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Superconductivity in layered lanthanum carbide halides: $La_2C_2(X,X')_2$ $(X,X'=Cl, Br, I)$

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Abstract

The superconducting properties of the layered lanthanum carbide halides $La_2C_2X_2$ (X=Br, I) and mixed halides are investigated. These compounds show superconductivity at 7.03(5) for X=Br and at ≈1.7 K for X=I, respectively. Selected compositions were investigated using high-resolution neutron powder diffraction measurements from room temperature to 1.5 K. Rietveld refinements of the powder patterns yield the structural parameters, in particular of the C atoms. These allow us to follow in detail the variation of the interatomic distances in the C_2 group. The low-temperature structural parameters are taken as inputs to perform Extended Hückel band structure calculations which allow us to identify a band of low dispersion along the Γ–N direction in the Brillouin zone. We discuss correlations of structural and electronic properties of the $La_2C_2(X,X')_2$ phase with the superconducting transition temperatures.

Keywords: Superconductivity; Rare-earth metal carbide halides; Neutron diffraction; Susceptibility

1. Introduction

Since superconductivity has been discovered in the rare earth metal carbide halides $RE_2C_2X_2$ (RE=Y, La; X=Cl, Br, I) [1] the majority of experiments concerning the superconducting properties of these compounds has been devoted to the yttrium-based compounds [2–9]. These investigations revealed a number of essential results: For example, it has been demonstrated for the mixed I–Br system, $Y_2C_2I_{2-x}Br_x$, that by adjusting the I/Br ratio to $x=0.5$ a superconducting transition temperature of $T_C=11.6$ K can be reached which is the highest transition temperature observed in the layered rare earth metal carbide halides, so far [2,8]. The crystal structure of the $RE_2C_2X_2$ phases is highly anisotropic, consisting of slabs of double layers of close-packed rare earth metal atoms which are sandwiched between layers of halogen atoms (Fig. 1) [10,11]. Such slabs stack along the crystallographic *c*-axis to form alternating double layers of metal and halogen atoms. Two different stacking sequences (1s- and 3s-type) have been found which differ in the number of double layers necessary to build a unit cell. C_2 dumbbells are located in the octahedral voids within the metal atom double layers. Backbonding from the C_2 group to the metal atoms leads to metallic conductivity which consequently may be expected to be strongly anisotropic and essentially confined to the metal–carbon substructure.

While the yttrium carbide halides have attracted particular attention, the lanthanum-based compounds are less well investigated. In a first study on $La_2C_2X_2$ (X=Br, I) and samples with halide mixtures we experienced a behavior which is somewhat different from that in the yttrium compounds [12]: The highest T_C of 7.2 K seen for lanthanum-based compounds, so far, has been met in the Br/Cl system ($La_2C_2Br_{1.7}Cl_{0.3}$) while $La_2C_2I_2$ did not show indications for a superconducting transition down to 2 K. To gain more insight into the relationship of structural and superconducting properties of these new superconductors we extended the investigation to temperatures of about 0.3 K. In this paper, we report on our study of neutron powder diffraction of $La_2C_2(X,X')_2$ (X,X'=Cl, Br and/or I) and use Extended Hückel tight-binding calculations to aid in an understanding of the superconducting behavior of the lanthanum carbide halide system.

2. Experiment

Polycrystalline samples of $La_2C_2X_2$(X=Br, I) were prepared by reacting stoichiometric mixtures of La metal,

