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Superconductivity and electronic instability at high pressure in $Sc_5Co_4Si_{10}$-type compounds

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The variation of the superconducting transition temperature (T_c) with hydrostatic pressure up to 23.7 kbar is reported for eleven ternary silicides and germanides with the $Sc_5Co_4Si_{10}$-type structure. Most of these compounds display a modest linear depression of T_c with pressure ($dT_c/dp \sim 10^{-5}$ K/bar); however, two materials, $Lu_5Ir_4Si_{10}$ and $Lu_5Rh_4Si_{10}$, undergo a discontinuous transformation to a state with a significantly higher T_c above a critical pressure of about 20 kbar. For $Lu_5Ir_4Si_{10}$, the pressure-enhanced T_c of 9.12 K is the highest transition temperature reported for this class of compounds.

I. INTRODUCTION

Ternary rare-earth transition-metal silicides and germanides crystallize in a great variety of structure types.[1] The occurrence of superconductivity in these compounds is also widespread with at least 11 distinct structure types having reported superconductors.[2] One intriguing property of some of these superconducting ternary silicides is their ability to incorporate elements from the traditionally magnetic $3d$ series of Fe, Co, and Ni while retaining their superconducting properties.[3–5] Previous work[6] has shown how modest pressures can affect the relative phase stability of superconductivity and an antiferromagnetically ordered state in $Tm_2Fe_3Si_5$. In this brief report we present experimental evidence of hydrostatic pressure affecting the relative stability of the low-T_c and high-T_c states of $Lu_5Ir_4Si_{10}$ and $Lu_5Rh_4Si_{10}$. In the case of $Lu_5Ir_4Si_{10}$, the effect of pressure is sufficiently dramatic to result in a record high transition temperature for this structure of 9.12 K. In addition, we report the discovery of another superconducting compound with this structure, $Lu_5Rh_4Si_{10}$, and the pressure dependence of T_c for all 11 ternaries in this class of materials.

II. EXPERIMENTAL METHODS

All samples were prepared from high-purity elements in a manner described previously.[7] Lattice parameters were determined by the method of least squares using 20 to 24 reflections including an internal silicon standard ($a = 5.43083$ Å). No impurity reflections were observed. The pressure dependence of T_c was determined using a piston-cylinder-type hydrostatic pressure clamp.[8] For each sample, the ambient pressure T_c was redetermined after the series of high-pressure measurements. In every instance, the original value was reproduced within experimental error indicating complete reversibility of the pressure effects on T_c.

III. RESULTS AND DISCUSSION

Results of the hydrostatic pressure measurements of T_c for five ternary silicides and five ternary germanides are displayed in Figs. 1 and 2, respectively. Below 20 kbar, all ten compounds exhibit a linear dependence of T_c with pressure. Only $Lu_5Ir_4Ge_{10}$ shows a slight rise in T_c with pressure, while for all of the other samples T_c is depressed by the application of external pressure. Two distinct transitions are observed for the sample $Lu_5Rh_4Si_{10}$ at 21 kbar.

The data for each of these ten compounds, as well as

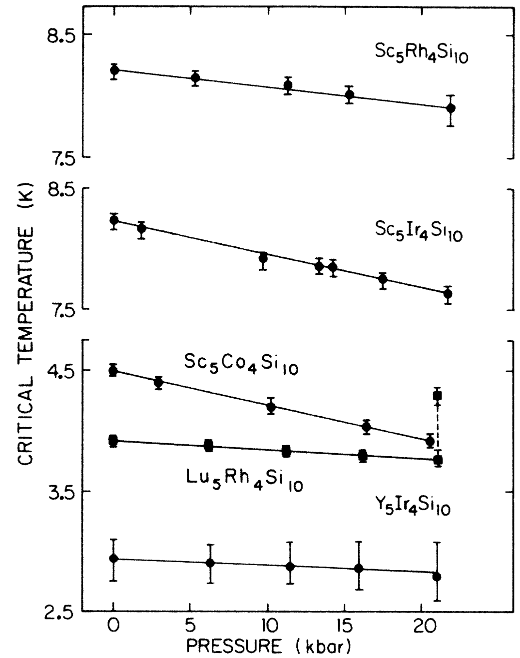

FIG. 1. Pressure dependence of the superconducting transition temperature for five ternary silicides with the $Sc_5Co_4Si_{10}$-type structure. Lines are least-squares fits to the data.

