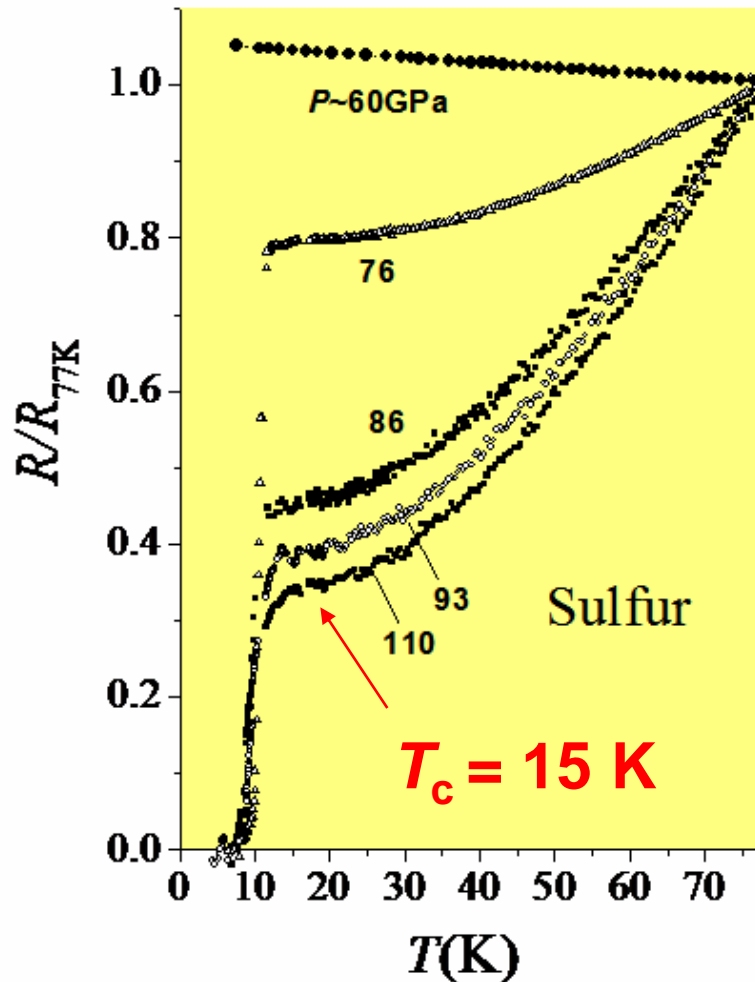


Oxygen  
Tc~0.5K



Bromine  
Tc~1.5K

# Superconductor from insulator



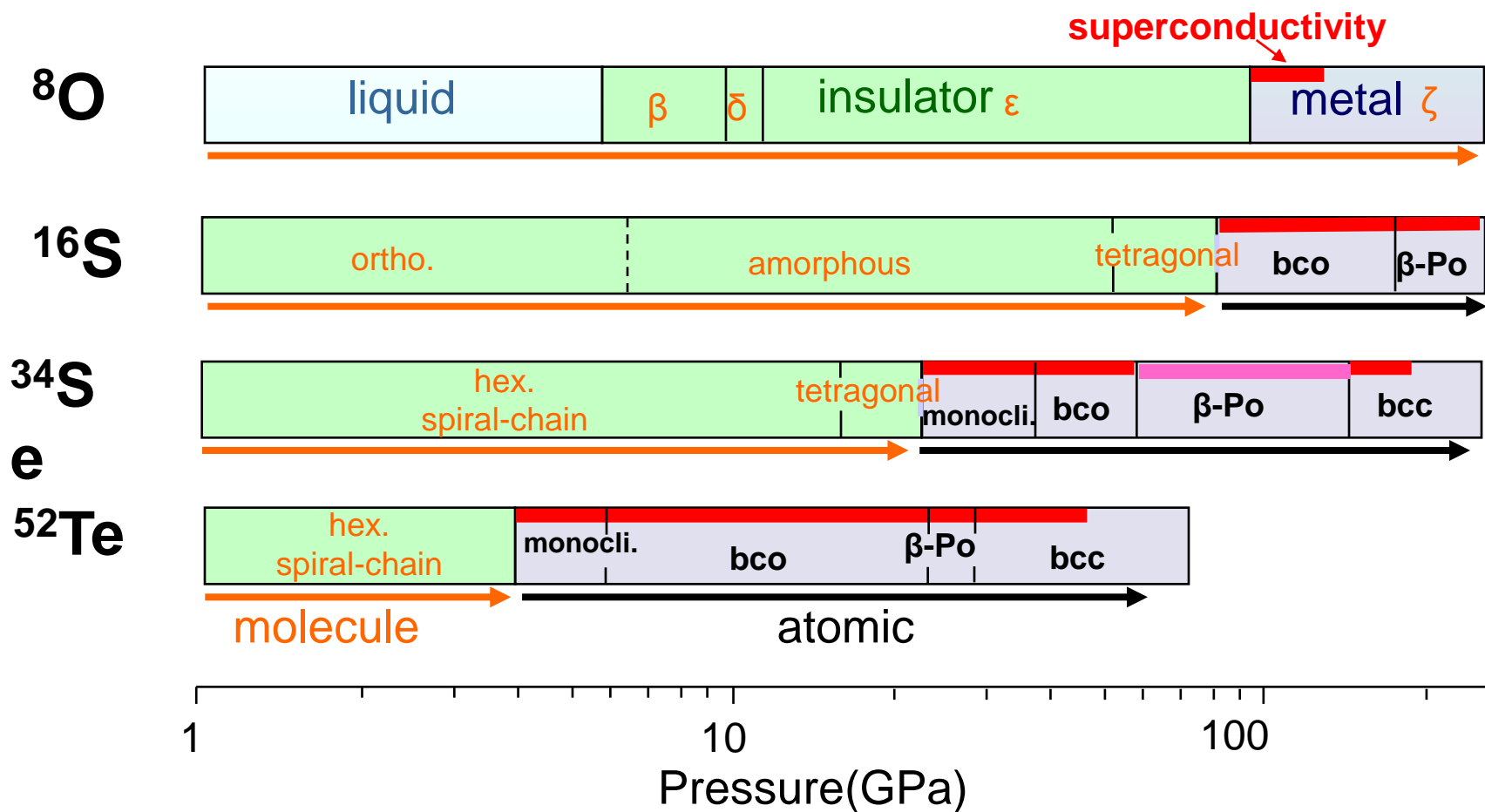
S. Kometani *et al.*, *J. Phys. Soc. Jpn.*, 66 (1997) 2564.



