

Polymorphism and superconductivity of LaIr_2Si_2

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LaIr_2Si_2 has a high-temperature form crystallizing in the primitive tetragonal CaBe_2Ge_2 -type structure (space group $P4/nmm$; $a=4.191 \text{ \AA}$, $c=9.944 \text{ \AA}$), and a low-temperature form of the body-centered tetragonal ThCr_2Si_2 type (space group $I4/mmm$; $a=4.109 \text{ \AA}$, $c=10.299 \text{ \AA}$). Both structures are BaAl_4 -type derivatives. The high-temperature modification may be quenched from above the transformation temperature of 1720°C and becomes superconducting at 1.6 K, while the low-temperature modification is normal down to 1 K. The structures of both modifications have been refined in single-crystal studies. The exceptional polymorphism of LaIr_2Si_2 is discussed, emphasizing structural relationships and the occurrence of superconductivity in the high-temperature modification.

I. INTRODUCTION

Over the last decade, the field of superconductivity in ternary compounds has received growing interest. The number of known superconducting ternary systems is rapidly increasing and has, in fact, more than doubled within the past three years.^{1,2} It is striking, then, how one of the largest families of ternary intermetallic compounds, that of the BaAl_4 -type derivative structures, is nearly devoid of superconducting members. A large subset of the BaAl_4 -type derivative structures has the general composition MT_2X_2 , where M is an alkaline-earth or rare-earth metal, T is a transition or post-transition element, and $X=\text{B, Ga, Si, Ge, Sn, P, As, or Sb}$. Of the known ternary rare-earth transition-metal borides, gallides, silicides, and germanides alone, more than 200 phases belong to this family.³ Nearly all these compounds crystallize with the body-centered tetragonal ThCr_2Si_2 type⁴; a few have the primitive tetragonal CaBe_2Ge_2 -type structure.⁵

An outstanding superconducting phase with the ThCr_2Si_2 -type structure is CeCu_2Si_2 , which has rather unusual and so far unique properties.⁶ Recently, superconductivity was reported for YbPd_2Ge_2 ,⁷ LaPd_2Ge_2 ,⁷ LaNi_2Ge_2 ,⁸ all with the ThCr_2Si_2 -type structure, and for LaPt_2Ge_2 (Ref. 7) whose structure was given as BaAl_4 related.

We were interested in the interplay between structural features and the occurrence of supercon-

ductivity in these intermetallic compounds. Some of the questions to be answered are the possibility of mixed-site occupancy⁹ between X and T , vacancies on one of the atom positions as reported, for example, in CeNiSi_2 -type compounds,¹⁰ and the structural transformations occurring between different BaAl_4 -type derivative structures.

A system particularly suitable for the study of these problems is La-Ir-Si. Several of the ternary phases in this system have structures deriving from the BaAl_4 type.¹¹ In particular, LaIr_2Si_2 shows polymorphism with a high-temperature phase (LaIr_2Si_2 -ht) of the CaBe_2Ge_2 type and a room-temperature phase (LaIr_2Si_2 -lt) of the ThCr_2Si_2 type. To our knowledge, this is the first observation of a polymorphic transition between these two structural types. We present the results of structural refinements of both phases and discuss their crystallographic relationship and possible consequences for the occurrence of superconductivity in LaIr_2Si_2 -ht.

II. SAMPLE PREPARATION AND CHARACTERIZATION

Several samples of LaIr_2Si_2 were prepared from high-purity elements (La, 99.99% purity; Ir, 99.9% purity; Si, 99.999% purity) by arc melting in an argon atmosphere. Melting losses were less than 0.3% in all cases. Homogenization and annealing was performed above 1000°C in an rf induction furnace

in vacuo, below 1000°C in sealed quartz capsules under argon. The high-temperature modification was retained by quenching with an argon jet. Differential thermal analysis (DTA) was carried out at temperatures up to 2000°C using W crucibles. Powder x-ray diffraction (Guinier camera and powder diffractometer, CuK α radiation) and metallography served to monitor sample purity and microstructure.