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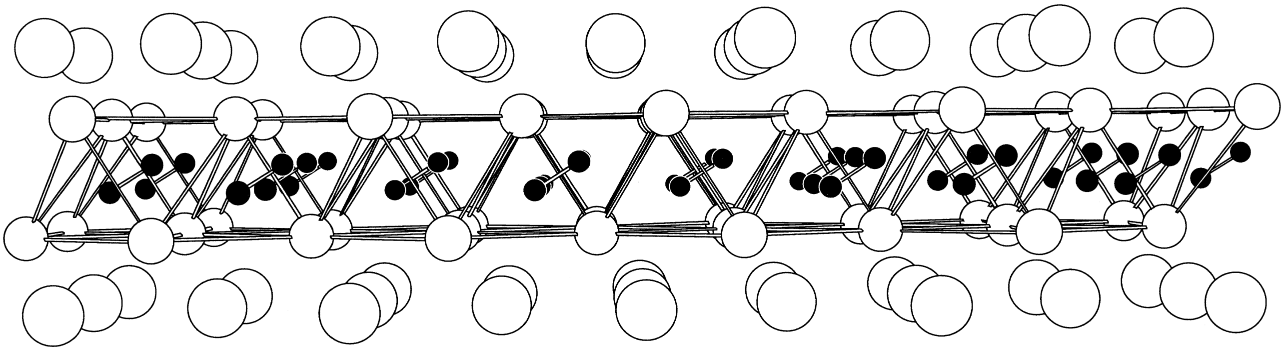


Fig. 1. Perspective view of a double layer of close-packed metal atoms (medium-sized circles) sandwiched between layers of halogen atoms (large circles) in the structure of $La_2C_2X_2$ (X=Br,I). C atoms (small circles) from C–C dumbbells octahedrally coordinated within the metal atom layers.

LaX_3 and carbon powder. In order to prepare 1s-$La_2C_2X_2$, stoichiometric mixtures with a 2% excess carbon powder were sealed in welded Ta tubes and heated to 980°C (X=Br) and 1050°C (X=I) for 2 weeks. An increased carbon content (≈10%) was found necessary to obtain the 3s-$La_2C_2I_2$ type. The 3s-$La_2C_2I_2$ samples were found to form into thin platelets up to 2 mm in diameter. Details of preparation of trihalides are described in elsewhere [13–15]. Since the trihalides and the products are extremely sensitive to moisture, all handling was done under dried