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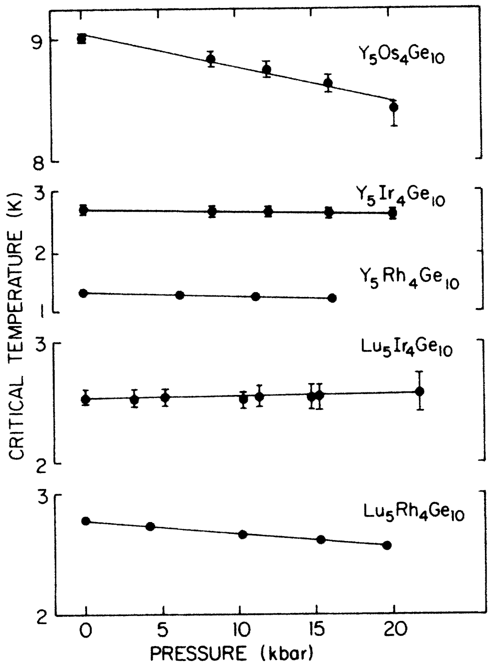

FIG. 2. Pressure dependence of the superconducting transition temperature for five ternary germanides with the $Sc_5Co_4Si_{10}$-type structure. Lines are least-squares fits to the data.

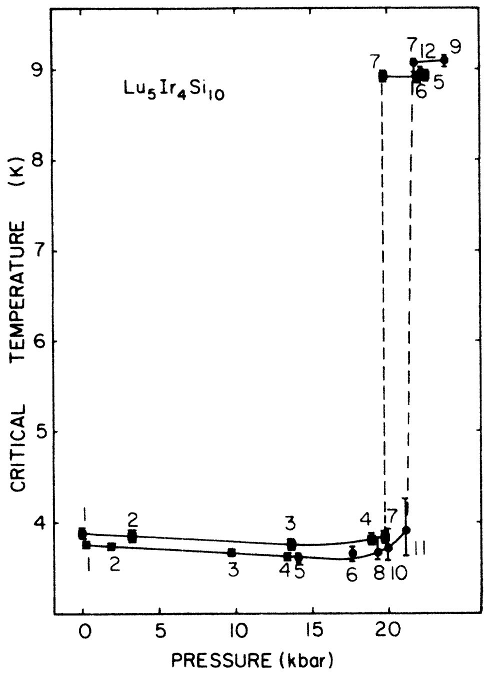

FIG. 3. Pressure dependence of the superconducting transition temperature for two samples of $Lu_5Ir_4Si_{10}$. Numbers next to the data points represent the order in which the data were taken for each sample.

the linear portion of the data for the two samples of $Lu_5Ir_4Si_{10}$ shown in Fig. 3, were fitted by the method of least squares to obtain the values of dT_c/dp listed in Table I. In the absence of any transformation, the effect of pressure on T_c is quite modest with values of dT_c/dp ranging from 0.21×10^{-5} K/bar to -3.42×10^{-5} K/bar.

In order to examine the volume effect on T_c, we begin with an expression for T_c based on the standard electron-phonon interaction[9]

$$T_c=\Theta e^{-1/g}, \tag{1}$$

where Θ is an average phonon frequency and g is the net attractive electron-electron interaction parameter which gives rise to superconductivity and depends on the repulsive Coulomb parameter μ^* and the attractive electron-phonon parameter λ. The general form of Eq. (1) has been retained in subsequent refinements of the BCS theory.[10–12] A successful specific form for Θ and g was given by McMillan[10] based on a solution of the Eliashberg equations for the spectrum of Nb and yields

$$\Theta=\Theta_D/1.45,\quad g=\frac{\lambda-\mu^*(1+0.62\lambda)}{1.04(1+\lambda)}, \tag{2}$$

where Θ_D is the Debye temperature. Utilizing this form, the volume dependence of T_c may be written in terms of the Grüneisen parameter $\gamma_G=-d\ln\Theta_D/d\ln V$ and the volume dependence of λ by differentiating Eq. (1) and taking $d\mu^*/dV=0$:

$$-\frac{B}{T_c}\frac{dT_c}{dp}=\frac{d\ln T_c}{d\ln V}=-\gamma+\ln\left[\frac{\Theta_D}{1.45T_c}\right]\left[\frac{\lambda(1+0.38\mu^*)}{(1+\lambda)[\lambda-\mu^*(1+0.62\lambda)]}\right]\frac{d\ln\lambda}{d\ln V}, \tag{3}$$

where B is the bulk modulus. We employ Eq. (3) to compute the values of $d\ln\lambda/d\ln V$ listed in Table I. In addition to our measured values of dT_c/dp, we take the experimental bulk modulus of 1370±70 kbar determined by Swenson and Anderson[13] for $Lu_5Ir_4Si_{10}$ below any pressure-induced transformation and typical transition-metal values[14] for γ_G of 2±1 and for $\mu^*=0.10$. Values for λ are obtained from Eqs. (1) and (2) using the experimental T_c's. Debye temperatures are known from low-temperature heat capacity measurements[15] for $Sc_5Co_4Si_{10}$, $Sc_5Rh_4Si_{10}$, and $Sc_5Ir_4Si_{10}$. Estimates of the Debye temperatures for the other components were made by scaling these measured values by the square root of the ratio of the masses of the known and unknown compounds and

TABLE I. Pressure effects on $Sc_5Co_4Si_{10}$-type superconductors.

