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SURVEY OF CHALCOGENIDE SUPERCONDUCTORS

S. Nagata[1*] *and T. Atake*[2]

[1]Department of Materials Science and Engineering, Muroran Institute of Technology
27-1 Mizumoto-cho, Muroran, Hokkaido, 050-8585
[2]Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho
Midori-ku, Yokohama, 226-8503 Japan

Abstract

The thread that runs through all research in the field of superconductivity is new physics through discovery of new materials. The knowledge of superconducting materials has become voluminous and complex. The comprehensive review of the superconducting materials is of particular importance. The main purpose of this report is to present the results of classification for chalcogenide superconductors. Superconducting critical temperature T_c, crystal-structure type and the references proper to these compounds are summarized. Brief survey of the superconductivity in chalcogen elements is also given. Furthermore, as representative sulfide and selenide, superconducting characteristics of $CuRh_2S_4$ and $CuRh_2Se_4$ will be shown.

Keywords: bibliography, critical temperature, crystal structure, $CuRh_2S_4$, $CuRh_2Se_4$, survey of chalcogenide superconductors

Introduction

The high-T_c oxide superconductivity appears to have thrown new light on the new superconducting materials. The discovery of high-T_c superconductors has led to unprecedented excitements. Intense research effort arises mainly from their potential for significant technological applications. With a new theoretical development to clarify the mechanism for the high-T_c superconductivity, the challenge is still manifold for the discovery of new superconductors. Much attention has been also paid to new sulfide superconductors and to other chalcogenides. It is our dream to understand and predict numerical value of the superconducting transition temperature T_c. Our primary purpose of this report is to survey and to present the results of classification of chalcogenide superconductors. Superconducting compounds of oxides, sulfides, selenides and tellurides will be listed [1–63]. Information regarding the superconducting chalcogenides has been clearly systematized by our classification. The data of superconducting materials can be reviewed comprehensibly in the light of these classifications.

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[*] Author for correspondence: e-mail: naga-sho@oyna.cc.muroran-it.ac.jp

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On the other hand, the superconductivity in the elements of oxygen, sulfur, selenium and tellurium is discussed [64–74]. A brief description of recent brilliant discoveries of superconductivity in oxygen and sulfur under combined extreme conditions of ultra-high pressure and very low temperature will be given.

In addition, as typical sulfide and selenide superconductors, the results of superconducting properties of $CuRh_2S_4$ and $CuRh_2Se_4$ will be shown with emphasis on thermal properties [39].

Classification of chalcogenide superconductors

The superconducting transition temperature T_c, crystal-structure type and the references proper to these chalcogenides are shown in Tables 1 to 4 [1–63]. The notation of the crystal-structure type is not unified in these tables, because we have regard for the original author's opinion about the notation and definition on the crystal-structure type. Our notation follows the original author's indication. Well-annealed specimens usually show sharper superconducting transition than strained or inhomogeneous specimens. It should be noted that most researchers choose the midpoint as the transition temperature T_c, while the others choose the onset temperature as T_c. The occasional scattered values of T_c quoted in our tables may lie in the variation in sample preparation and the purity of sample itself. This survey attempts to provide the simple and clear classification. It is stressed that this survey has mainly focused on the conventional superconductors, not on the high-T_c oxide superconductors. With only a few exceptions, this survey does not cover (1) organic superconductors, (2) amorphous superconductors, (3) superconductors appeared only under high pressure, (4) intercalation, (5) thin-film preparations.

Since advances in the development of new superconducting materials are largely associated with physics and chemistry, it is hoped that this survey will lead to stimulus and fruitful discussion for further researches. The world general literature previously complied and published for the superconducting materials are given [75–80]. The present paper is an advanced version of our original monograph [79]. The readers should have critical eye and be careful for the conflict in the data values such as T_c in the references. Errors in all the tables are greatly regretted by the authors and hopefully readers will point these out to be corrected.

Superconductivity in O, S, Se and Te

The oxygen, sulfur, selenium and tellurium belong to the same VI-b group in the periodic table. These chalcogen elements become superconducting only under high pressure, as shown in Table 5 [64–74]. Solid oxygen exhibits superconductivity at pressure around 100 GPa with T_c=0.6 K, which is a recent brilliant experimental achievement under combined extreme conditions of ultra-high pressure and very low temperature below 1 K developed by Amaya and co-workers at Osaka University [64–65]. It is noted that solid oxygen shows the antiferromagnetism at low temperature with spin S=1 per one molecule, however, under high pressure the magnetic moment of solid oxygen seems to disappear. Struzhkin *et al.* [67] have shown that sulfur becomes superconducting at 157 GPa with 17 K which is the highest transition temperature T_c of an elemental solid reported so far.