The transformation temperature of stoichiometric LaIr₂Si₂ was determined by DTA to be 1720±10°C. No other transition was detected between 700°C and the solidus temperature of 1890±10°C, also determined by DTA. Preliminary results on non-stoichiometric samples indicate a dependence of the transformation temperature on composition. A stoichiometric sample Ar-jet quenched from 1750°C consisted of pure LaIr₂Si₂-ht and was found to have transformed completely to the low-temperature modification after a 6-d anneal at 1000°C. Metallographic examination shows the presence of a small quantity (<5 vol %) of intergranular impurity phases in the as-quenched and annealed samples, which do not show up in powder diffraction photographs.

LaIr₂Si₂-ht had platelike crystallites up to 0.1 mm thick and 0.5 mm wide. The growth morphology of LaIr₂Si₂-ht is retained in samples annealed at 1000°C, however, the primary grains transform into multiple crystallites of small size (<30 μm). Larger crystallites of LaIr₂Si₂-lt, suitable for an x-ray single-crystal study, were obtained after a modified heat treatment: recrystallization of the high-temperature phase at about 1800°C, slow cooling through the transformation temperature to permit the formation of large homogeneous grains, and an ordering heat treatment at 1000°C for 6 d.

Superconducting critical temperatures were determined by ac susceptibility measurements. The high-temperature modification LaIr₂Si₂-ht, quenched from 1750°C, is superconducting with an onset temperature of 1.58 K (10% superconducting signal) and a transition width of 0.18 K (10–90% signal). The superconducting transition was measured on a 340-mg piece, and on the same material after reduction to a powder (<85 μm) with no significant change in the onset temperature, transition width, or magnitude of the diamagnetic signal, indicating that the observed superconductivity is due to the majority phase. No trace of superconductivity was found, down to 1 K, in LaIr₂Si₂-lt.

III. STRUCTURE DETERMINATION

The intermetallic compound LaIr₂Si₂ has a room-temperature modification (LaIr₂Si₂-lt) with

body-centered tetragonal ThCr₂Si₂-type⁴ structure, and a high-temperature modification (LaIr₂Si₂-ht) with primitive tetragonal CaBe₂Ge₂-type⁵ structure. Accurate lattice parameters were obtained from the Guinier photographs, with Si as an internal standard by least-squares refinement.¹² Both modifications have similar cell dimensions (Table I).

Apart from the shift in line positions, the main difference in the powder patterns of the two phases lies in a different intensity distribution and the appearance of reflections with odd *hkl* sum for the high-temperature phase. If these additional reflections were mistakenly interpreted as arising from some impurity phase, the powder pattern of LaIr₂Si₂-ht might be indexed on the basis of the ThCr₂Si₂-type structure, with the assumption of a statistical distribution of the Ir and Si atoms over the available sites in order to explain the observed intensities. For this reason, the definitive structure determination of the two modifications of LaIr₂Si₂ was carried out on single crystals.

Integrated intensities were collected on an automatic four-circle diffractometer (Philips PW1100, MoK α radiation, graphite monochromator) in the ω - 2θ scan mode up to a limit of $(\sin \theta)/\lambda = 1.0 \text{ \AA}^{-1}$. Spherical absorption corrections were applied, and the atomic positional parameters, anisotropic thermal parameters, and a scale factor were refined in least-squares cycles.¹³ A summary of the results¹⁴ is given in Table I.

The structure refinement of LaIr₂Si₂-ht was based on 463 unique measured reflections. Of these, 12 having intensities below the threshold (3σ) were considered as unobserved, and two more [(220) and (200)] were rejected as suffering from extinction. The final agreement factor $R = \sum |\Delta F| / \sum |F_o|$, with the use of unit weights, was 0.049. There is no indication for mixed-site occupation between Ir and Si or vacancies on either site.