Compound	a (Å)	c (Å)	$T_c(0)^a$ (K)	dT_c/dp (10^{-5} K/bar)	Θ_D (K)	$\frac{d\ln\lambda}{d\ln V}$
$Sc_5Co_4Si_{10}$	12.01(1)	3.936(5)	4.53–4.46	-2.70 ± 0.04	580	2.3 ± 0.3
$Sc_5Rh_4Si_{10}$	12.325(6)	4.032(3)	8.27–8.16	-1.53 ± 0.04	450	1.5 ± 0.3
$Sc_5Ir_4Si_{10}$	12.316(5)	4.076(3)	8.29–8.16	-2.56 ± 0.04	400	2.2 ± 0.3
$Y_5Ir_4Si_{10}$	12.599(8)	4.234(5)	3.10–2.76	-0.62 ± 0.04	370^b	1.1 ± 0.3
$Lu_5Rh_4Si_{10}$	12.502(2)	4.137(1)	3.95–3.87	-0.70 ± 0.04	340^b	1.2 ± 0.3
$Lu_5Ir_4Si_{10}$	12.475(8)	4.171(4)	3.91–3.84	-0.98 ± 0.04	330^b	1.5 ± 0.3
$Y_5Rh_4Ge_{10}$	12.953(3)	4.272(2)	1.35–1.34	-0.86 ± 0.04	340^b	2.0 ± 0.3
$Y_5Ir_4Ge_{10}$	12.927(5)	4.308(5)	2.76–2.71	-0.59 ± 0.04	320^b	1.2 ± 0.3
$Y_5Os_4Ge_{10}$	13.006(8)	4.297(5)	9.06–8.99	-3.42 ± 0.04	320^b	2.9 ± 0.3
$Lu_5Rh_4Ge_{10}$	12.850(8)	4.208(3)	2.79–2.76	-1.07 ± 0.04	300^b	1.8 ± 0.3
$Lu_5Ir_4Ge_{10}$	12.831(8)	4.252(3)	2.60–2.49	0.21 ± 0.04	290^b	0.2 ± 0.3

[a] Values represent 10–90% transition widths.

[b] Estimated, see text for details.

are listed in Table I. Our calculated values of $d\ln\lambda/d\ln V$ fall between 0 and 3, while the corresponding values of $\phi \equiv d\ln g/d\ln V$ lie between 0.2 and 2.0, with the majority in the range 1.3 ± 0.3. These values of ϕ support the assumption that d-band electrons make an important contribution to the occurrence of superconductivity in this class of compounds.[16]

The most remarkable effect of pressure on the superconducting state of these materials occurs for the compound $Lu_5Ir_4Si_{10}$ and is apparent in the data of Fig. 3. For two distinct samples, we observe a discontinuous, but reversible increase in T_c from a value of 3.7 K to a value in excess of 9 K. The complete reversibility of this transformation from low-T_c to high-T_c material is illustrated by the order in which the data were taken. For one sample at one specific pressure (point 7), there are two discrete transitions separated by more than 5 K indicating that only a portion of the sample has transformed. This is similar to the $Lu_5Rh_4Si_{10}$ sample shown in Fig. 1. The partial transformation to the high-T_c phase may be attributed to small composition variations within a sample which are present in bulk samples, even following the annealing process. A second factor which could broaden the transition into the high-T_c phase is a pressure gradient within the high-pressure cell estimated to be ≤ 1 kbar.

The exact nature of this pressure-induced transformation and the reason for its dramatic effect on superconductivity are yet to be determined. Isothermal bulk modulus measurements[13] taken up to 26 kbar at four different temperatures ranging from 293 to 14 K reveal no volume anomaly within the sensitivity of the measurement of $\Delta V/V \sim 1/10\%$. This indicates that the transformation responsible for the striking enhancement of T_c is probably electronic in nature with no major effect on the cohesive energy of the crystal.

Results of two alloy studies on $(Lu_{1-x}Sc_x)_5Ir_4Si_{10}$ and $Lu_5(Ir_{1-x}Rh_x)_4Si_{10}$ shown in Fig. 4 provide additional evidence as to the origin of this transformation. A rapid initial increase in T_c occurs with the substitution of either Sc or Rh into $Lu_5Ir_4Si_{10}$, regardless of whether the other end member in the series has a higher T_c than $Lu_5Ir_4Si_{10}$. We have also observed a similar enhancement of T_c when Ir is replaced by Co. These data indicate that the ambient pressure T_c of $Lu_5Ir_4Si_{10}$ is depressed from an expected value based on its isostructural neighbor compounds. Powder x-ray diffraction experiments performed down to 21 K reveal no detectable deviation from the primitive tetragonal symmetry observed at room temperature, thus reducing the possibility of a crystallographic phase transformation. The nonlinear behavior of T_c versus composition for both curves in Fig. 4 occurs while the room-temperature lattice parameters and unit-cell volume follow Vegard's Law.