Table 1 Superconductivity of oxides

Compounds	Structure (type)	T_c/K	Ref.
TiO	f.c.c.	0.65–0.94	[1]
NbO	simple cubic	1.61	[1]
$Ca_{0.1}WO_3$	hexagonal	1.4–3.4	[2]
(many Tungsten-oxide bronzes)			
K_xMoO_3	tetragonal	4.2	[3]
K_xReO_3	hexagonal	3.6	[3]
Zr_3V_3O	Fe_3W_3C	7.5	[4]
$Zr_{0.61}Rh_{0.285}O_{0.105}$	Fe_3W_3C	11.8	[4]
$Li_{0.9}Mo_6O_{17}$	hexagonal	1.9	[5]
$Li_{0.45}NbO_2$	layered	5.5	[6]
$Ag_7O_8NO_3$	clathrate	1.04	[7]
(many anions: NO_3, HF_2, ClO_4, F, BF_4)			
$LiTi_2O_4$	spinel	13.7	[8]
$Li_{2.6}Ti_{1.9}O_4$		11.2	[9]
$SrTiO_{3-x}$	perovskite	0.3	[10]
$BaPb_{1-x}Bi_xO_3$	perovskite	13	[11]
$Ba_{1-x}K_xBiO_3$	perovskite	34	[12]
$(La,Ba)_2CuO_4$	K_2NiF_4	35	[13]
$YBa_2Cu_3O_{7-x}$	layered	92	[13]
$Bi_2Sr_2Ca_2Cu_3O_{10+x}$	layered	110	[13]
$Tl_2Ba_2Ca_2Cu_3O_{10}$	layered	125	[13]
$HgBa_2Ca_2Cu_3O_{8+x}$	layered	135	[14]
(many high-T_c cuprates)			
Sr_2RuO_4	K_2NiF_4	1.0	[15]
$KCa_2Nb_3O_{10}$(Li)	intercalation	~1.0	[16]
$Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.8}$	spin ladder	12	[17]
(under high pressure)			

These results of simple molecular and elemental substances may provide crucial test of the origin and mechanisms of superconductivity.

Table 2 Superconductivity of sulfides

Compounds	Structure (type)	T_c/K	Ref.
$ScS_{1.1}$	NaCl	4.5	[18]
CuS	CuS	1.62	[19]
YS	NaCl	1.3–1.9	[20]
$ZrS_{1.1}$	NaCl	2.5–4.5	[21]
LaS	NaCl	0.84	[22]
LuS	NaCl	0.8–1.1	[20]
$(SN)_x$		0.33	[23]
CuS_2	pyrite	1.48–1.53	[24]
CuSSe	pyrite	1.5–2.0	[24]
Nb_3S_4	Nb_3S_4	4.0	[25]
La_3S_4	Th_3P_4	8.25	[22]
$In_{0.69}V_6S_8$	Nb_3S_4	3.7	[26]
$Rh_{17}S_{15}$	$Pd_{17}Se_{15}$	5.8	[27]
$Pd_{2.2}S$	cubic	1.63	[28]
2H-NbS_2	2H-NbS_2	6.1	[29]
2H-TaS_2	2H-NbS_2	0.8	[29]
$TaS_2(C_5H_5N)_{0.5}$	intercalation	3.4	[29]
$SnTaS_2$	intercalation	2.95	[29]
$Cs_{0.3}MoS_2$	intercalation	6.9	[30]
$Li_xTi_{1.1}S_2$	Ti_3S_4	10–13	[31]
$SnNbS_3$	tetragonal	2.85	[32]
$SnTaS_3$	tetragonal	2.96	[32]
$(PbS)_{1.13}TaS_2$	misfit layer	3.08	[33]
$PbNbS_3$	$PbTiS_3$	2.62	[34]
$PbTaS_3$	$PbTiS_3$	3.07	[34]
$Na_2Cu_3S_3$		0.3	[35]
KCu_4S_3	tetragonal	1.4	[35]
Mo_6S_8	Chevrel	1.8	[36]
$PbMo_6S_8$	Chevrel	15	[36]
$LaMo_6S_8$	Chevrel	5.8	[37]
(many Chevrel phases)			

Table 2 Continued

Compounds	Structure (type)	T_c/K	Ref.
$K_2Mo_{15}S_{19}$	$K_2Mo_{15}S_{19}$	3.32	[36]
Ag_2Pd_3S	β-Mn	1.13	[38]
$CuRh_2S_4$	spinel	4.70	[39]
$BaTa_2S_5$	hexagonal	2.88	[40]
$SrTa_2S_5$	hexagonal	2.75	[41]

