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Angaben zur Veröffentlichung / Publication details:

Henn, R. W., K. Ahn, Hans-Albrecht Krug von Nidda, R. K. Kremer, and A. Simon. 2000. "Pressure dependence of the transition temperature of the layered superconductors Y2C2Br2−xIx." *Physica C: Superconductivity* 341-348 (2): 719–22. https://doi.org/10.1016/s0921-4534(00)00659-6.

Pressure Dependence of the Transition Temperature of the Layered Superconductors $Y_2C_2Br_{2-x}I_x$

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We report the effect of hydrostatic pressure up to 1.5 GPa on the superconducting transition temperatures T_c of four compounds in the series $Y_2C_2Br_{2-x}I_x$ ($0<x<2$) and of $La_2C_2Br_2$. Depending on halogen composition, the $Y_2C_2(X,X')_2$ (X=Br,I) display a linear variation in T_c with a pressure coefficient dT_c/dP changing in magnitude and sign. This finding is discussed along with a cusp in the electronic density of states close to Fermi energy.

1. Introduction

Superconductivity in the carbide halides of rare earth metals $RE_2C_2X_2$, RE being Y or La and X being Cl, Br or I was discovered in 1991 [1]. In the following years, the superconducting state of these materials was investigated by means of heat capacity, dc-magnetization, and resistivity measurements [2–4,6–9]. The $RE_2C_2X_2$ compounds exhibit layered crystal structures (see Fig. 1) with units of bilayers of closely-packed rare earth metal atoms which are sandwiched between sheets of halogen atoms. The octahedral voids in the metal-atom bilayers are occupied by dimeric C-C dumbbells. Such X-RE-C_2-RE-X units stack with bonding via van der Waals forces and crystallize in a monoclinic structure with space group $C2/m$ [5]. The C_2 units were proposed to be of essential importance regarding the electronic properties of the $RE_2C_2X_2$ superconductors: An overlap of antibonding C_2-π^* molecular orbitals with energetically neighboring RE-d states causes a shortening of the C-C double bond. This covalency on one hand gives rise to electron delocalization and metallic behavior. On the other hand, the quasi-free conduction electrons are "tied" to the C_2-π^* orbital through backbonding from RE-d with a tendency to localize and to enhance the electron-phonon coupling [6]. So far, the highest T_c was found in the homogeneous series $Y_2C_2Br_{2-x}I_x$. With increasing x, T_c first rises to a maximum

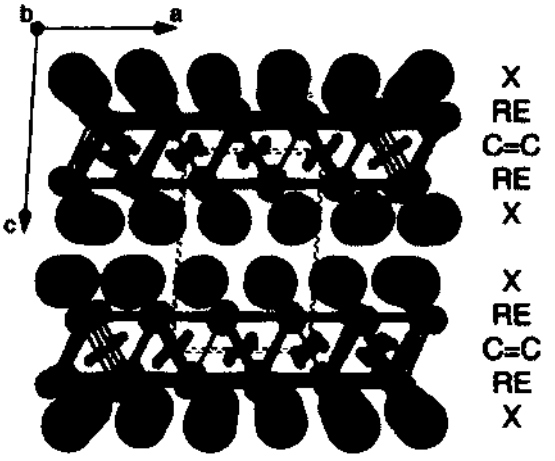

Figure 1. Perspecitve projection of the $RE_2C_2X_2$ crystal structure.

of 11.6 K for $Y_2C_2Br_{0.5}I_{1.5}$ and then decreases to 9.97 K for $Y_2C_2I_2$. The lowest T_c of 5.05 K is observed for $Y_2C_2Br_2$. LMTO band-structure calculations for $Y_2C_2Br_2$ reveal a peak in the DOS at the Fermi-energy, which is due to a hyperbolic saddle point at the Fermi-surface [7]. Experimental support for such a structure in $N(\epsilon)$ was gained from a nonlinear temperature dependence of the ^{13}C-NMR Korringa relaxation of $Y_2C_2Br_2$ [8].