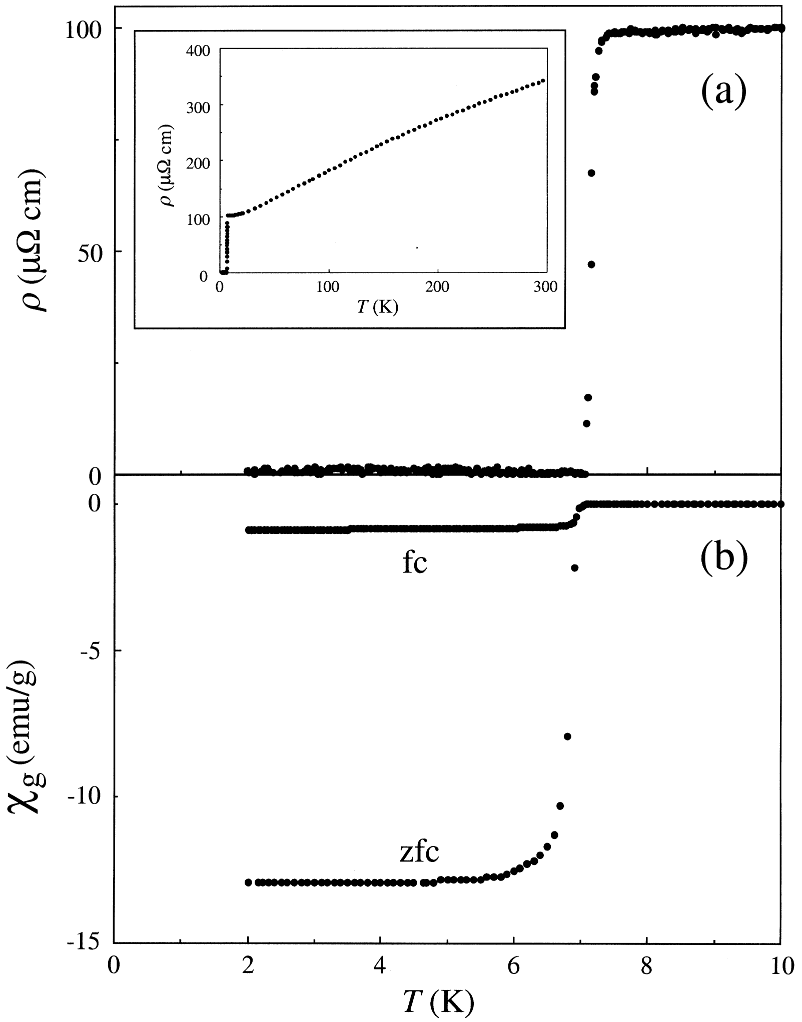


Fig. 2. (a) Electrical resistivity, and (b) DC magnetic susceptibility of $La_2C_2Br_2$. In (b) 'fc' and 'zfc' refer to field cooled and zero-field cooled susceptibility, respectively.

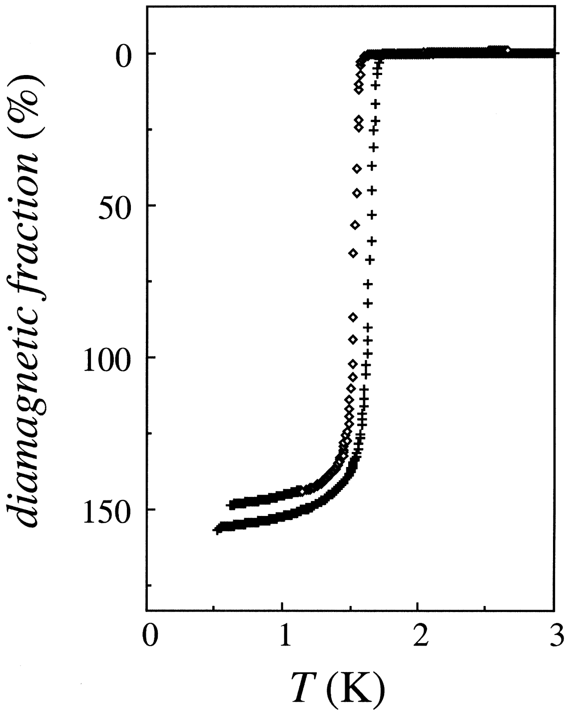


Fig. 3. AC susceptibility of a sample of 1s-$La_2C_2I_2$ (◇, $T_C \approx 1.6$ K) and 3s-$La_2C_2I_2$ (+, $T_C \approx 1.7$ K).

argon gas atmosphere. Details of measurements of the AC and DC magnetic susceptibility have been reported elsewhere [12,16]. Electrical resistivity was determined on sintered pellets of 5 mm diameter and a thickness of about 1 mm using the van der Pauw method. The pellets were enclosed in a vacuum tight copper can and pressed onto four gold-plated spring pins.

3. Results and discussions

Fig. 2 displays the electrical resistivity and DC susceptibilities of a sample of 1s-$La_2C_2Br_2$ which is monophasic according to a neutron powder diffraction study. Zero-resistivity is reached at 7.03(5)K. Diamagnetic shielding is complete while the Meissner fraction amounts to about 10% of the expected value. This difference is frequently observed and may be attributed to strong pinning effects at grain boundaries or crystal imperfections in the sample. The AC susceptibilities of 1s-$La_2C_2I_2$ and 3s-$La_2C_2I_2$ samples show transitions to superconductivity below 2 K. For both samples the transitions to superconductivity are remarkably sharp (Fig. 3). In contrast to $La_2C_2Br_2$ the two differently prepared samples [16], exhibiting 1s- and 3s-stacking, respectively, show a slight difference in the onset temperature $\Delta T_C^{\text{onset}} \approx 0.12(5)$K. Flux exclusion is complete at lowest temperatures for both samples.