Table 3 Superconductivity of selenides

Compounds	Structure (type)	T_c/K	Ref.
ScSe		3.7	[42]
YSe	NaCl	2.5	[20]
LaSe	NaCl	1.02	[22]
LuSe	NaCl	0.56	[20]
$AgSnSe_2$	NaCl	4.5–6.9	[43]
$CuSe_2$	pyrite	2.30–2.43	[24]
CuSeTe	pyrite	1.6–2.0	[24]
$RhSe_{1.75}$	pyrite	6.0	[4]
SbPdSe	pyrite	1.0	[44]
BiPdSe	pyrite	1.0	[44]
BiPtSe	pyrite	1.45	[44]
RhSeTe	pyrite	2.9	[44]
$TaSe_3$	monoclinic	2.0	[45]
$NbSnSe_3$	tetragonal	3.09	[32]
Nb_2Se_3	Mo_2S_3	2.1	[46]
Nb_3Se_4	Nb_3Se_4	2.0	[25]
La_3Se_4	Th_3P_4	8.6	[47]
2H-$NbSe_2$	2H-NbS_2	7.3	[29]
2H-$TaSe_2$	2H-NbS_2	0.15	[29]
Pd_4Se	Pd_4Se	0.42	[48]
$Pd_{2.5}Se$		2.3	[28]
$TlMo_3Se_3$	$TlFe_3Te_3$	4.0	[49]
$CuRh_2Se_4$	spinel	3.48	[39]
Mo_6Se_8	Chevrel	6.2	[36]

Table 3 Continued

Compounds	Structure (type)	T_c/K	Ref.
$PbMo_6Se_8$	Chevrel	6.7	[36]
$LaMo_6Se_8$	Chevrel	11.4	[36]
(many Chevrel phases)			
$In_{2.9}Mo_{15}Se_{19}$	$In_3Mo_{15}Se_{19}$	4.24	[36]
$K_2Mo_{15}Se_{19}$	$K_2Mo_{15}Se_{19}$	2.45	[36]
(many other phases: K, Ba, In, Tl)			
$BaNb_2Se_5$	hexagonal	2.5	[50]

Table 4 Superconductivity of tellurides

Compounds	Structure (type)	T_c/K	Ref.
YTe	NaCl	2.05	[20]
PdTe	NiAs	3.85	[48]
InTe	NaCl	3.2–3.45	[51]
LaTe	NaCl	1.48	[47]
IrTe	NiAs	3.0	[48]
PtTe	orthorhombic	0.59	[48]
TlTe	tetragonal	0.19	[52]
$CuTe_2$	pyrite	1.3	[24]
$NbTe_2$	$NbTe_2$	0.50	[53]
$MoTe_2$	$MoTe_2$	~0.3	[46]
$RhTe_2(\alpha)$	pyrite	1.51	[4]
$PdTe_2$	CdI_2	1.69	[48]
PdSbTe	pyrite	1.2	[44]
BiPdTe	pyrite	1.20	[44]
BiPtTe	pyrite	1.15	[44]
$BiTlTe_2$		0.14	[54]
$ZrTe_3$	monoclinic	~3.0	[55]
$AgTe_3$	cubic	2.6	[56]
$IrTe_3$	defect pyrite	1.18	[48]
Pd_3Te		0.76	[48]
Bi_3Te		0.75–1.0	[57]

Table 4 Continued

Compounds	Structure (type)	T_c/K	Ref.
Rh_3Te_2	Rh_3Te_2	0.49	[46]
Ge_xTe_{1-x}	NaCl	0.07–0.42	[58]
Sn_xTe_{1-x}	NaCl	0.02–0.22	[58]
$Pb_{1+x}Te$		5.19	[59]
Ge_3Te_4	rhombohedral	1.55–1.80	[60]
Nb_3Te_4	Nb_3Se_4	1.8	[25]
In_3Te_4	rhombohedral	1.15–1.25	[61]
La_3Te_4	Th_3P_4	5.3	[47]
Au_3Te_5	cubic	1.62	[56]
Tl_5Te_3	cubic	2.23	[62]
In_2SbTe_2	NaCl	1.06	[63]
Mo_6Te_8	Chevrel	1.7	[36]
$Mo_6Te_5I_3$	Chevrel	2.4	[36]
(many Chevrel phases)			