A comparison between the volume dependence of T_c in these alloys and the volume dependence of T_c for $Lu_5Ir_4Si_{10}$ due to external pressures is shown in Fig. 5.

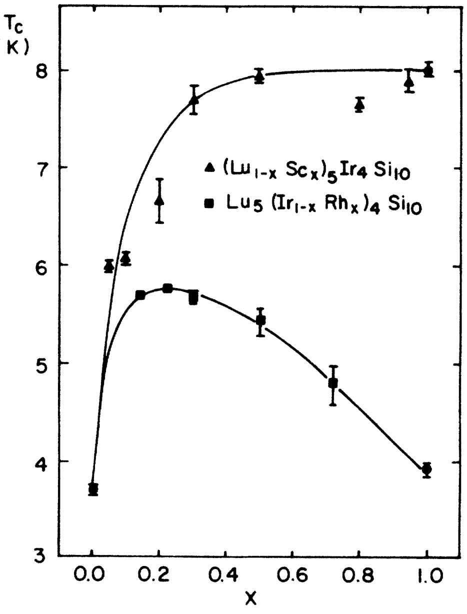

FIG. 4. Superconducting transition temperature versus alloy concentration for the pseudoternary systems: ▲ $(Lu_{1-x}Sc_x)_5Ir_4Si_{10}$ and ■ $Lu_5(Ir_{1-x}Rh_x)_4Si_{10}$.

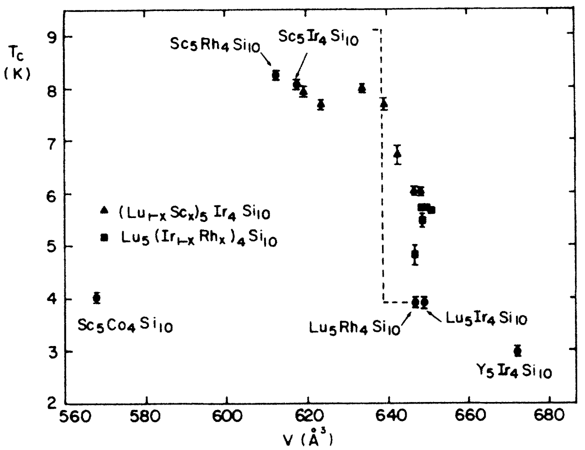

FIG. 5. Superconducting transition temperature versus unit-cell volume for ternary silicides with the $Sc_5Co_4Si_{10}$-type structure. The dashed line indicates the behavior of T_c under pressure for the pure ternary $Lu_5Ir_4Si_{10}$ (see Fig. 3).

The sharp jump in T_c due to pressure which occurs at a critical volume of about $V_c \approx 639$ Å^3 is smeared into a broader curve when volume changes are caused by alloying on the rare-earth sublattice. The data presented in Figs. 4 and 5 may be understood if one postulates the existence of a sharp feature in the electronic density of states of $Lu_5Ir_4Si_{10}$ which lies just above the Fermi energy. A reduction in unit-cell volume results in an increase in E_F, moving the Fermi level into this sharp feature. Application of hydrostatic pressure is a particularly clean method of obtaining a volume reduction since no atomic disorder or chemical effects are introduced. Thus, the extremely sudden strong increase in T_c at V_c may reflect this sharp structure in the electronic density of states. In the case of the pseudoternary alloys, although T_c is ultimately limited by the values of the end member compounds ($Sc_5Ir_4Si_{10}$ and $Lu_5Rh_4Si_{10}$), the critical temperature does increase rapidly at low concentrations, consistent with minimal disorder being favorable for higher T_c values. Sublattice disorder due to alloying causes a broadening of any sharp electronic feature in the density of states. This broadening effect is evident by comparing the $(Lu_{1-x}Sc_x)_5Ir_4Si_{10}$ data to the pressure enhanced T_c of the pure $Lu_5Ir_4Si_{10}$ in Fig. 5. The sharp increase in $T_c(p)$ of $Lu_5Ir_4Si_{10}$ at V_c is smeared into a broader curve of T_c versus V in the alloy system. The difference in T_c at V_c between the pressure-induced high T_c state of $Lu_5Ir_4Si_{10}$ and the alloy $(Lu_{0.7}Sc_{0.3})_5Ir_4Si_{10}$ is approximately 1.4 K and provides a rough measure of the effect of sublattice disorder on optimizing T_c. Theoretical electronic band-structure calculations would be of great value in understanding the experimental properties of this class of materials.

ACKNOWLEDGMENTS

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