The structure of each compound was refined from neutron powder diffraction patterns (instrument D1A, ILL) in the monoclinic space group $C2/m$ using the Rietveld method. Lattice parameters are listed in Table 1. The structure type is well known from the $Gd_2C_2Br_2$ [10,11], either in its 1s- and 3s-stacking variants. All diffraction patterns showed no evidence for impurity phases, e.g. starting materials or decomposition products above the level of sensitivity of powder diffraction measurements. For mixed halide samples the occupation factors were also refined and the resulting composition was found to be in good agreement with values expected from the initial ratio of the trihalides in the starting mixtures. On cooling from room temperature to 1.5 K, apart from a monotonic decrease of the lattice parameters no indications for structural phase transitions were observed in the diffraction patterns of all samples. Fig. 4 shows the result of the final Rietveld refinement of the diffraction pattern of $La_2C_2Br_{0.5}I_{1.5}$ taken at 1.5 K.

Within the Zintl–Klemm concept, the chemical bonding for the phases $La_2C_2X_2$ may be approximated by the formula $(La^{3-})_2C_2^{4-}(X^-)_2$ suggesting semiconducting behavior. From the molecular point of view, the metallic behavior has been attributed as due to backbonding from occupied C_2-π^* state to empty d-states of the metal atoms. The metallic character of $La_2C_2X_2$ (X=Br, I) is verified by the results of our Extended Hückel calculations. Fig. 5(a) displays the total density of states (DOS) calculated for the observed crystal structure of the 3s-type of $La_2C_2I_2$. The local maximum in the DOS around E_F originates from bands of low dispersion along Γ–N (=−1/2, 1/2, 0) [Fig. 5(b)]. The direction Γ–N corresponds to the direction of the crystallographic *a*-axis or the projection of the C–C group onto the crystallographic *a*–*b* plane. We consider this in-plane band of low dispersion to be essential for superconductivity in these phases.

Table 1
Lattice constants (pm) and C–C distances (pm) of the investigated $La_2C_2(X,X')_2$ samples at 1.5 K and their superconducting transition temperatures

Composition		*a*	*b*	*c*	*β* (°)	T_C^{onset} (K)	d_{C-C}
$La_2C_2Br_2$	1s	746.09(5)	404.93(3)	1001.16(9)	94.163(5)	7.03(5)	134.1(7)
$La_2C_2I_2$	1s	761.90(3)	412.52(2)	1075.13(7)	93.143(4)	1.60(5)	132.2(5)
$La_2C_2I_2$	3s	761.32(2)	413.24(1)	1085.90(4)	100.835(2)	1.72(5)	128.4(4)
$La_2C_2Br_{0.5}I_{1.5}$	1s	758.57(3)	409.81(2)	1067.82(5)	93.272(2)	1.65(3)	131.5(4)
$La_2C_2Cl_{0.5}I_{1.5}$	1s	757.64(3)	407.58(2)	1072.66(5)	93.384(3)	1.82(3)	129.7(5)