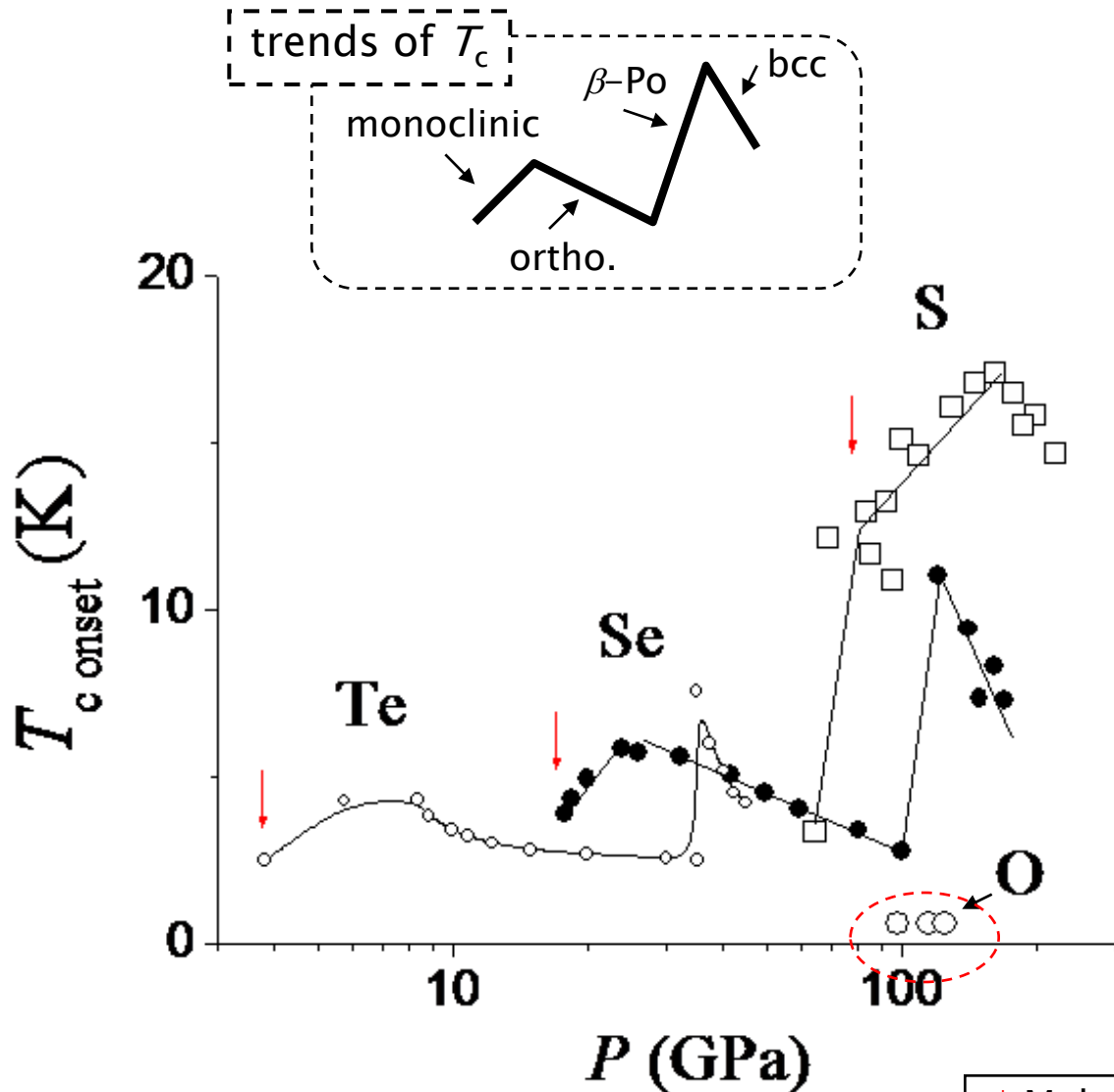
$^{16}\text{S}$  17 K at 200 GPa

$^{34}\text{Se}$  8 K at 150 GPa

$^{56}\text{Te}$  7.4 K at 35 GPa



Lighter elements; higher  $T_c$  at higher  $P$



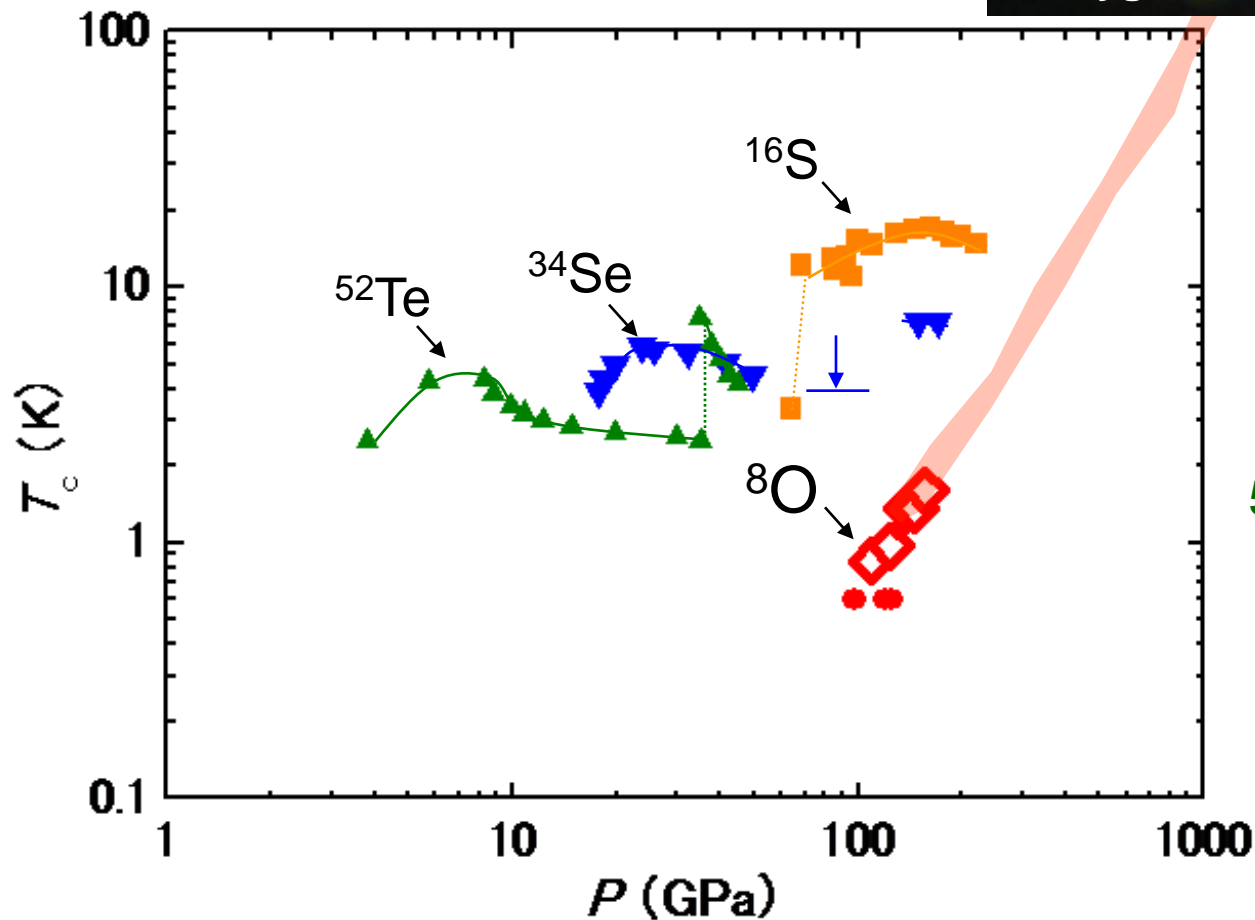
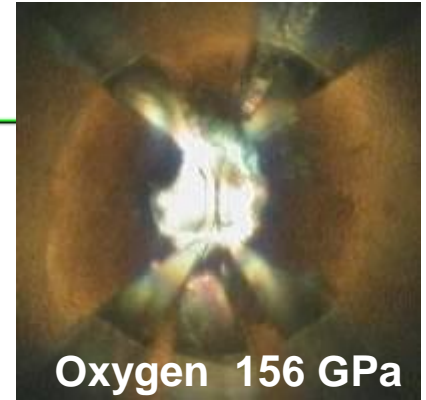
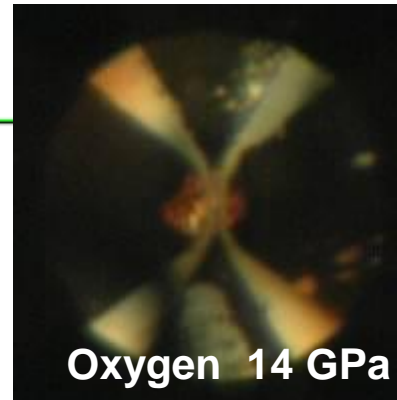
VIIb

<sup>7</sup> N	<sup>8</sup> O	<sup>9</sup> F
<sup>15</sup> P	<sup>16</sup> S	<sup>17</sup> Cl
<sup>33</sup> As	<sup>34</sup> Se	<sup>35</sup> Br
<sup>51</sup> Sb	<sup>52</sup> Te	<sup>53</sup> I
<sup>83</sup> Bi	<sup>84</sup> Po	<sup>85</sup> At

Oxygen may need much higher pressure

↓ Molecular dissociation, (=metallization)

# New data for metallic oxygen



$^{8}\text{O}$  1.6 K at 156 GPa

$^{16}\text{S}$  17 K at 200 GPa

$^{34}\text{Se}$  8 K at 150 GPa

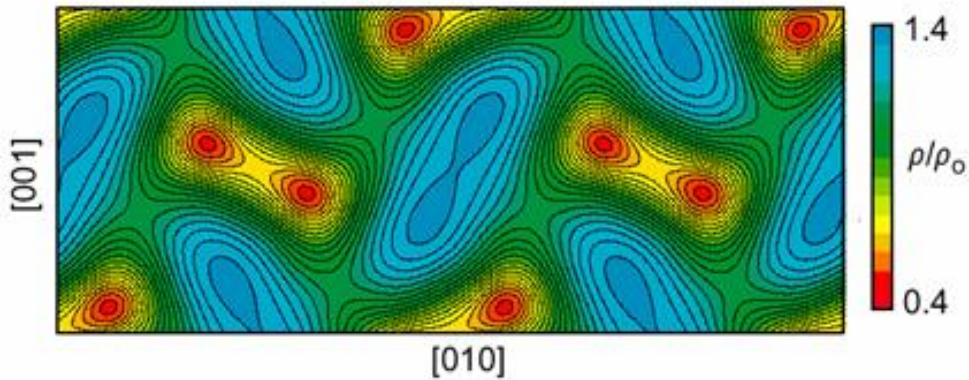
$^{56}\text{Te}$  7.4 K at 35 GPa



Mizobata

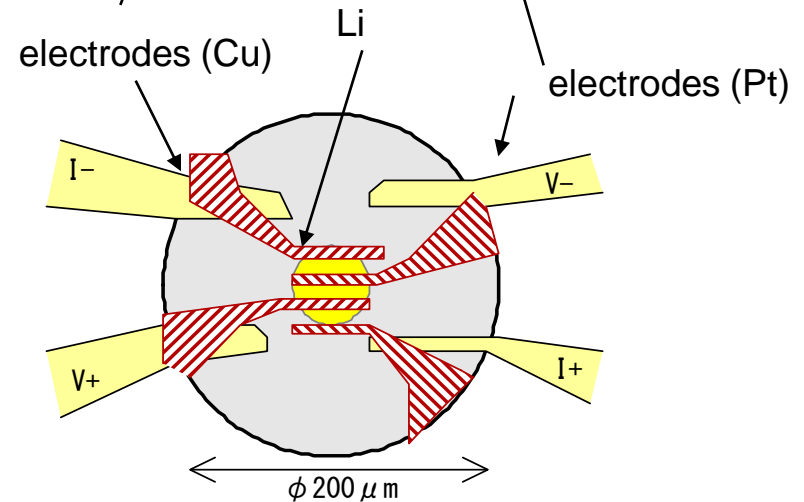
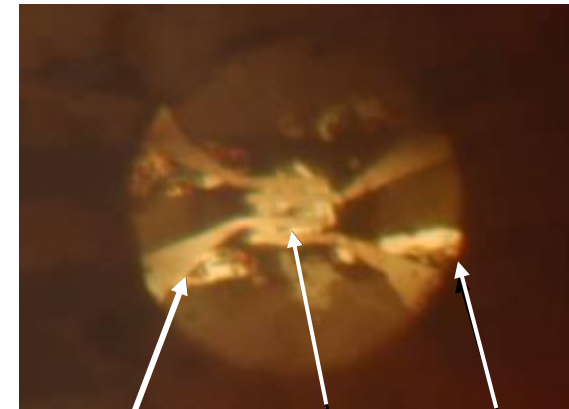