Table 5 Superconductivity of chalcogens

Elements	T_c/K	Pressure	Ref.
O	0.6	115 GPa	[64][65]
S	12	100 GPa	[64][66]
S	17	157 GPa	[67]
S	10	?	[68]
Se(II)	6.95	130 kbar	[69]
Te(II)	2.5–3.9	40–70 kbar	[70]
Te(II)	2.05–3.4	43–50 kbar	[71][72][73]
Te(II)	2.4–5.1	38–55 kbar	[74]
Te(III)	4.15–4.28	68–80 kbar	[70][71]
Te(III)	4.1–4.2	53–62 kbar	[74]
Te(IV)	3.3–4.3	80–100 kbar	[70][71]
Te(IV)	4–4.72	63–80 kbar	[74]

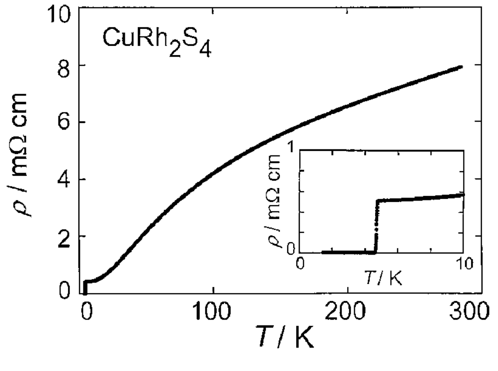

Fig. 1 Resistivity of $CuRh_2S_4$

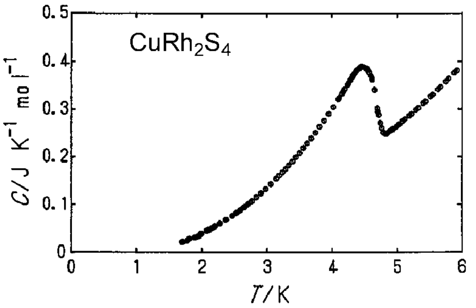

Fig. 2 Measured molar heat capacity of $CuRh_2S_4$

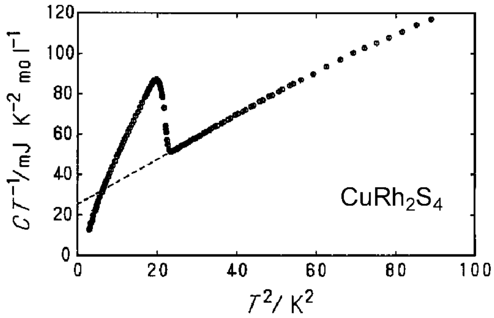

Fig. 3 Heat capacity of $CuRh_2S_4$, plotted as C/T *vs.* T^2

Representative sulfide and selenide superconductors

$CuRh_2S_4$ and $CuRh_2Se_4$

For typical examples of sulfide and selenide superconductors, results of recent intense systematic research on the normal spinel-type compounds $CuRh_2S_4$ and

$CuRh_2Se_4$ are shown, which have been extensively studied in our laboratory [39]. Here, only representative experimental results are exhibited with emphasis on thermal properties.

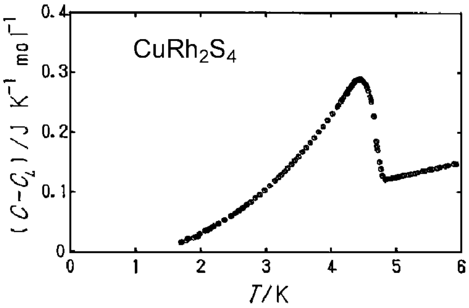

Fig. 4 Electronic part of the heat capacity, C_{es} =C–C_L , after the subtraction of lattice part C_L

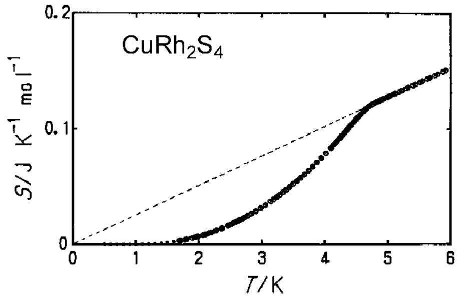

Fig. 5 Entropy S of the electronic part as a function of temperature

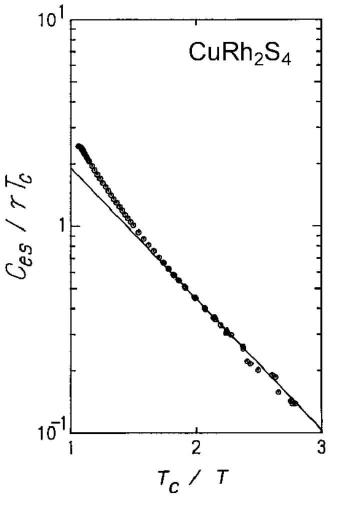

Fig. 6 The normalized electronic part of the heat capacity, C_{es} , in the superconducting state, plotted on a log scale *vs*. T_c /T. The exponential dependence on 1/T is evident