Here, we present investigations of the pressure dependence of T_c in the $RE_2C_2X_2$ superconduc-

tors in order to gain further experimental insight in the electronic structure of these systems.

2. Experimental details

Single phase samples of $RE_2C_2X_2$ were prepared in sealed tantalum crucibles from RE metal chips (99.99% Johnson-Matthey), RE trihalides and graphite powder as described previously [11]. Carbon was used with its natural isotope abundance, ^{nat}C, (Aldrich Chemie). Due to the sensitivity of precursors and compounds to air and moisture, all handling had to be done under dry argon atmosphere. In the first instance, all samples were characterized by x-ray powder diffraction. Additionally, samples No. 1,4,5 (see Tab 1) were investigated by neutron powder diffraction [4,9,10].

The magnetic susceptibilities of powder samples of about 5 mg were measured in zero field cooled (zfc) runs with a MPMS7 SQUID-magnetometer (Quantum Design) in an applied field of 0.05 mT. The $Y_2C_2X_2$ samples together with small polycrystalline pieces of Pb or Sn were immersed in silicon oil in a Delrin container (outer diameter 3 mm) which was placed in a Cu-Be piston type pressure cell. The pressure was determined from the superconducting transition of the Pb/Sn manometer.

3. Results and Discussion

Figure 2 shows the onset of diamagnetic shielding for $Y_2C_2Br_2$ and $La_2C_2Br_2$. The transition of the Pb/Sn manometer has been subtracted for clarity of arrangement. The superconducting transition temperatures were gained from the intersection of the zero line with the linear part of the zfc susceptibility just below T_c. Other criteria for extracting T_c were also applied and are qualitatively in agreement with the present results. All samples exhibit a linear dependence of T_c with pressure. For $Y_2C_2I_2$ T_c increases with a rate of dT_c/dP=1.05(2) K/GPa, while for $Y_2C_2Br_2$, T_c decreases with a significantly smaller pressure coefficient dT_c/dP=−0.13(1) K/GPa. Figure 3 displays the normalized pressure dependencies of T_c for all

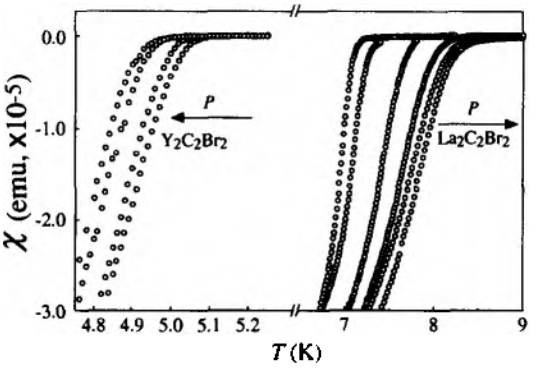

Figure 2. Diamagnetic shielding of samples No. 1 and 5 (Tab 1). The arrows indicate the shift in T_c when applying hydrostatic pressure of 0, 0.46, 0.79, 0.99, and 0.04, 0.16, 0.55, 0.83, 0.93, 0.99 GPa to $Y_2C_2Br_2$ and $La_2C_2Br_2$, respectively.

investigated samples. Results of the analyses of dT_c/dP are compiled in Tab. 1.

Specific heat analyses of the $Y_2C_2X_2$ superconductors reveal a strong electron phonon coupling which allows to discuss the $T_c(P)$ dependence in the scope of the Allen-Dynes equation [12] with the transition temperature $T_c(\lambda, \mu^*, \omega_{ph}, \omega_{ln})$ being a function of the electron-phonon coupling coefficient λ, the Coulomb pseudo potential μ^* and the generalized moments of the electron-phonon spectral densities ω_{ph} and ω_{ln}. Pressure dependence of μ^* may be neglected, while ω_{ph} and ω_{ln} may be expected to decrease monotonically with P. Thus, the change in sign of dT_c/dP in the $RE_2C_2X_2$ series must be related to the pressure dependence of the electron-phonon coupling constant λ which was introduced by McMillan [13].

$$\lambda = \frac{N(\epsilon_F)\,\langle g^2 \rangle}{M\,\langle \omega^2 \rangle} \qquad (1)$$

We assume that the electron matrix element $\langle g^2 \rangle$ is independent of pressure and the average squared phonon frequency $\langle \omega^2 \rangle$ increases smoothly with pressure due to lattice stiffening. The large variation of dT_c/dP (about one order of magnitude in the $Y_2C_2Br_{2-x}I_x$ system) and the change in sign of dT_c/dP must be attributed to a volume effect which mainly affects $N(\epsilon_F)$. The denominator in eq. (1) contains the ionic mass M.