The refinement of LaIr₂Si₂-lt is based on 234 unique reflections, averaged over two symmetry equivalent sets. The reflections (200), (002), and (004), whose intensities were consistently too low, were omitted from the final refinement cycles, leading to an agreement factor of 0.061. There is no evidence for an Ir population on the 4(*e*) site. Conversely, the presence of up to 4 at.% Si or vacancies on the 4(*d*) site cannot be excluded.

IV. COMPARISON OF BOTH STRUCTURE TYPES

The structures of LaIr₂Si₂-lt (ThCr₂Si₂ type), and LaIr₂Si₂-ht (CaGe₂Be₂ type) are shown in Fig. 1. Both structure types are ordered ternary derivatives of the binary BaAl₄-type structure. In both cases, the Ba sites are occupied by the La atoms and the Al

TABLE I. Crystallographic data of the two LaIr_2Si_2 modifications.

	$\text{LaIr}_2\text{Si}_2\text{-lt}$				$\text{LaIr}_2\text{Si}_2\text{-ht}$			
Pearson symbol	<i>tI</i> 10				<i>tP</i> 10			
Structure type	ThCr_2Si_2				CaBe_2Ge_2			
Lattice parameters ^a	$a = 4.109(1) \text{ \AA}, c = 10.299(3) \text{ \AA}$ $c/a = 2.506(1)$				$a = 4.191(1) \text{ \AA}, c = 9.944(4) \text{ \AA}$ $c/a = 2.373(1)$			
Space group	<i>I</i> 4/ <i>mmm</i>				<i>P</i> 4/ <i>nmm</i> (origin at center)			
Atomic positions ^{a,b}	x	y	z	<i>U</i> (\AA^2)	x	y	z	<i>U</i> (\AA^2)
Si	0	0	0.3733(7)	1.17(9)	$\frac{1}{4}$	$\frac{1}{4}$	0.3745(1)	0.84(2)
Ir	0	$\frac{1}{2}$	$\frac{1}{4}$	0.90(2)	$\frac{1}{4}$	$\frac{1}{4}$	0.1262(7)	0.66(10)
La	0	0	0	0.98(3)	$\frac{3}{4}$	$\frac{3}{4}$	0	0.61(1)
Refinement	Single crystal				Single crystal			
Radiation	Mo <i>K</i> α				Mo <i>K</i> α			
Absorption correction	Isotropic, $\mu R = 2.0$				Isotropic, $\mu R = 2.24$			
Contributing reflections	231				449			
Variables	8				14			
Agreement factor <i>R</i>	0.061				0.049			

^aEstimated standard deviation given in parentheses.^bThe isotropic temperature factor is $T = \exp[-8\pi^2(10^{-3}U\lambda^{-2})\sin^2\theta]$.

