Influence of pressure on the properties of the layered superconductors $RE_2C_2Br_{2-x}I_x$ (RE = Y, La)

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Since the seminal papers by Ginzburg and Kirznits it is widely believed that two-dimensional layered materials provide optimum conditions for superconductivity with high T_c. Well known examples are the cuprate superconductors and more recently the 40 K superconductor MgB_2. Other superconductors with quasi-two-dimensional layered structures are the Ta and Nb dichalcogenides as well as organic superconductors which, however, display less spectacular transition temperatures. Of particular interest for superconductivity in layered materials is the question how the superconducting properties depend on the interlayer coupling. A variation of the coupling between the layers can be achieved by chemical means, as for example by doping with oxygen as demonstrated for the high-T_c cuprates or by intercalation as investigated for the dichalcogenides.

Another way to vary interlayer coupling and to change the superconducting properties is to apply external pressure. For example, the highest T_c of 164 K among the superconducting cuprates was obtained by applying pressure of 30 GPa to $HgCa_2Ba_2Cu_3O_{8+\delta}$. Superconductivity in the carbide halides of the rare earth metals $RE_2C_2X_2$ (RE = Y, La; X = Cl, Br, I) was discovered by Simon and coworkers in 1991 [see annual report I-77/1991]. The $RE_2C_2X_2$ compounds crystallize with layered structures with units of bilayers of close-packed rare earth metal atoms which are sandwiched between doublelayers of halogen atoms. The octahedral voids in the metal atom doublelayers 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 with a monoclinic structure. The C_2 orbitals are of essential importance regarding the electronic properties and the superconductivity of the $RE_2C_2X_2$ compounds: Overlap of antibonding $C_2 - \pi^*$

molecular orbitals with energetically neighboring RE–d states causes a shortening of the C–C distance with respect to an ordinary molecular C–C double bond. This covalency gives rise to electron delocalization and metallic character of the $RE_2C_2X_2$ compounds. To gain further insight into the electronic structure and superconducting properties we have carried out detailed pressure experiments.
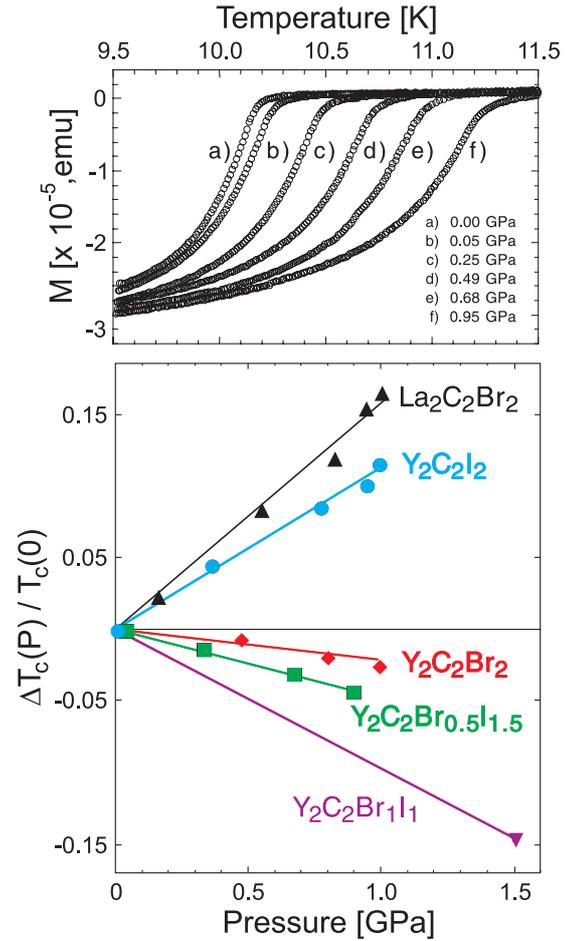

Figure 1: *Top: Magnetization of a sample of $Y_2C_2I_2$ at various pressures as indicated as obtained in a magnetic field of ≈ 0.5 mT. Bottom: Variation of T_c of various $RE_2C_2X_2$ with pressure.*

Depending on the particular system application of pressure may raise or decrease the critical temperature T_c. Figure 1 displays the magnetization of $Y_2C_2I_2$ as function of pressure indicating a rather sizable *increase* of T_c with pressure. An even larger relative pressure increase of T_c is observed for $La_2C_2Br_2$ showing a T_c of 7.03(5) K at ambient pressure. $Y_2C_2Br_2$ and other phases with a mixed halogen composition, however, undergo a decrease of T_c when pressure is applied.

Via the electron-phonon coupling constant λ this pressure dependence of T_c may be related to the variation of the electronic and the phononic system

$$\lambda \propto \frac{N(E_F)\langle g^2 \rangle}{\langle \omega^2 \rangle} \ . \tag{1}$$

If we assume that the electron-phonon matrix element $\langle g^2 \rangle$ and the average squared phonon frequency $\langle \omega^2 \rangle$ increase smoothly with pressure the large observed increase of T_c for $La_2C_2Br_2$ and $Y_2C_2I_2$ indicates a sizable increase of the electronic density of states $N(E_F)$ when the cell volume is reduced by applying pressure indicating a remarkably structured $N(E)$ close to the Fermi energy E_F.
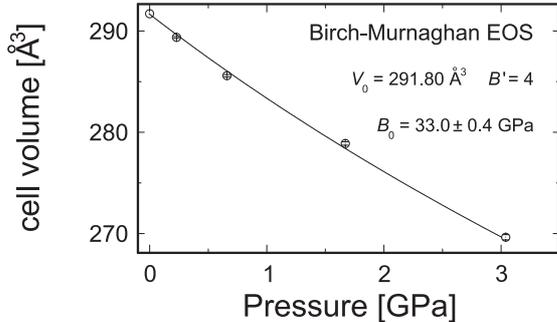

Figure 2: *Birch-Murnaghan fit (full line) to the pressure dependent cell volume data of $Y_2C_2I_2$ (POLARIS ISIS facility).*

To study the response of the lattice to pressure and to gain an estimate of $\langle \omega^2 \rangle$ we performed detailed powder neutron experiments under pressure of $Y_2C_2I_2$ ($T_c \approx 10$ K) using a Paris-Edinburgh type pressure cell at the ISIS POLARIS TOF diffractometer. Up to a pressure of ≈ 3 GPa we observe a monotonous decrease of the cell volume shown in Fig. 2. A least-squares fit to a Birch-Murnaghan relation converged to a bulk-modulus of 33.0(4) GPa.