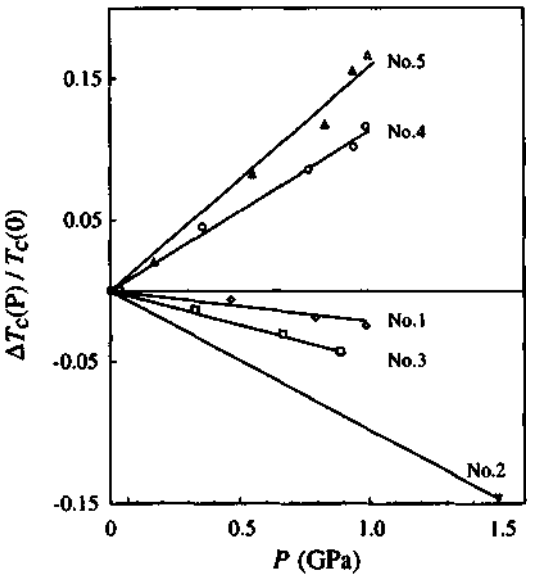

Figure 3. Normalized change in T_c versus the applied pressure. See tab. 1 for sample notation

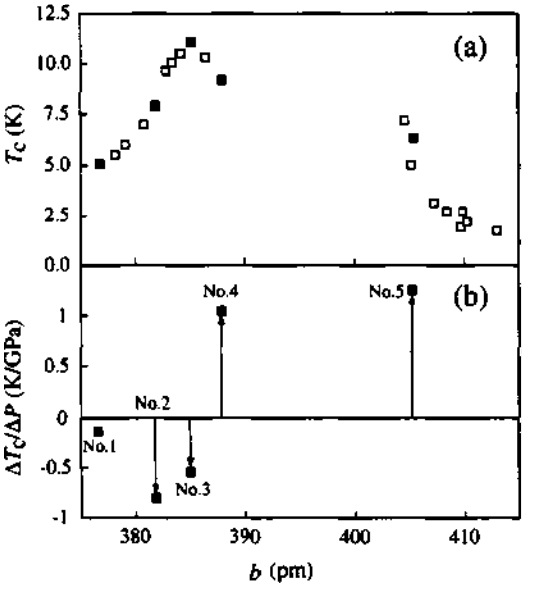

Figure 4. T_c versus b in the $Y_2C_2Br_{2-x}I_x$ and $La_2C_2Br_{2-y}I_y$ systems (a). The arrows indicate the pressure coefficient for the compounds which are depicted below (b). See tab. 1 for sample notation.