# Li: metal-hydrogen-like metal?



**LDA 2s charge density in Cmca structure**

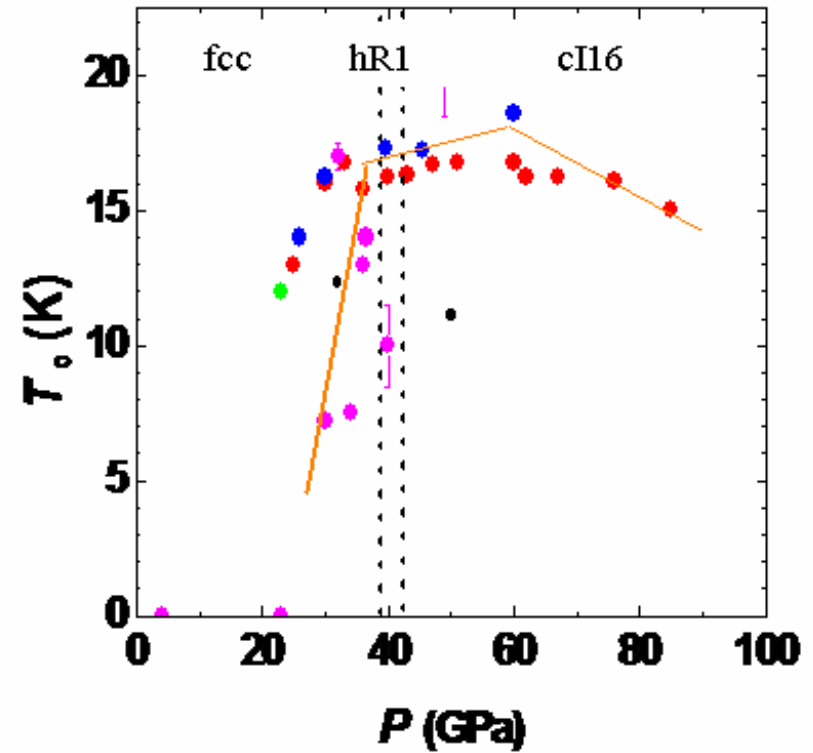
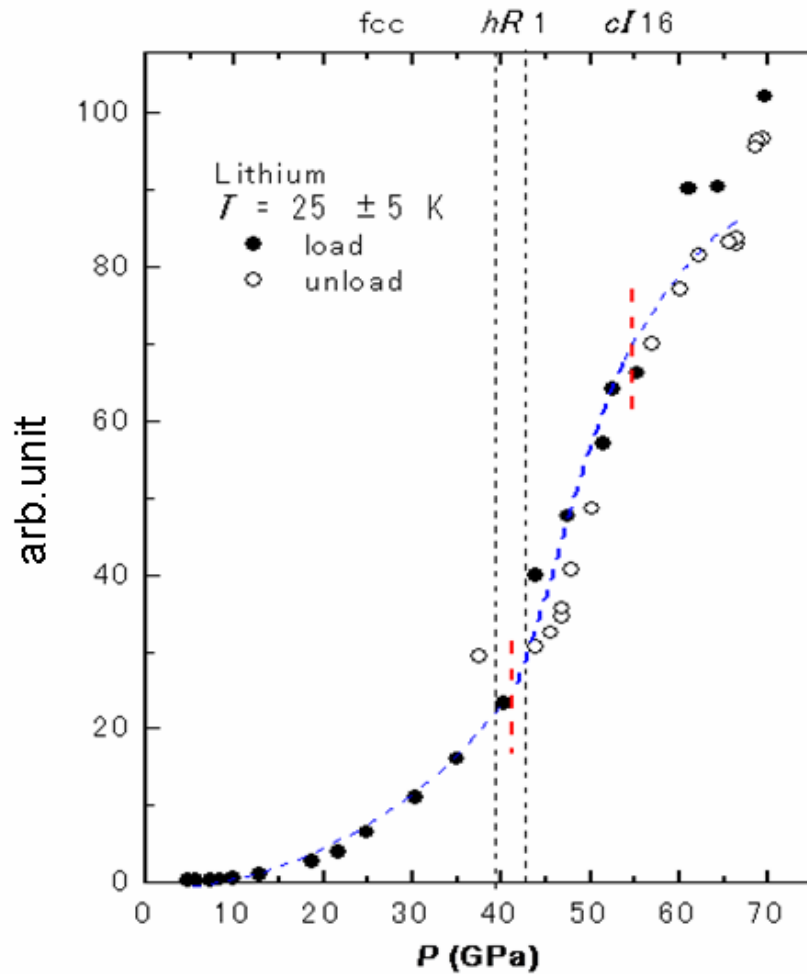
J.B.Neaton and Ashcroft, Nature 400, 141 (1999)



High chemical activity

Fine deposited electrodes enables true 4-probe method.

# Lower symmetry, lower conductivity

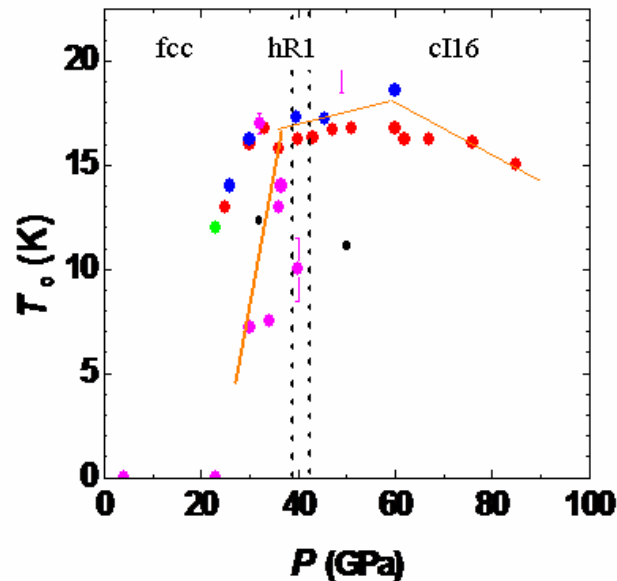


K. Shimizu *et al.*, Nature 419 (2002) 597.

The significant increase of  $\rho$ .

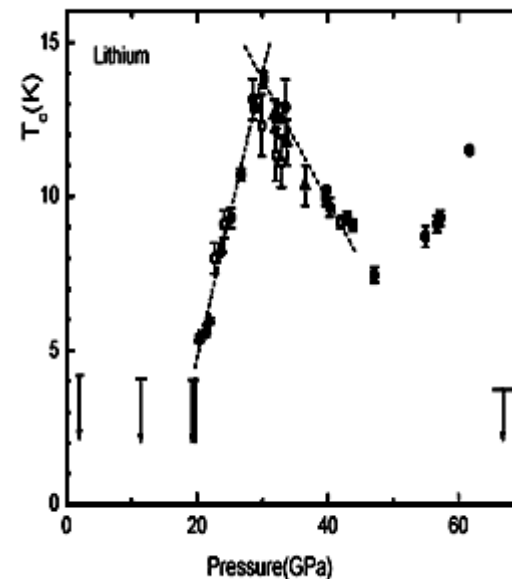
# Lithium: $T_c$ - $P$

Resistance measurement  
non-hydrostatic (no pressure medium)



K. Shimizu *et al.*, Nature 419 (2002) 597.

Magnetization measurement  
hydrostatic (Helium pressure medium)



S. Deemyad and J. S. Schilling

Hydrostaticity, **Structural effect**, Further transition at high pressure



# x-ray diffraction + resistance measurement @ SP8

SPring-8 BL10XU



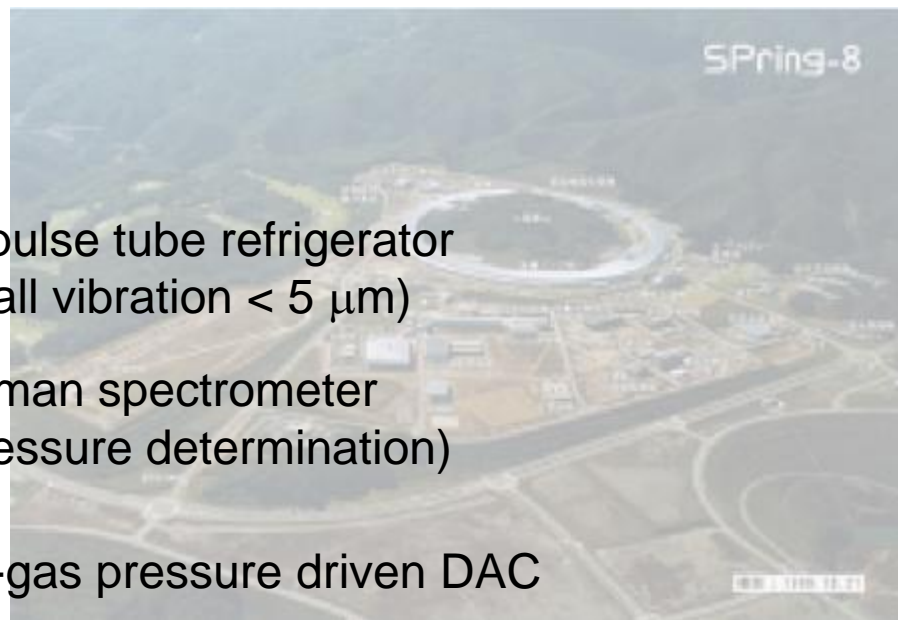
x-ray

15 $\mu\text{m}\phi$

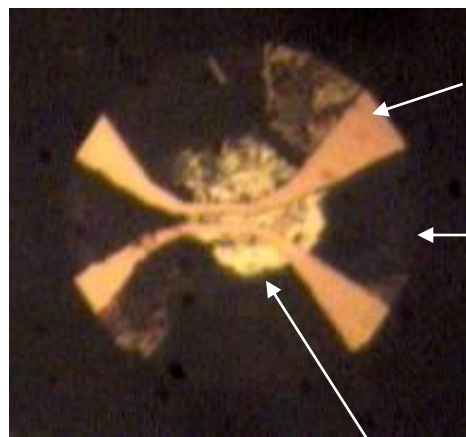
4K-pulse tube refrigerator  
(small vibration < 5  $\mu\text{m}$ )

Raman spectrometer  
(pressure determination)