Table 6 Superconducting and normal-state characteristics for $CuRh_2S_4$ and $CuRh_2Se_4$

Property	Units	$CuRh_2S_4$	$CuRh_2Se_4$
Lattice const. a	Å	9.787	10.269
u parameter		0.384	0.384
V_m	cm^3/mol	70.58	81.54
T_c	K	4.70	3.48
γ	mJ/K^2 mol f.u.	25	26
Θ	K	230	211
$N(\varepsilon_F)$ (from γ)	states/eV atom	0.90	0.96
λ_{ep}		0.68	0.64
χ_o	10^{-4} emu/mol f.u.	3.4	3.2
S (Seebeck)	μV/K	+25	+7.3
$\Delta C / (\gamma T_c)$		1.82	1.31
$H_{c2}(0)$	kOe	20.0	4.40
$C_{es} = (a\gamma T_c)\exp[-bT_c/T]$		a=8.73	a=3.00

Table 6 Continued

Property	Units	$CuRh_2S_4$	$CuRh_2Se_4$
$(T < 0.5T_c)$		b=1.50	b=1.02
$H_c(0)$ (from free energy)	Oe	704	445
$H_c(0) = [\gamma T_c^2 / (0.170 V_m)]^{1/2}$	Oe	680	470
$2\Delta(0) / k_B T_c = \frac{4\pi}{\sqrt{3}} \left[\frac{H_c(0)^2 V_m}{8\pi\gamma T_c^2} \right]^{1/2}$		3.51	3.51
$\xi_{GL}(0)$	Å	128	274
$\lambda(0)$	Å	2670	1810
$\kappa(0) = \lambda / \xi_{GL}$		21	6.6
$H_{c1}(0) = \frac{\Phi_o \ln\kappa}{4\pi\lambda^2}$	Oe	70	95

The normal spinel-type compounds $CuRh_2S_4$ has T_c=4.70 K as shown in Fig. 1. The value of cubic lattice constant of $CuRh_2S_4$ at room temperature is 9.787 Å. The results of molar heat capacity are shown in Figs 2 to 6. The heat capacity C has the form $C=C_L+C_{es}$, here C_L is the lattice part and C_{es} is the electronic contribution to the heat capacity. The Debye temperature θ of $CuRh_2S_4$ is 230 K and the value of electronic heat capacity constant γ is 25 mJ/K^{2}mol f.u. According to the BCS theory, the electronic contribution C_{es} is approximated by the next formula:

$$C_{es}=(a\gamma T_c)\exp[-b\,T_c/T] \text{ for } T<0.5\,T_c,$$

where a and b are constants. Their magnitudes are a=8.73 and b=1.50, respectively. The value of energy gap ratio $2\Delta(0)/k_B T_c$ is 3.51. The copper nuclear spin-lattice relaxation rate exhibits distinctly a coherence peak. Lower and upper critical fields at T=0 K are 70 Oe and 20.0 kOe. The thermodynamic critical field H_c at T=0 K is 704 Oe. The value of electron-phonon interaction parameter λ_{ep} is obtained to be 0.68 using the McMillan formula. This compound $CuRh_2S_4$ is not strong-coupling superconductor but exists between weak- and intermediate-coupling superconductor, which is driven through the electron-phonon interaction. The Ginzburg-Landau coherence length $\xi_{GL}(0)$ is 128 Å and the penetration depth λ (0) is 2670 Å at T =0 K. The Ginzburg-Landau parameter κ(0) is 21 and then $CuRh_2S_4$ has typical characteristics of type - II superconductor which is clearly understood on the basis of the BCS theory.

