ACADEMIC
PRESS

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Solid State Chemistry 171 (2003) 367–370

JOURNAL OF
SOLID STATE
CHEMISTRY

http://elsevier.com/locate/ jssc

Pressure dependence of T_C of the layered superconductor $Y_2C_2I_2$: lattice versus electronic effects

Kyungsoo Ahn,[a] Andrzej Grzechnik,[a] Reinhard K. Kremer,[a,*] Arndt Simon,[a]
and William G. Marshall[b]

[a] Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany
[b] ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK

Received 7 May 2002; received in revised form 1 September 2002; accepted 4 September 2002

Abstract

The response to application of pressure of the crystal structure of the 10 K layered rare-earth carbide halide superconductor $Y_2C_2I_2$ is studied. We find an anisotropic response with largest compression perpendicular to the metal atom layers. From the decrease of the cell volume with pressure the equation of state is established using a bulk modulus of 37(1) GPa. It is concluded that the large increase of T_C with pressure ($1/T_C\,\mathrm{d}T_C/\mathrm{d}P = 0.13(1)\ \mathrm{GPa}^{-1}$) is due to a growth of the electronic density of states with pressure for which a value of $1/N(E_F)\,\mathrm{d}N(E_F)/\mathrm{d}P$ to ≈ 0.12 states/eV GPa is estimated.

Keywords: Superconductivity; Layered superconductors; Rare-earth carbide halides; Pressure dependence; Bulk modulus; Equation of state; Neutron powder diffraction; X-ray powder diffraction

It is generally believed that compounds with layered structures provide optimal conditions for superconductivity with high T_C [1–3]. Well-known examples are the high-T_C oxocuprate superconductors and the recently discovered 40 K superconductor MgB_2 [4]. The interlayer coupling plays a crucial role for the superconducting properties. Variation of the coupling between the layers can be achieved by chemical means, as e.g. by doping with oxygen as for the high-T_C oxocuprates or by intercalation with *pd* donors. Another efficient way to tune the interlayer coupling and by this to enhance T_C is to apply external pressure. For example, the highest T_C reached in the oxocuprates so far was obtained in $HgCa_2Ba_2Cu_3O_{8+\delta}$ at 30 GPa hydrostatic pressure [5].

In the past years, our group has intensively investigated the chemical and physical properties of the carbide halides of the rare-earth metals, $RE_2C_2X_2$ (X = Cl, Br, I and RE being a rare-earth metal) [6]. These phases crystallize with layered structures which contain double layers of close-packed metal atoms with C_2 units occupying the RE octahedral voids [7,8]. These double layers are sandwiched by layers of halogen atoms to form X–RE–C_2–RE–X slabs which connect via van der Waals forces in stacks along the crystallographic *c*-axis (cf. Fig. 1). Compounds containing the nonmagnetic rare-earth metals Y and La are superconductors with a maximum T_C of 11.6 K which was achieved by adjusting the composition in the quasi-ternary phases $Y_2C_2(X,X')_2$ [9].

In a preceding paper we have reported the pressure dependence of T_C of several $RE_2C_2X_2$ (RE = La, Y; X = Br I) [10]. The variation of the T_C's with pressure was found markedly different for this series, not only in magnitude but also in sign: an increase of 20% and 10% for $1/T_C\,\mathrm{d}T_C/\mathrm{d}P$ has been detected for $La_2C_2Br_2$ and $Y_2C_2I_2$, respectively, while T_C decreases with pressure for $Y_2C_2Br_2$ and $Y_2C_2Br_{0.5}I_{1.5}$ by about 3–4%. The increase of T_C with pressure as observed for $Y_2C_2I_2$ and $La_2C_2I_2$ is remarkable and parallels the findings e.g. in the high-T_C oxocuprates $YBa_2Cu_4O_8$ and underdoped $YBa_2Cu_3O_x$ ($x<7$) but also for *fcc*-La for which similar values for the relative increase of T_C, $1/T_C\,\mathrm{d}T_C/\mathrm{d}P$, have been detected (see e.g. Ref. [11]).

A decrease of T_C with pressure as observed in $Y_2C_2Br_2$ and $Y_2C_2Br_{0.5}I_{1.5}$ can be understood as a consequence of lattice stiffening upon pressure. The increase of T_C with pressure seen for $Y_2C_2I_2$ and

---

*Corresponding author. Fax: +49-711-689-1689.
E-mail address: rekre@cesux.mpi-stuttgart.mpg.de (R.K. Kremer).