He-gas pressure driven DAC



Matsuoka

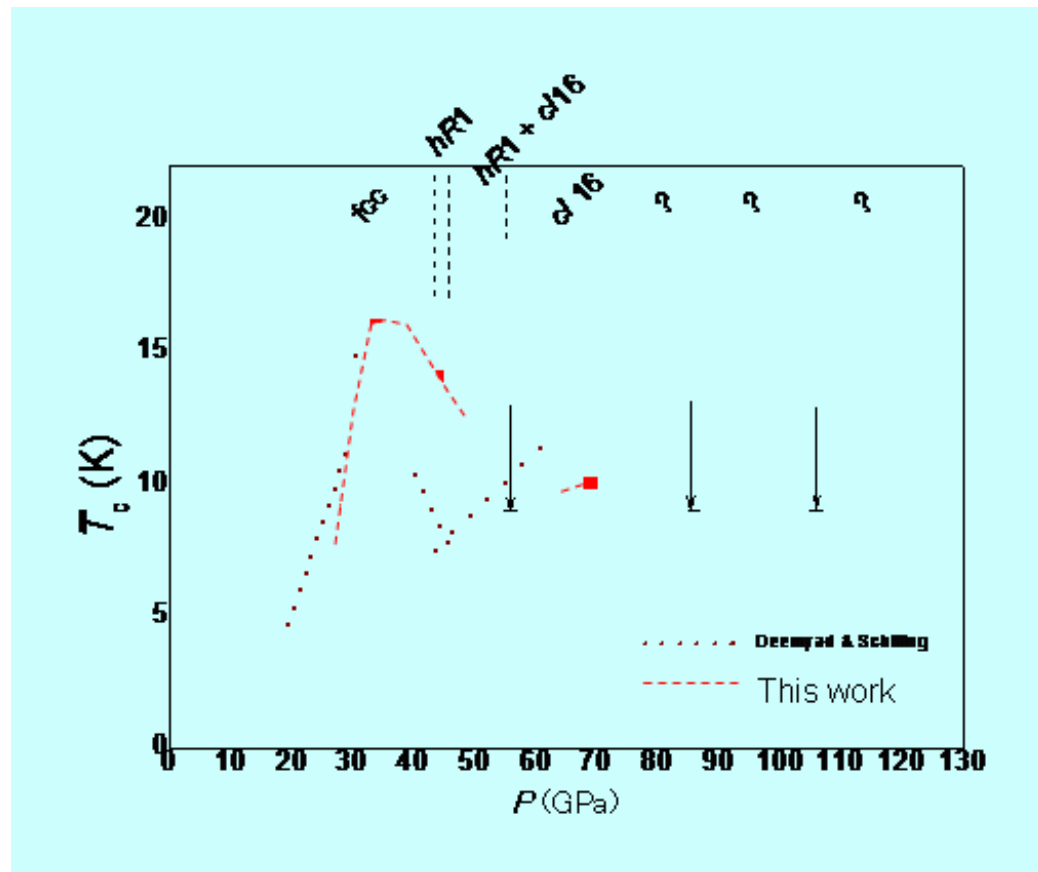
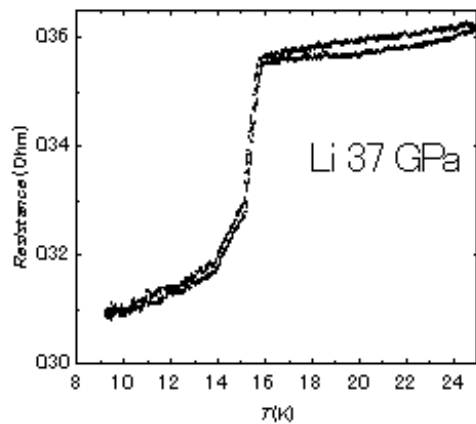
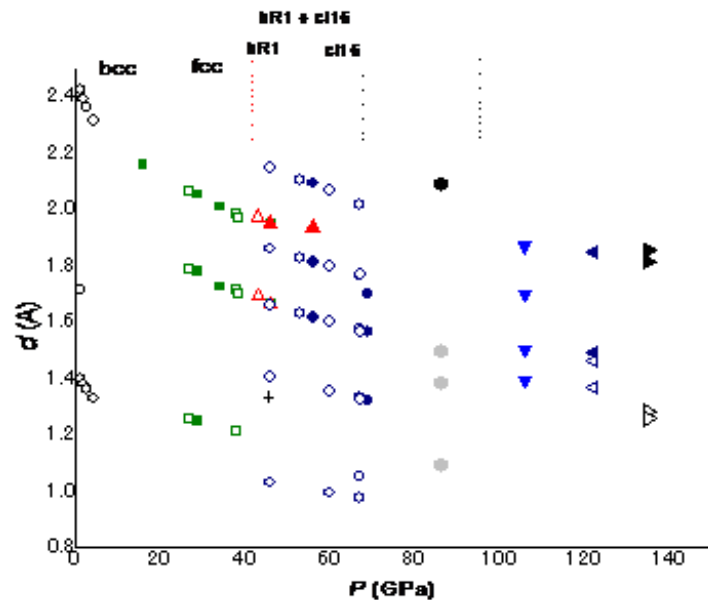


Deposited electrodes  
(Cu)

Beveled anvil  
( $\phi 100 - 300\mu\text{m}$ )

Sample (Li)  $\phi 30\mu\text{m} \times 20\mu\text{m}^t$

# $T_c$ vs. Pressure and structural sequences

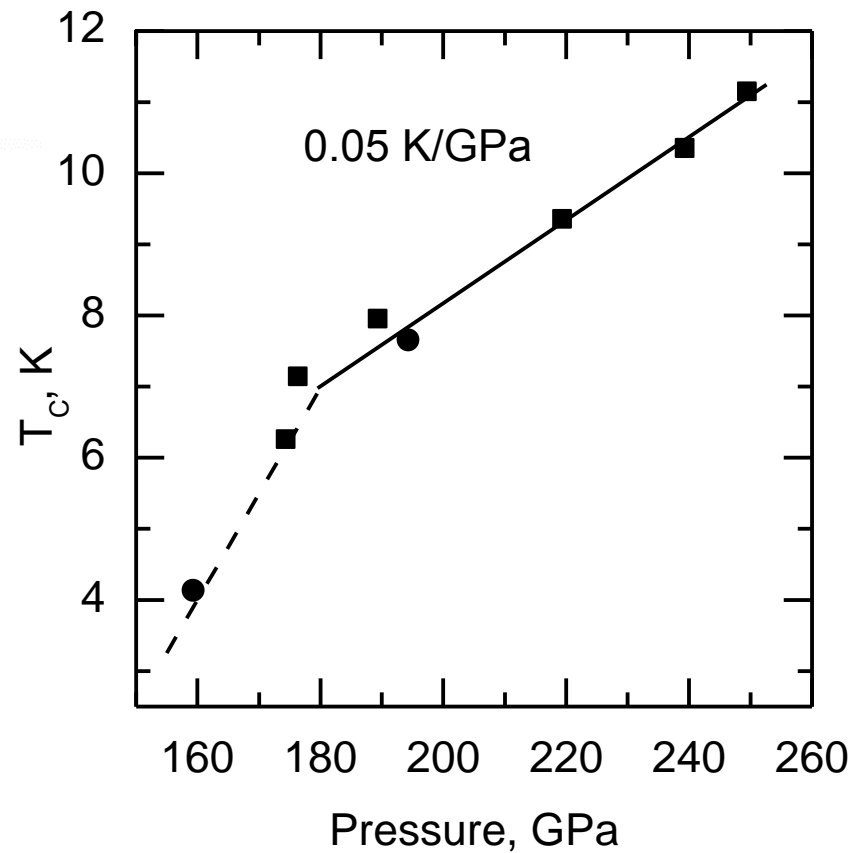
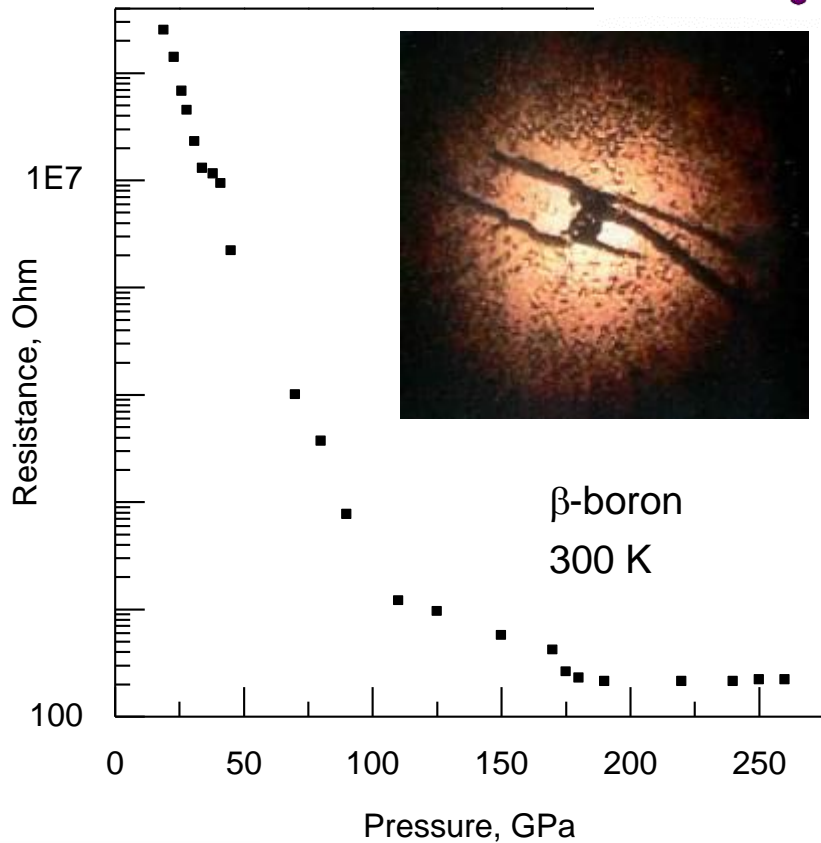
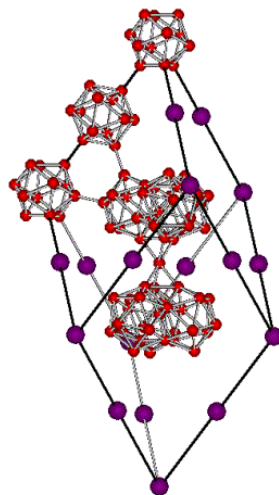