Band-structure calculations predict a van-Hove type peak in the DOS close to the Fermi energy for $Y_2C_2Br_2$ [7]. An analysis of the band structure via the fat-band representation reveals, that the involved flat bands at ϵ_F have mainly C-p and Y-d character. A rigid-band model may be assumed for the $Y_2C_2X_2$ system where the shape of the peak in the DOS around the Fermi-energy is nearly unchanged by halogen atom replacement. The Fermi level sweeps across this peak due to the volume expansion which is induced by increasing x in the $Y_2C_2Br_{2-x}I_x$ series. The cusp in T_c(x) was explained as due to this shift of ϵ_F through the peak in the DOS [6]. In Fig. 4(a), T_c is plotted versus the b-lattice parameter. This plot allows to extend the $Y_2C_2Br_{2-x}I_x$ series (b<400 pm) to the $La_2C_2Br_{2-y}I_y$ system (b>400 pm). The full squares indicate those compounds which have been used for the investigation of $T_c(P)$. The arrows in Fig. 4(b) show the pressure coefficients dT_c/dP for these compounds. For a low value of b, $T_c(b)$ increases slowly. A pressure coefficient of dT_c/dP=-0.13(1) K/GPa has been measured for $Y_2C_2Br_2$. The transition temperature then rises steeply with increasing b to reach a minimum value of dT_c/dP=-0.79(7) K/GPa for $Y_2C_2Br_1I_1$. For $Y_2C_2Br_{0.5}I_{1.5}$ the pressure coefficient dT_c/dP=-0.54(4) K/GPa is still negative though less than for $Y_2C_2Br_1I_1$. A further increase of b results in a downshift of T_c to 9.97 K for $Y_2C_2I_2$. This compound exhibits a large positive pressure coefficient of dT_c/dP=1.05(2) K/GPa. The $La_2C_2Br_{2-y}I_y$ series adds to the $Y_2C_2Br_{2-x}I_x$ system, however, well separated in the $T_c(b)$ plot. This is due to the change in the lattice parameters when replacing Y atoms by the larger La atoms. For the $La_2C_2Br_{2-y}I_y$ series $T_c(b)$ shows a sharp drop with increasing b. The largest dT_c/dP of 1.26(5) K/GPa has been observed for $La_2C_2Br_2$.

Applying hydrostatic pressure to the $RE_2C_2X_2$ systems obviously just reverses the band-structure effect induced by the replacement of

Table 1
Transition temperatures and pressure coefficients for the investigated samples with estimated errors in parentheses.

No.	compound	$T_c(0)$ (K)	dT_c/dP (K/ GPa)	$1/T_c(0)\cdot dT_c/dP$ (1/ GPa)
1	$Y_2C_2Br_2$	5.03(2)	-0.13(1)	-0.026(2)
2	$Y_2C_2Br_1I_1$	8.08(4)	-0.79(7)	-0.098(8)
3	$Y_2C_2Br_{0.5}I_{1.5}$	11.6(1)	-0.54(4)	-0.047(5)
4	$Y_2C_2I_2$	9.97(2)	1.05(2)	0.105(3)
5	$La_2C_2Br_2$	7.03(5)	1.26(5)	0.18(1)

Br by I. The shift of the Fermi energy by applying hydrostatic pressure or by halogen atom replacement scans the peak in the DOS which is paralleled by the observed variation in $T_c(b)$ and dT_c/dP respectively. In the case of $Y_2C_2Br_2$, the Fermi level is situated at the high-energy side of the peak. In the $Y_2C_2Br_{2-x}I_x$ series the crystal volume expands by increasing x (replacement of Br by the larger I) which is paralleled by a downshift of the Fermi energy. At $x \approx 1.5$, the Fermi level crosses the maximum of the peak in the DOS which is indicated by the maximum observed T_c=11.6 K for $Y_2C_2Br_{0.5}I_{1.5}$. A further expansion of the crystal volume then shifts ϵ_F to the low-energy side of the peak. In $T_c(b)$ regions with a high slope, $|dT_c/dP|$ is large, while it has smaller values for flat $T_c(b)$ regions. The sign of dT_c/dP is inverted with respect to the sign of $dT_c(b)/db$. A comparison of the $T_c(x)$ curve with the pressure coefficients gives a correspondence of the hydrostatic pressure of 1 GPa to the chemical pressure induced by a replacement of x=0.3±0.1 I by Br atoms in the $Y_2C_2Br_{2-x}I_x$ system.

In summary, we have measured the pressure coefficients dT_c/dP in the $RE_2C_2X_2$ systems, which vary strongly in amount and sign. This finding could be qualitatively explained as due to a distinct peak in the DOS at the Fermi level. Due to a volume effect, the Fermi energy sweeps through this peak by halogen atom replacement or by applying hydrostatic pressure in the $Y_2C_2Br_{2-x}I_x$ series. The interpretation is carried out in the scope of the Allen-Dynes formalism for strong coupling superconductors.

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