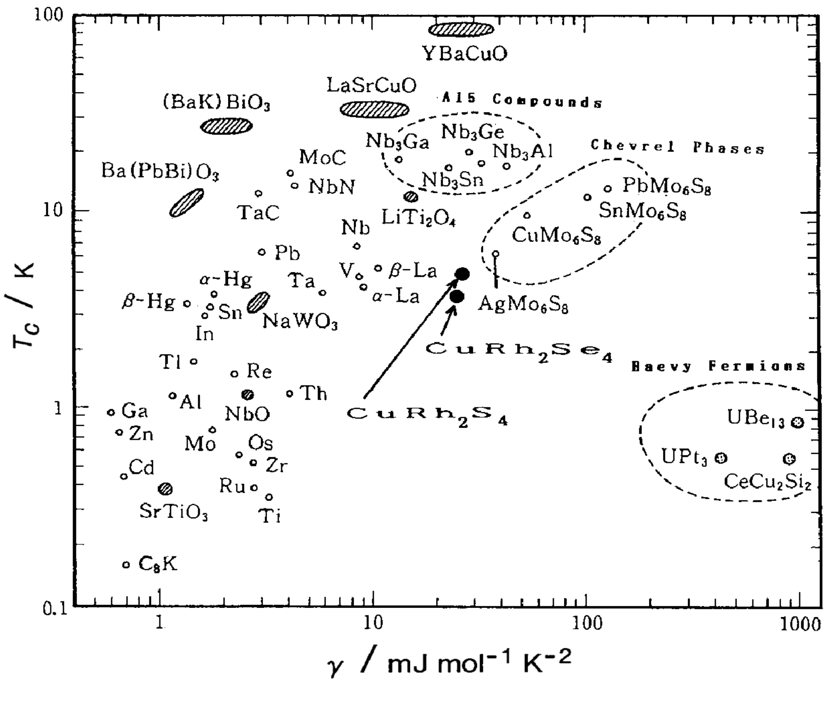

Fig. 7 T_c *vs.* γ plot for various superconductors

The summary of superconducting and normal-state properties of $CuRh_2S_4$ and $CuRh_2Se_4$ is shown in Table 6. The T_c *vs.* γ plot is shown in Fig. 7 as a perspective overview of various superconductors. These sulfides $CuRh_2S_4$ and $CuRh_2Se_4$ are located close to the molybdenum Chevrel-phase sulfides group.

References

1 A. M. Okaz and P. H. Keesom, Phys. Rev., B12 (1975) 4917.
2 P. E. Bierstedt, T. A. Bither and F. J. Darnell, Solid State Commun., 4 (1966) 25.
3 A. W. Sleight, T. A. Bither and P. E. Bierstedt, Solid State Commun., 7 (1969) 299.
4 B. T. Matthias, T. H. Geballe and V. B. Compton, Rev. Mod. Phys., 35 (1963) 1.
5 M. Greenblatt, W. H. McCarroll, R. Neifeld, M. Croft and J. V. Waszczak, Solid State Commun., 51 (1984) 671.
6 M. J. Geselbracht, T. J. Richardson and A. M. Stacy, Nature, 345 (1990) 324.
7 M. B. Robin, K. Andres, T. H. Geballe, N. A. Kuebler and D. B. McWhan, Phys. Rev. Lett., 17 (1966) 917.
8 D. C. Johnston, J. Low Temp. Phys., 25 (1976) 145.
9 S. Foner and E. J. McNiff Jr., Solid State Commun., 20 (1976) 995.
10 J. F. Schooley, H. P. R. Frederikse, W. R. Hostler and E. R. Pfeiffer, Phys. Rev., 159 (1967) 301.
11 A. W. Sleight, J. L. Gillson and P. E. Bierstedt, Solid State Commun., 17 (1975) 27.
12 L. F. Mattheiss, E. M. György and D. W. Johnson Jr., Phys. Rev., B37 (1988) 3745.
13 J. Evetts, Magnetic & Superconducting Materials, Pergamon Press, Oxford, 1992 p. 423.
14 A. Schilling, M. Cantoni, J. D. Guo and H. R. Ott, Nature, 363 (1993) 56.
15 Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz and F. Lichtenberg, Nature, 372 (1994) 532.
16 Y. Takano, S. Takayanagi, S. Ogawa, T. Yamadaya and N. Mori, Solid State Commun., 103 (1997) 215.
17 M. Uehara, T. Nagata, J. Akimitsu, H. Takahashi, N. Mori and K. Kinoshita, J. Phys. Soc. Jpn., 65 (1996) 2764.
18 A. R. Moodenbaugh, D. C. Johnston and R. Viswanathan, Mat. Res. Bull., 9 (1974) 1671.
19 W. Buckel and R. Hilsch, Z. Phys., 128 (1950) 324.
20 F. Hulliger and G. W. Hull Jr., Solid State Commun., 8 (1970) 1379.
21 D. C. Johnston and A. R. Moodenbaugh, Phys. Lett., 41A (1972) 447.
22 R. M. Bozorth, F. Holtzberg and S. Methfessel, Phys. Rev. Lett., 14 (1965) 952; J. Appl. Phys., 37 (1966) 1433.
23 G. B. Street, H. Arnal, W. D. Gill, P. M. Grant and R. L. Greene, Mat. Res. Bull., 10 (1975) 877.
24 T. A. Bither, C. T. Prewitt, J. L. Gillson, P. E. Bierstedt, R. B. Flippen and H. S. Young, Solid State Commun., 4 (1966) 533.
25 E. Amberger, K. Polborn, P. Grimm, M. Dietrich and B. Obst, Solid State Commun., 26 (1978) 943.
26 W. Bensch and J. Koy, Mater. Res. Bull., 30 (1995) 1217.
27 B. T. Matthias, E. Corenzwit and C. E. Miller, Phys. Rev., 93 (1954) 1415.
28 Ch. J. Raub, W. H. Zachariasen, T. H. Geballe and B. T. Matthias, J. Phys. Chem. Solids, 24 (1963) 1093.
29 J. A. Wilson, F. J. DiSalvo and S. Mahajan, Adv. Phys., 24 (1975) 117; F. J. DiSalvo, G. W. Hull Jr., L. H. Schwartz, J. M. Voorhoev and J. V. Waszczak, J. Chem. Phys., 59 (1973) 1922.
30 J. A. Woollam and R. B. Somoano, Phys. Rev., B13 (1976) 3843.
31 H. E. Barz, A. S. Cooper, E. Corenzwit, M. Marezio, B. T. Matthias and P. H. Schmidt, Science, 175 (1972) 884.