structure

$T_c$

structure	fcc	<i>hR1</i>	<i>cI16</i>	?	?	?
$T_c$	↗	↘	↗	? < 9K	? < 9K	? < 9K

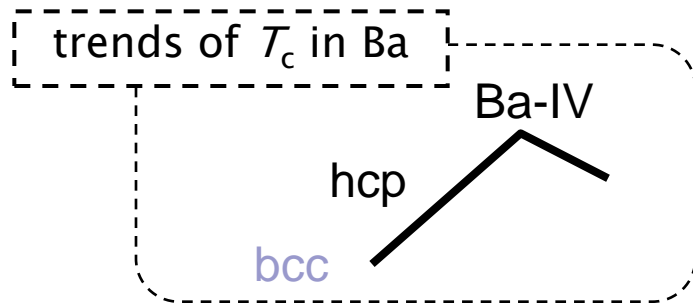
# Boron, $\beta$ -boron



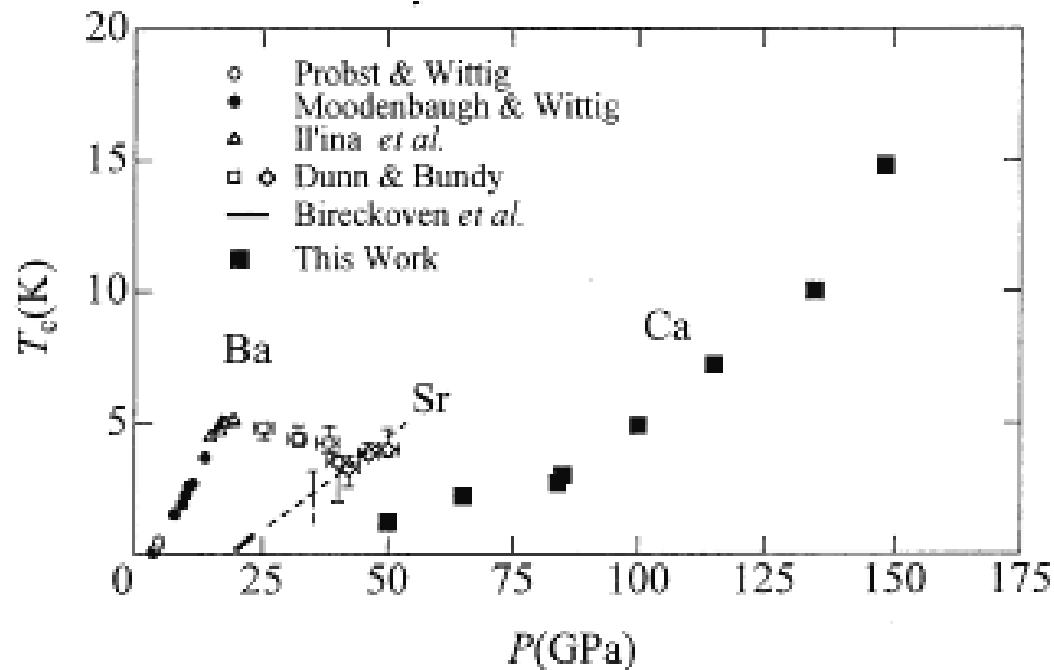
M. I. Erements *et al.* Science **293** (2001) 272.



# Superconductivity in heavy alkaline (IIa) metals

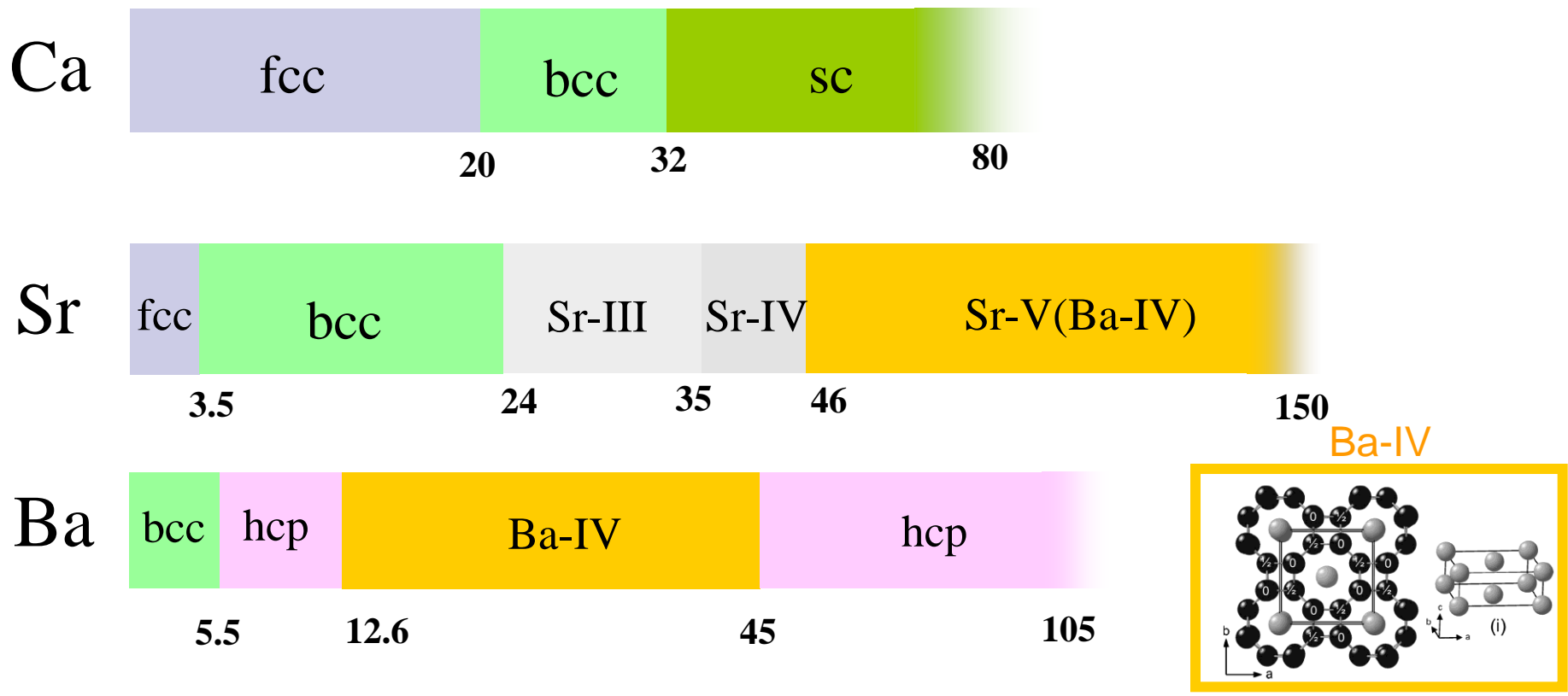
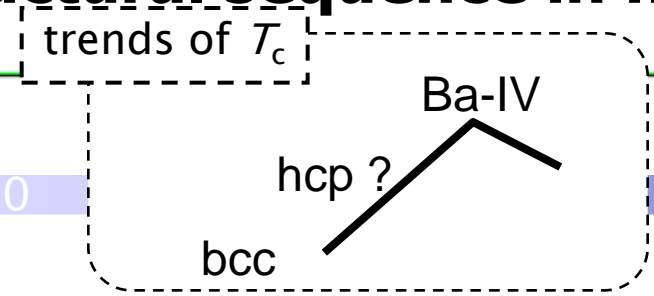


$^{12}\text{Mg}$
$^{20}\text{Ca}$
$^{38}\text{Sr}$
$^{56}\text{Ba}$



S. Okada *et al.*, J. Phys. Soc. Jpn. 65 (1996) 1924.

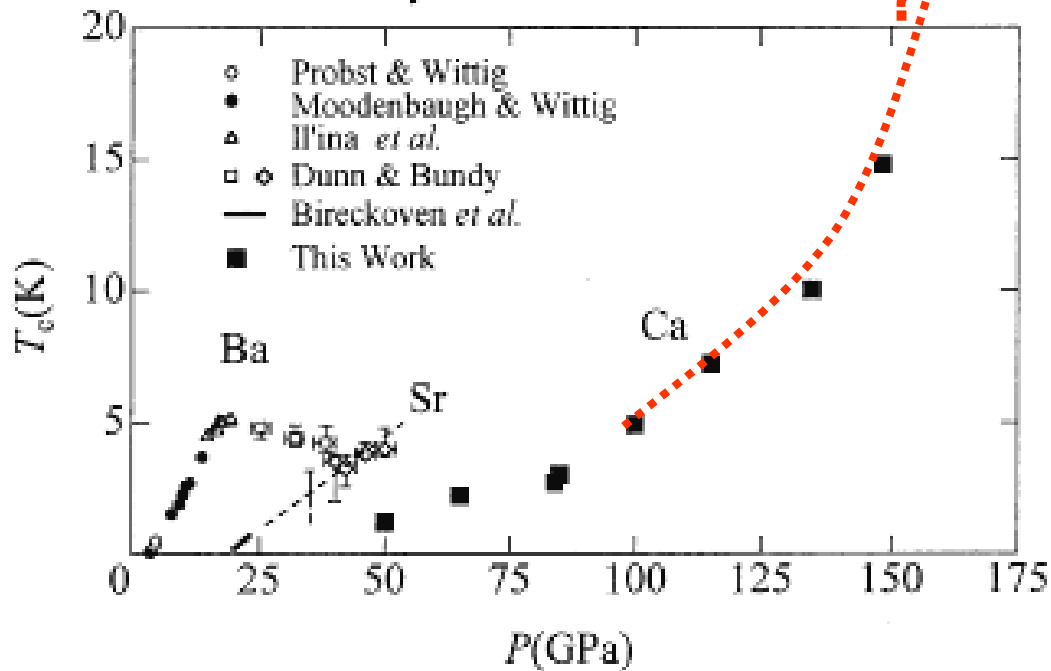
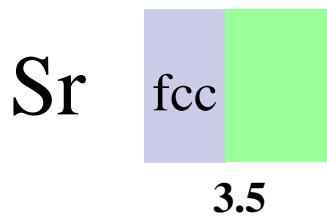
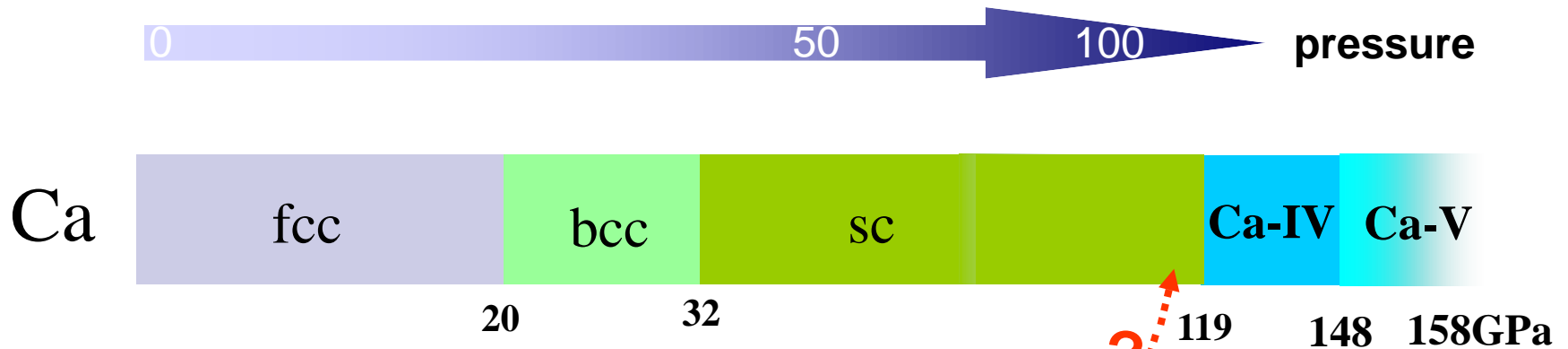
# Structural sequence in heavy alkaline (IIa) metals