Profile refinements with the Rietveld method of the neutron powder diffraction patterns collected with applied pressure provide the pressure dependent atomic coordinates and cell parameters (Figs. 3(a) and (b)). These data were used as input to calculate the electronic structure of $Y_2C_2I_2$ with high precision. The results verify a growth of the density of states at E_F by about 50% and demonstrate that the characteristic valley structure at E_F observed for $Y_2C_2I_2$ is gradually filled. Quantitative estimates with a reasonable assumption for the mode Grüneisen parameter reveal that lattice stiffening reduces the increase of T_c by about 30% due to the sheer pressure changes of the electronic structure.

Above ≈ 3.5 GPa we discover a new high-pressure phase of $Y_2C_2I_2$ (Fig. 3(d)). The diffraction pattern at 3.03 GPa shows loss of intensity, especially, of the peaks around 2.3 and 2.8 Å, respectively, and the emergence of a new peak at ≈ 2.5 Å (Fig. 3(c)). The pressure-induced structural phase transition is reversible but appears to leave considerable strain after pressure release and, in particular, sizable disorder between the layers. The pressure released samples have a reduced T_c of about 7 K. $T_c \approx 10$ K can be restored by reannealing the samples for 1 day at 1050°C.

Detailed further investigations using neutron powder and X-ray powder techniques are underway to solve the crystal structure of the new high pressure phase of $Y_2C_2I_2$ and to search for pressure-induced phase transitions in the other phases of the superconducting layered rare earth carbide halides.
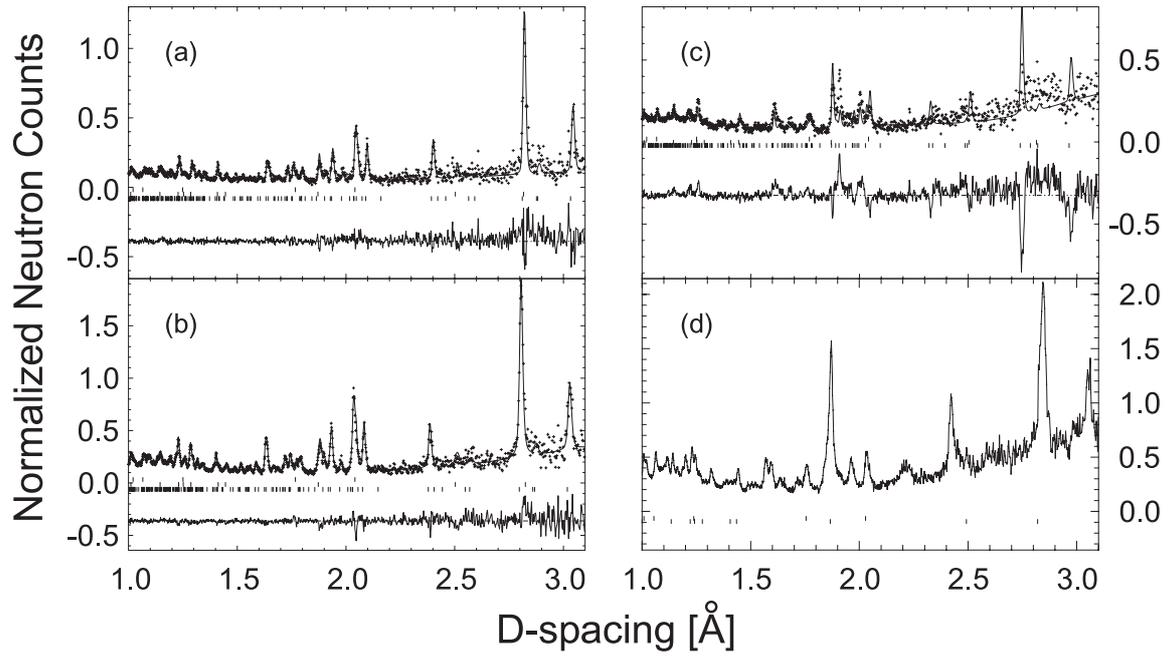
Figure 3: *Neutron powder patterns of a sample of $Y_2C_2I_2$ at (a) 0.14 GPa, (b) 0.72 GPa, respectively. Data collected at $2\theta = 90°$ are shown as dots. The solid lines are the results of Rietveld profile refinements. Vertical bars indicate the position of the reflections used to generate the patterns. Upper bar row, medium bar row and low bar row indicate the reflections of the Ni gasket, WC anvils and of the $Y_2C_2I_2$ samples, respectively. The lower solid lines represent the difference between the observed and calculated patterns. Diffraction patterns at (c) 3.03 GPa show the results of comparison with a theoretical pattern indicating significant deviations from the ambient pressure to be present. (d) Diffraction pattern at 6.0 GPa evidences the new high-pressure phase. (The reflections emerging from the Ni gasket and the WC anvils are indicated by the vertical bars.)*