32 M. H. Van Maaren, Phys. Lett., 40A (1972) 353.

33 D. Reefman, J. Baak, H. B. Brom and G. A. Wiegers, Solid State Commun., 75 (1990) 47.

34 L. Schmidt, Phys. Lett., 31A (1970) 551.

35 W. Rudorff *et al.*, Z. Anorg. Allg. Chem., 269 (1952) 141.

36 Φ. Fischer and M. B. Maple, Superconductivity in Ternary Compounds I, Springer-Verlag, Berlin, 1982, p. 1.

37 Φ. Fischer, Appl. Phys., 16 (1978) 1.

38 H. R. Khan, H. Trunk, Ch. J. Raub, W. A. Fertig and A. C. Lawson, J. Less-Common Metals, 30 (1973) 167.

39 T. Hagino, Y. Seki, N. Wada, S. Tsuji, T. Shirane, K. Kumagai and S. Nagata, Phys. Rev., B51 (1995) 12673.

40 H. Nozaki, M. Saeki and M. Onoda, J. Solid State Chem., 116 (1995) 392.

41 N. Kijima, K. Morie, S. Nagata and I. Shimono, J. Low Temp. Phys., 105 (1996) 1511; N. Kijima, M. Takahashi, N. Matsumoto and S. Nagata, J. Solid State Chem., 135 (1998) 325.

42 A. R. Moodenbaugh, D. C. Johnston and R. Viswanathan, Bull. Amer. Phys. Soc., 22 (1977) 52.

43 D. C. Johnston and H. Adrian, J. Phys. Chem. Solids, 38 (1977) 355.

44 E. M. Savitskii, V. V. Baron, Yu. V. Efimov, M. I. Bychkova and L. F. Myzenkova, Superconducting Materials, Plenum Press, New York, London 1973, p. 107; F. Hulliger and J. Müller, Phys. Lett., 5 (1963) 226.

45 S. Nagata, S. Ebisu, T. Aochi, Y. Kinoshita, S. Chikazawa and K. Yamaya, J. Phys. Chem. Solids, 52 (1991) 761; T. Sambongi, M. Yamamoto, K. Tsutsumi, Y. Shiozaki, K. Yamaya and Y. Abe, J. Phys. Soc. Jpn., 42 (1977) 1421.

46 F. Hulliger, Structure and Bonding, Vol. 4, Springer-Verlag, Berlin, Heidelberg, New York 1968, p. 83.

47 E. Bucher, K. Andres, F. J. DiSalvo, J. P. Maita, A. C. Gossard, A. S. Cooper and G. W. Hull Jr., Phys. Rev., B11 (1975) 500; J. K. Hulm, M. Ashkin, D. W. Deis and C. K. Jones, Prog. in Low Temp. Phys., 6 (1970) 205.

48 Ch. J. Raub, V. B. Compton, T. H. Geballe, B. T. Matthias, J. P. Maita and G. W. Hull Jr., J. Phys. Chem. Solids, 26 (1965) 2051.