- Max.  $T_c$  in Ba-IV type structure
- *s-d* electronic transfer

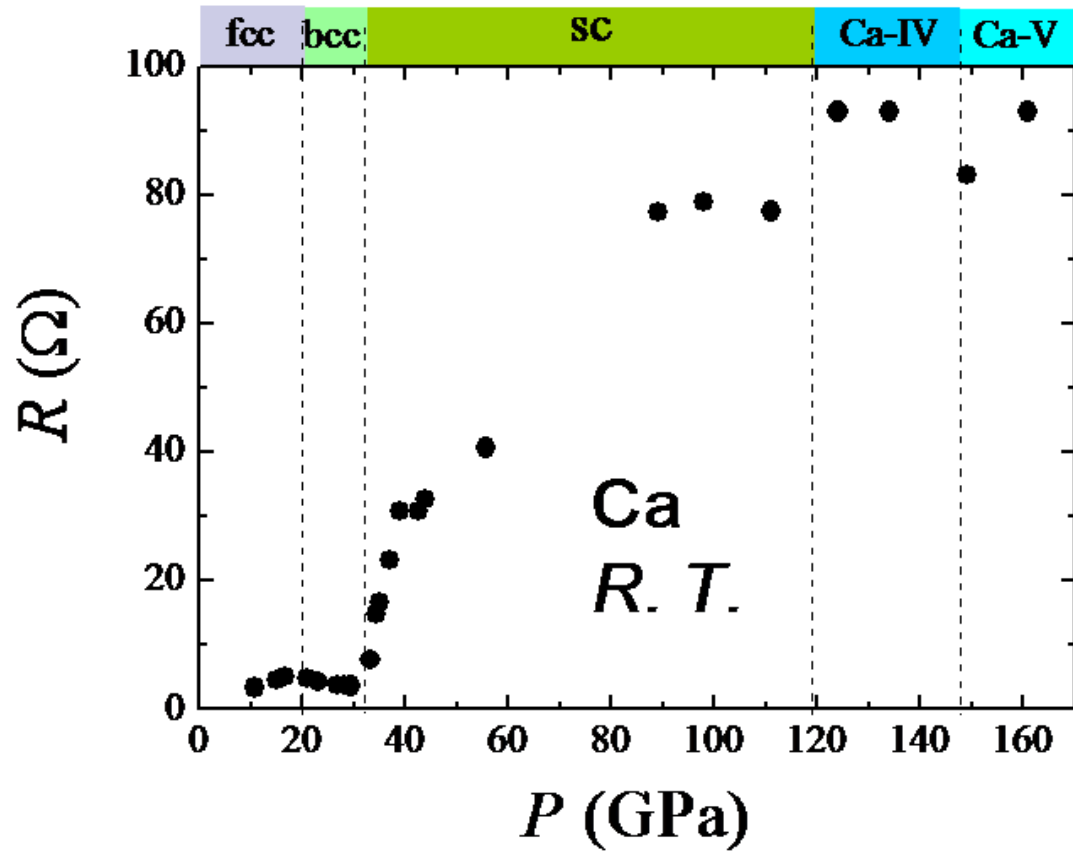
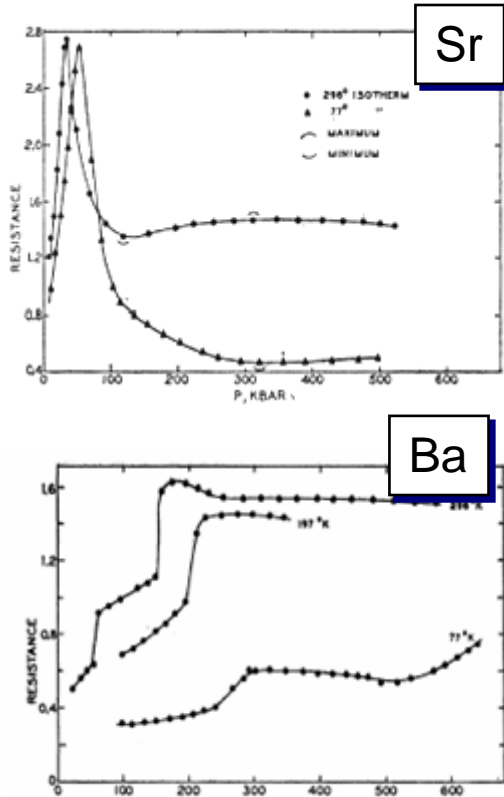
M. Winzenick and W. B. Holzapfel, *High Pressure Science & Technology*, p384-p386 (1995).  
 M. I. McMahon *et al.*, *Phys. Rev. B* **61**, 3135 (2000).

# New structure in calcium at megabar pressure



T. Yabuuchi *et al.*, *J. Phys. Soc. Jpn.* 74 2391 (2005).

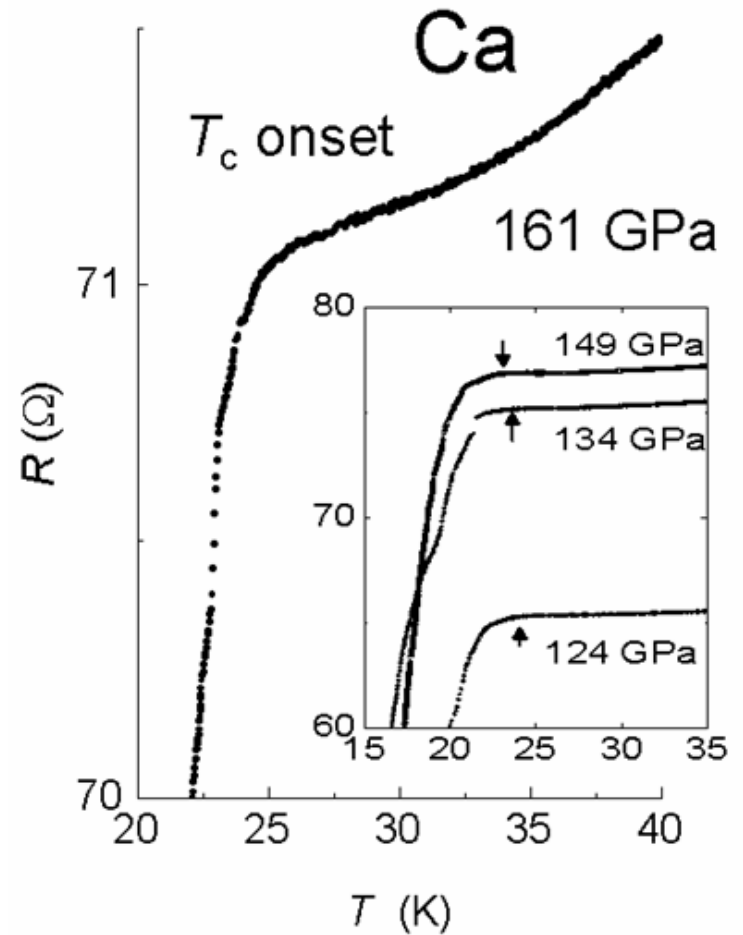
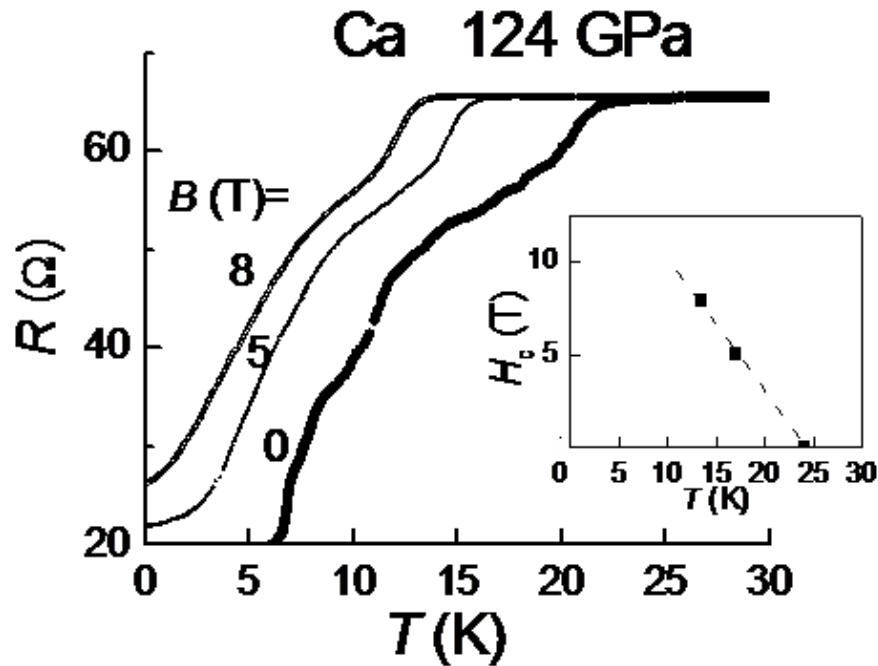
# Resistance at room temperature