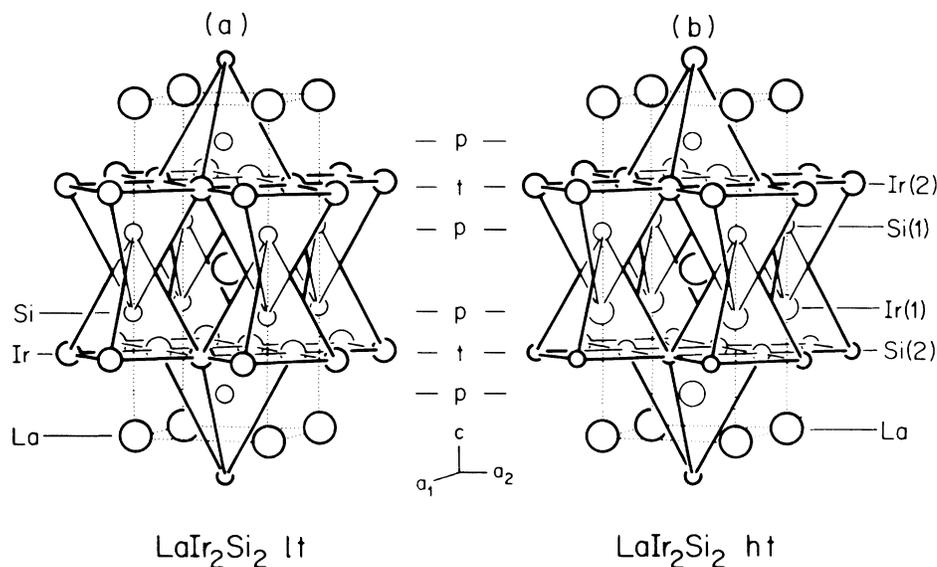


FIG. 1. Structures of the two modifications of LaIr_2Si_2 . The distribution of Ir and Si on the tetrahedral (t) and pyramidal (p) sites is indicated, the inner coordination pyramids are outlined. The unit cell origin of LaIr_2Si_2 -ht has been shifted by $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$.

positions by Ir and Si, the distinction between the two ternary structures arising from the different distribution of Ir and Si atoms over the available Al sites.

A brief discussion of the Al framework of BaAl_4 will facilitate the comparison of the two ternary structure types. There are two types of coordination of the Al sites: double tetrahedral coordination by 4 Al and 4 Ba, and double pyramidal coordination by 5 Al and 5 Ba (Fig. 2). What we call a site with pyramidal coordination is usually designated as a site with antiprismatic coordination, since the bases of the Ba and Al pyramids form a square antiprism.¹⁵ We prefer the notion of a pyramidal coordination, since in the present compounds the interatomic distances between the central atom and all five Al-equivalent nearest neighbors are very nearly equal.

In the further discussion, we will consider only

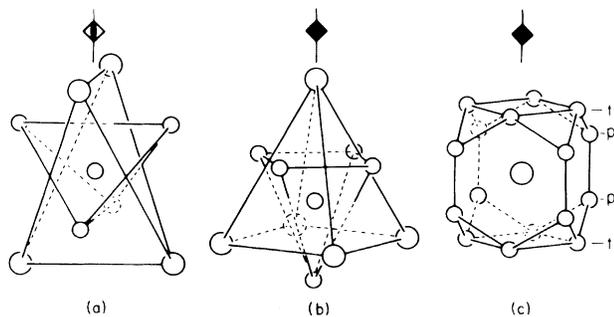


FIG. 2. Coordination of the three different sites in BaAl_4 : (a) tetrahedral Al site; (b) pyramidal Al site; (c) Ba site. Large circles: Ba; small circles: Al.

the inner coordination polyhedra, viz., a simple tetrahedron and a simple pyramid formed by atoms that correspond to the Al atoms in BaAl_4 . Only the inner pyramids are indicated in Fig. 1. The tetrahedrally coordinated sites form a square planar net perpendicular to c , each square representing the base of a pyramid. Adjacent pyramids point to different sides of the square net, alternating up and down. The upward pointing pyramids of one layer intersect the downward pointing pyramids of the next layer, the apex of one pyramid being at the center of the other, and vice versa. The M atoms approximately center the holes between four pairs of intersecting pyramids and have a quite regular 16-atom-coordination polyhedron, shown in Fig. 2(c) for BaAl_4 .

If we denote pyramidally coordinated sites by p and tetrahedrally coordinated sites by t , the structure is characterized by the sequence of layers $ptpptp$ stacked along the c direction (Fig. 1). In BaAl_4 , all p and t sites are occupied by Al. In the ternary derivative MT_2X_2 with ThCr_2Si_2 -type structure, the tetrahedral sites are exclusively occupied by T , the pyramidal sites exclusively by X : $XTXXTX$. In the CaBe_2Ge_2 -type structure, both types of sites are occupied by both types of atoms, in the sequence $TXTXTX$.