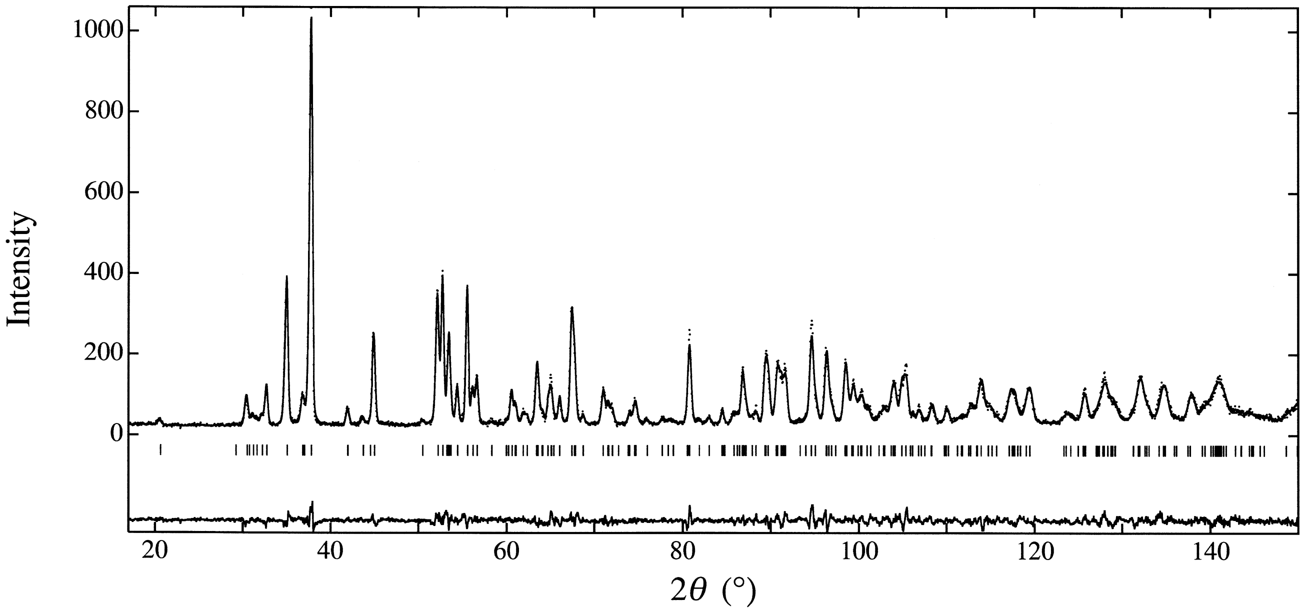
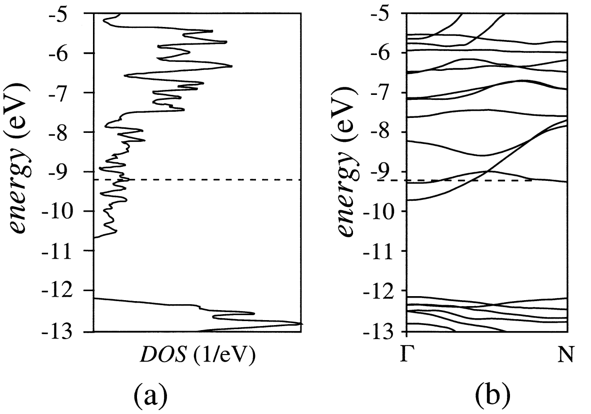


Fig. 4. Observed (•), calculated (full line) and difference neutron diffraction pattern (instrument D1A, ILL) for $La_2C_2Br_{0.5}I_{1.5}$ (1s-type) at 1.5 K. Vertical bars indicate the positions of the reflections used to simulate the pattern.

4. Summary and conclusion

In summary, the onset of superconductivity in $La_2C_2Br_2$ is found close to 7 K in a set of three samples prepared under different conditions. $La_2C_2I_2$ crystallizes in structures with different stacking sequences, 3s- and 1s-type, with slightly different lattice parameters, interatomic distances and different superconducting transition temperatures. The observation that pure 3s-type samples of $La_2C_2I_2$ can only be prepared using a considerable excess of carbon while mixed 1s-/3s-type samples result when the carbon excess is reduced close to stoichiometric mixtures strongly suggests that the 1s-type samples exhibit a slight carbon deficiency, $La_2C_{2-x}I_2$. Rietveld refinements assuming this structure model, however, failed to reveal scattering density in the center of the octahedra beyond the level of sensitivity of the method. According to the calculations, the replacement of C_2 by C may at most amount to 0.3(6)%. Extended Hückel band calculations can explain the metallic behavior of the $La_2C_2X_2$ system. From the band structure calculations we identify a band of low dispersion in the direction (Γ–N) which corresponds to the direction of the crystallographic *a*-axis. We note that the flat band originates from orbital interaction within the layer and not from interactions perpendicular to the layers.



(a) (b)

Fig. 5. (a) Density of states (DOS) (Fermi level at −9.2 eV), and (b) band dispersion for 3s-$La_2C_2I_2$ plotted for the Γ–N (−1/2, 1/2, 0) direction in the Brillouin zone.

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