R. A. Stager and H. G. Drickamer, Phys. Rev. 131, 2524 (1963).

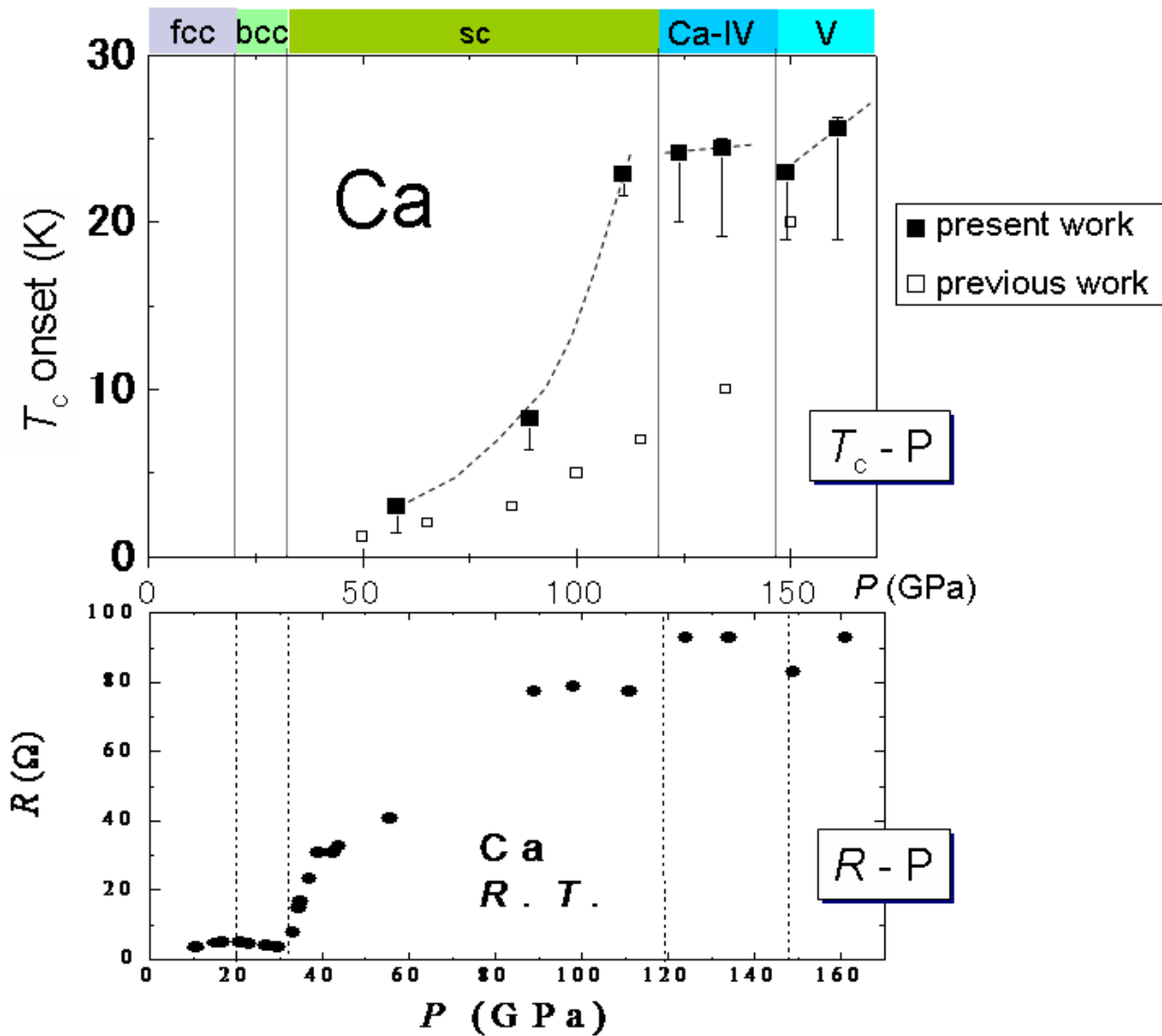


# Superconductivity in Ca



T. Yabuuchi et al., J. Phys. Soc. Jpn. 75 (2006).

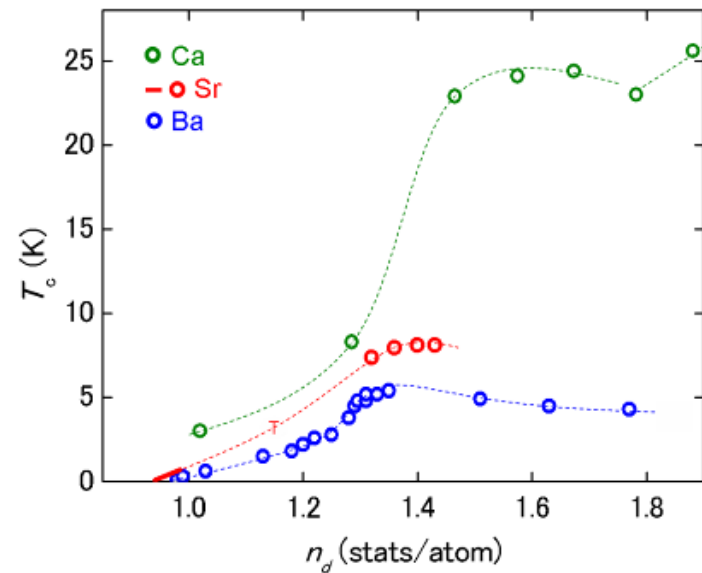
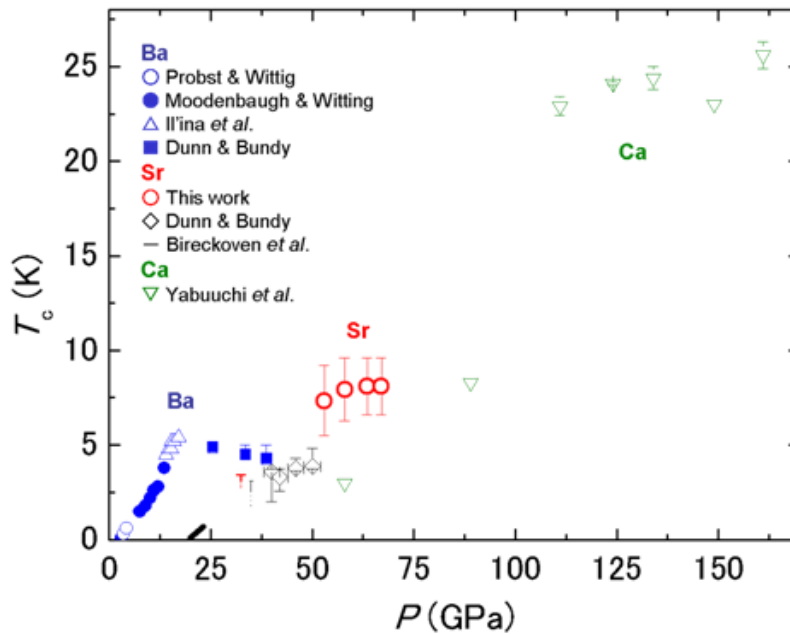
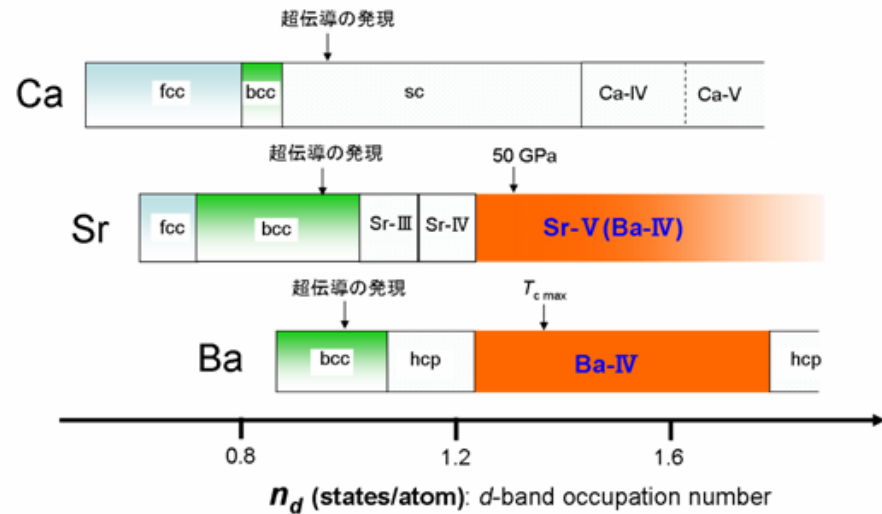
# Pressure dependence of $T_c$



# heavy alkaline

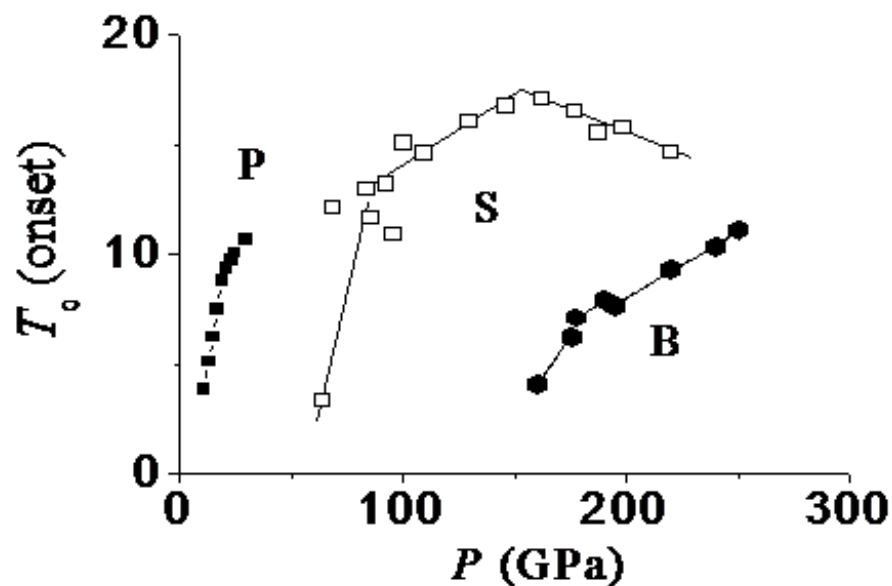


Mizobata

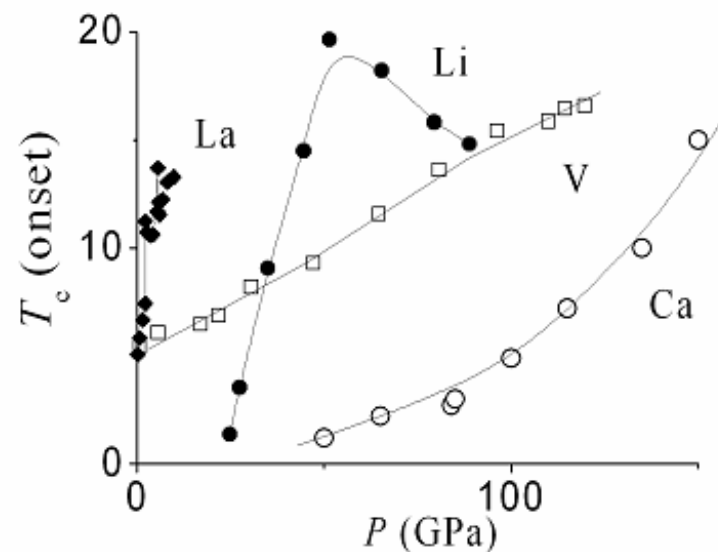


# High $T_c$ elements ( $\equiv T_c > 10$ K) at $P > 100$ GPa

from insulator



from metal



[P] I. Shirovani *et al.*, Phys. Rev. B 50 (1994) 16274.

[S] S. Kometani *et al.*, J. Phys. Soc. Jpn. 66 (1997) 2564.

[B] M. I. Erements *et al.*, Science 293 (2001) 272.

[La] V. G. Tissen, Phys. Rev. B 53 (1996) 8238.

[Li] K. Shimizu *et al.*, Nature 419 (2002) 597.