The alternating of transition metal and metalloid in subsequent layers in the CaBe_2Ge_2 -type structure has several interesting consequences. First, the high symmetry of the ThCr_2Si_2 type, characterized by body centeredness and centrosymmetry, is lost in the CaBe_2Ge_2 type, which has a primitive Bravais lat-

tice. However, were both sites p and t occupied by a statistical mixture of T and X , the original high symmetry would be restored. As a second consequence of this alternation of $TXTX$ in the CaBe_2Ge_2 -type structure, the nearest neighbors of one atom type, X or T , are always atoms of the other type, T or X . This is not the case in the ThCr_2Si_2 -type structures, where Si pairs are formed. Finally, the inner coordination polyhedra in the CaBe_2Ge_2 -type structure are all built by one type of atom: all inner coordination pyramids are built by 5 X 's or by 5 T 's, all coordination tetrahedra are built by 4 X 's or by 4 T 's, all coordination polyhedra are centered by the opposite types of atom. The ThCr_2Si_2 -type structure also has tetrahedra built by 4 X 's and centered by T , whereas the coordination pyramids are built by 4 T 's (the base), one X (the apex) and centered by X . The difference in the occupation of the pyramidal site and its coordination distinguishes the two structure types and might well be the reason for their different physical properties. This distinction will be diminished in the case of site exchange disorder between X and T in the ThCr_2Si_2 -type structure, if such disorder involves more than just a few percent of the atoms.

In Table II, we compare the observed interatomic distances of LaIr_2Si_2 with hypothetical distances, calculated with the use of covalent radii for Ir and Si, and the metallic radius for La. The differences Δ are nearly zero for all atoms belonging to the coordination polyhedra as defined above. A notable exception occurs for the pyramidally coordinated sites. In both modifications, the apex atom of the La pyramid is much farther removed from the center atom than the four basis atoms, the elongation being more pronounced for Si-centered pyramids than for Ir-centered pyramids. A similar elongation along c is observed for the inner coordination pyramids of LaIr_2Si_2 -lt, where the homonuclear bond between the center and apex Si atoms is much longer than the heteronuclear bonds between the center Si and the basis Ir atoms. In LaIr_2Si_2 -ht, where only heteronuclear bonds occur, all these distances are equal for pyramids centered by Si or Ir. The elongation of the coordination pyramids in the low-temperature phase is reflected in its higher c/a ratio (Table I). Both structures may be described as consisting of a three-dimensional framework with short bond distances, built by Ir and Si, the La occupying the largest open spaces.

V. SUPERCONDUCTIVITY AND STRUCTURE

Short bond distances between silicon and transition metals, in the order of the sum of their covalent radii, are common in ternary and binary silicides, including the binary iridium silicides. However, in none of the known phases in the binary Ir-Si system does Ir have a pyramidal coordination. None of these compounds is superconducting above 1 K.¹¹ In ternary rare-earth-transition-metal silicides, the short silicon-transition-metal bonds frequently form three-dimensional frameworks, in which the rare-earth ions are embedded. One of these silicides is $\text{Sc}_5\text{Co}_4\text{Si}_{10}$, the prototype structure¹⁶ of a series of superconducting compounds,^{17,18} and itself a superconductor at 4.9 K. In this structure type, the transition metal (Co, Rh, Ir) has a double pyramidal coordination polyhedron consisting of 5 Si and 5 Sc, which, although slightly distorted, is completely analogous to the coordination figure of the pyramidal site in BaAl_4 and its ternary derivatives [Fig. 2(b)]. $\text{Sc}_5\text{Ir}_4\text{Si}_{10}$ becomes superconducting at 8.4 K.¹⁸

Of the two LaIr_2Si_2 modifications, only the high-temperature form has Ir atoms centering a pyramid of 5 Si. Further, only in the high-temperature form do Ir and Si atoms alternate on adjacent sites of a three-dimensional framework, and it is this modification that becomes superconducting. It is therefore tempting to speculate that the transition-metal coordination in these silicides is linked with and may be crucial for the occurrence of superconductivity in these compounds.

VI. SUMMARY

Polymorphism is observed for the compound LaIr_2Si_2 between a high-temperature phase of the primitive tetragonal CaBe_2Ge_2 -type structure and a low-temperature phase of the body-centered tetragonal ThCr_2Si_2 -type structure. A link is suggested between the formation of a three-dimensional Ir-Si framework with a fivefold Si coordination of Ir and the superconductivity of the high-temperature phase.

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