49 W. Honle, H. G. von Schnering, A. Lipka and K. Yvon, J. Less-Common Metals, 71 (1980) 135.

50 T. Ohtani, S. Honji and M. Takano, J. Solid State Chem., 132 (1997) 188.

51 S. Geller, A. Jayaraman and G. W. Hull Jr., Appl. Phys. Lett., 4 (1964) 35.

52 V. G. Kantser, N. S. Popovich and A. S. Sidorenko, Sov. J. Low Temp. Phys., 11 (1985) 568.

53 S. Nagata, T. Abe, S. Ebisu, Y. Ishihara and K. Tsutsumi, J. Phys. Chem. Solids, 54 (1993) 895.

54 R. A. Hein and E. M. Swiggard, Phys. Rev. Lett., 24 (1970) 53.

55 S. Takahashi, T. Sambongi and S. Okada, J. Physique, 44 (supplement) (1983) C3 1733.

56 H. L. Luo, M. F. Merriam and D. C. Hamilton, Science, 145 (1964) 581.

57 B. T. Matthias, A. Jayaraman, T. H. Geball, K. Andres and E. Corenzwit, Phys. Rev. Lett., 17 (1966) 640.

58 I. A. Chernik and S. N. Lykov, Sov. Phys. Solid State, 23 (1981) 817.

59 B. LaLevic, Phys. Lett., 16 (1965) 206.

60 S. Geller and G. W. Hull Jr., Phys. Rev. Lett., 13 (1964) 127.

61 S. Geller, A. Jayaraman and G. W. Hull Jr., J. Phys. Chem. Solids, 26 (1965) 353.

62 W. H. Haemmerle, W. A. Reed, A. Juodakis and C. R. Kannewurf, J. Appl. Phys., 44 (1973) 1356; A. Juodakis and C. R. Kannewurf, J. Appl. Phys., 39 (1968) 3003.

63 A. Rabenau, K. Deneke and M. M. Van Der Meij, Angew Chem. Internat. Edit., 3 (1964) 588.

64 K. Amaya, K. Shimizu, N. Takeshita, S. Kometani, M. I. Eremets, A. Onodera, T. C. Kobayashi, T. Mizutani, M. Ishizuka, S. Endo, M. Takai, N. Hamaya and I. Shirotani, Proc.

of Inter. Conf. on High Pressure Science and Technology (-AIRAPT-16 and HPCJ-38-) Kyoto, Japan Aug. 25-29, 1997; Rev. High Pressure Sci. Technol., 7 (1998) 688; K. Shimizu, M. I. Eremets, K. Suhara and K. Amaya, Rev. High Pressure Sci. Technol., 7 (1998) 784; K. Shimizu, K. Suhara, K. Amaya and S. Endo, J. Phys. Soc. Jpn., 65 (1996) 1527.

65 K. Shimizu, K. Suhara, M. Ikumo, M. I. Eremets and K. Amaya, Nature, 393 (1998) 767.

66 S. Kometani, M. I. Eremets, K. Shimizu, M. Kobayashi and K. Amaya, J. Phys. Soc. Jpn., 66 (1997) 2564.

67 V. V. Struzhkin, R. J. Hemley, H. K. Mao and Y. A. Timofeev, Nature, 390 (1997) 382.

68 G. N. Stepanov and E. N. Yakovlev, JETP Lett., 32 (1981) 643.

69 J. Wittig, Phys. Rev. Lett., 15 (1965) 159.

70 I. V. Berman, Zh. I. Bynzarov and Yu. P. Kurkin, Sov. Phys.-Solid State, 14 (1973) 2192.

71 M. A. Il'ina and E. S. Itskevich, JETP Lett., 13 (1971) 15.

72 T. Nakajima, E. Kanda and Y. Ohki, Proc. 12th Inter. Conf. on Low Temp. Phys. Kyoto, Japan Sep. 4-10, 1970, (ed. E. Kanda) KEIGAKU Pub. Co., Tokyo 1971, p. 293.

73 B. T. Matthias and J. L. Olsen, Phys. Lett., 13 (1964) 202.

74 M. A. Il'ina and E. S. Itskevich, Fiz. Tverd. Tela, 17 (1975) 3461; translation Sov. Phys. Solid State, 17 (1975) 2266.

75 B. W. Roberts, J. Phys. Chem. Ref. Data, 5 (1976) 581.

76 B. W. Roberts, Properties of Selected Superconductive Materials, 1978 Supplement, National Bureau of Standards Technical Note, NBS Technical Note, 983 1978, p. 1-93.

77 R. C. Weast, CRC Handbook of Chemistry and Physics, CRC Press Inc., Boca Raton, Florida 1983, p. E-78 (There are new editions.).

78 Landolt-Börnstein, Superconductors: Transition Temperatures and Characterization of Elements, Alloys and Compounds, new series III/21a (1990).

79 S. Nagata, N. Kijima, T. Komatsu, H. Hirosaki, A. Matsuda and S. Ebisu, Proc. of the 10th Inter. Symp. on Superconductivity (ISS'97), Gifu, Japan, Oct. 27-30, 1997. Advances in Superconductivity X, (K. Osamura and I. Hirabayashi, Eds.) Vol. 1 Springer-Verlag, Tokyo 1998, p. 293-296.

80 S. Nagata, Kotaibutsuri (Solid State Physics), 33 (1998) 790 (in Japanese).