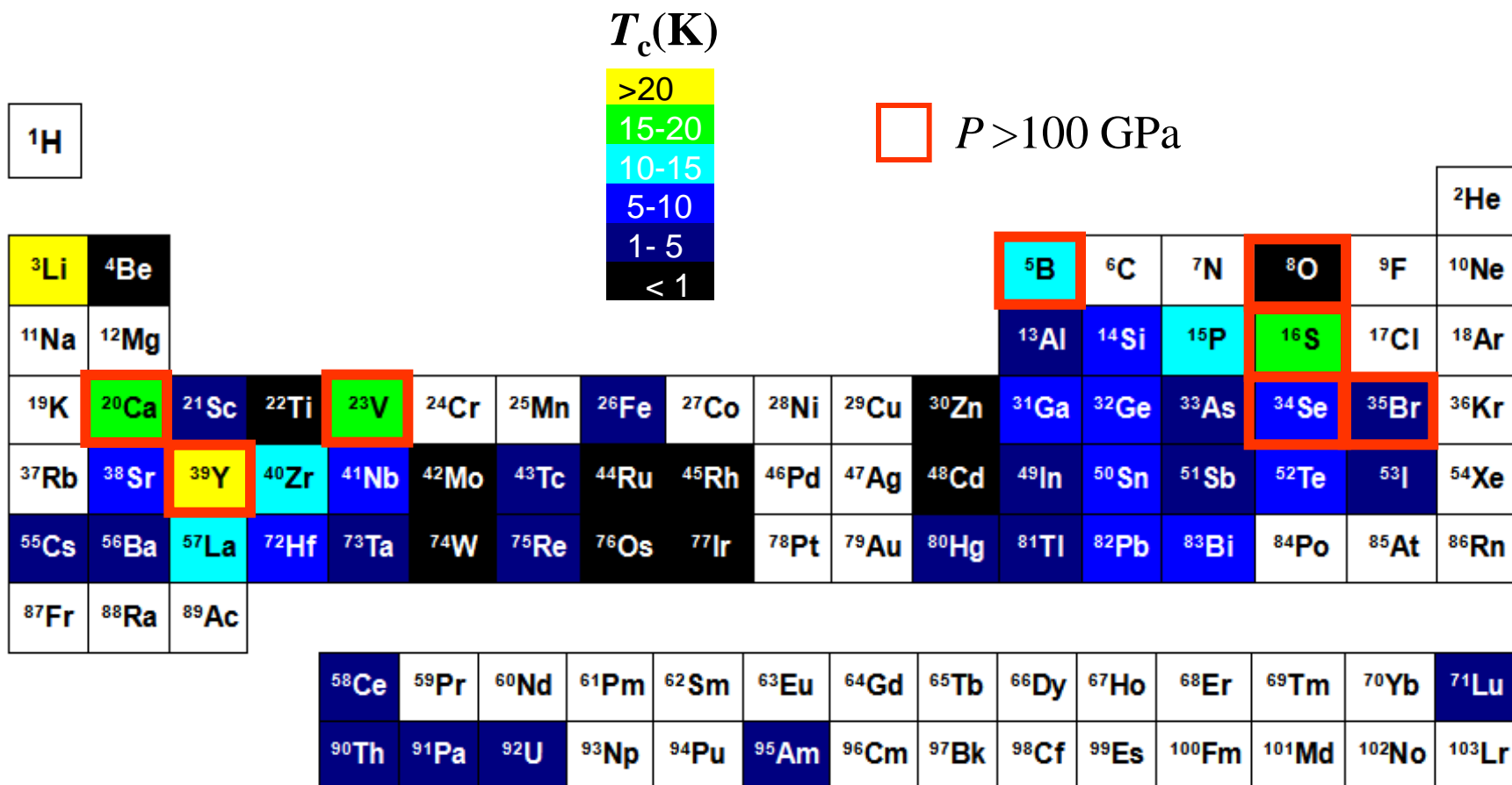
[V] M. Ishizuka *et al.*, Phys. Rev. B 61 (2000) R3823.

[Ca] S. Okada *et al.*, J. Phys. Soc. Jpn. 65 (1996) 1924.

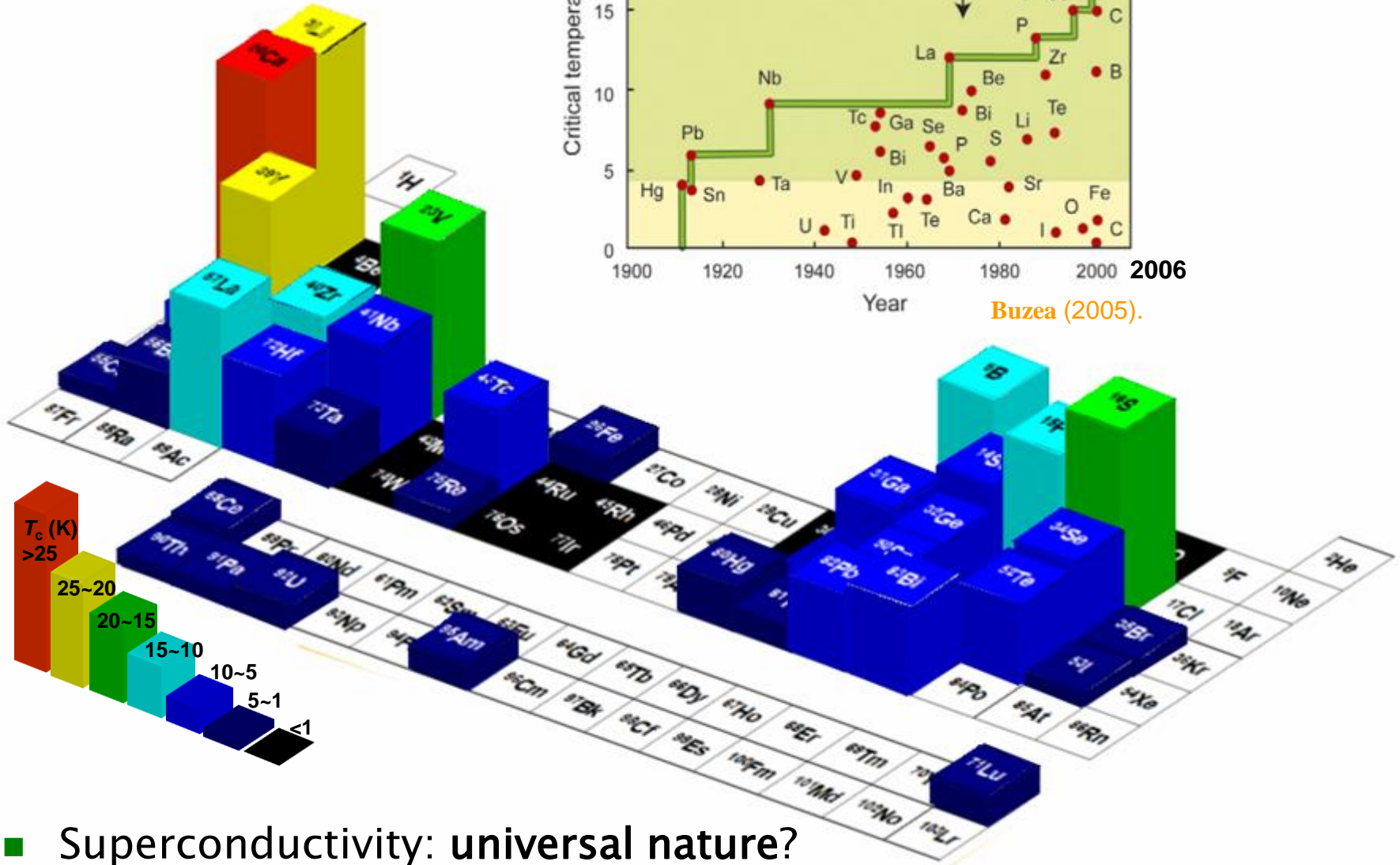
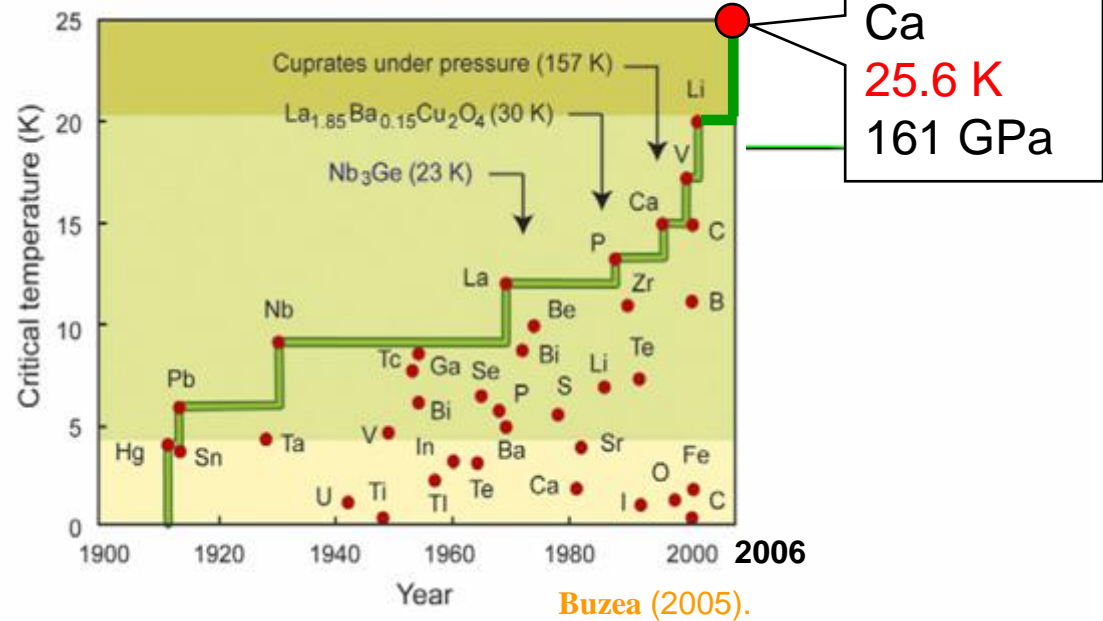




# Observed the highest $T_c$



# Summary



■ Superconductivity: universal nature?

■ Transition metals become good superconductors.

# and future



## ■ Challenging subjects

- Hydrostaticity  $\Leftrightarrow$  uniaxial compression
- Higher P ( $> 300$  GPa)
- *In situ* & precise measurements ( SC , +X-ray , Heat Capacity , + Thermal expansion, ...)