0022-4596/03/$ - see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S0022-4596(02)00214-1

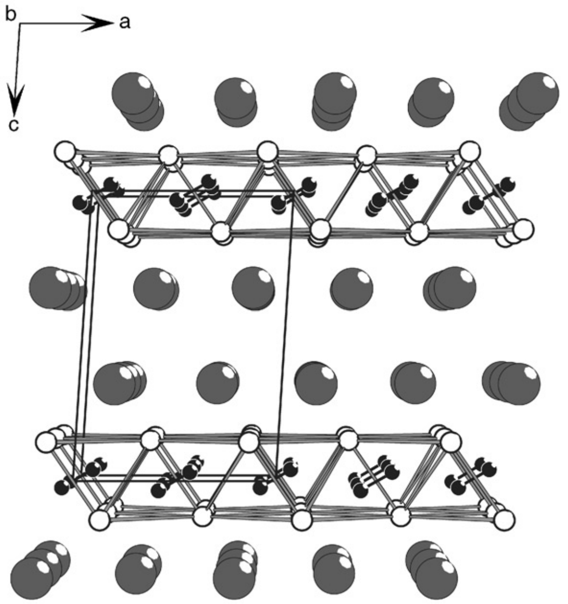

Fig. 1. Crystal structure of 1s-$Y_2C_2I_2$ with a unit cell outlined. C, Y, and I are displayed with increasing size.

$La_2C_2I_2$ was qualitatively assigned to a peak in the electronic density of states which by applying pressure sweeps through the Fermi energy and outweighs the lattice stiffening effect [10]. We expect that lattice stiffening would lead to a decrease of T_C similar to that observed for $Y_2C_2Br_2$ and $Y_2C_2Br_{0.5}I_{1.5}$. A more quantitative analysis of the two opposing effects, however, could not given in Ref. [10] since detailed compressibility data were missing.

Here, we report a study of the pressure dependence of the structural properties of $Y_2C_2I_2$. $Y_2C_2I_2$ exhibits the highest T_C of 10 K among all ternary $RE_2C_2X_2$ phases. In addition, a very large pressure-induced increase of T_C is observed. The objective of this study is to estimate the effect of pressure on the lattice vibrations and to derive the magnitude of the electronic contribution to the T_C increase with pressure by a comparison with the experimental results.

Polycrystalline samples of $Y_2C_2I_2$ were prepared from appropriate mixtures of Y, YI_3 and carbon powder as described in detail elsewhere [12]. A slight excess of carbon ($\approx 5\%$) was added to achieve a T_C slightly above 10 K [13]. The superconducting properties of the sample at ambient pressure were determined by electrical resistivity, dc susceptibility (Quantum Design MPMS) and heat capacity experiments (Quantum Design PPMS). The dependence of T_C on pressure $P \leqslant 1$ GPa was obtained from the dc susceptibility of a sample of ≈ 1 mg $Y_2C_2I_2$ employing a piston-type Cu–Be pressure cell [14][1] and Fluorinert as pressure medium. The pressure was determined by simultaneously measuring T_C of a small splinter of high-purity Pb following the data of Eiling et al. [15]. Neutron powder diffraction at room temperature was carried out at the ISIS POLARIS TOF diffractometer at Rutherford Appleton Laboratory using a Paris–Edinburgh-type pressure cell. Pressures were determined from the pressure dependence of the lattice parameters of NaCl added as an internal standard [16]. Angle-dispersive X-ray powder patterns were measured on the ID9 beamline at the European Synchrotron Radiation Facility. Monochromatic radiation at $\lambda = 0.416425$ Å was used for pattern collection on image plates. The images were integrated using the program FIT2D [17] to yield intensities. The instrumental resolution (minimum full-width at half-height of diffraction peaks) was 0.03°. To improve powder averaging, the diamond anvil cell was rotated by ±3°. The ruby luminescence method was used for pressure determination [18]. The moisture sensitivity of the samples always precluded use of a pressure medium.

The magnitude of the heat capacity anomaly at T_C is similar to that reported previously for an early sample confirming bulk superconductivity for the present specimen [19,20]. The anomaly of the present sample, however, is somewhat sharper pointing to a reduced scatter of T_C over the sample and even more remarkably, the onset of superconductivity is found at 10.2 K, and clearly exceeds the T_C of all samples investigated so far. We attribute the increased T_C to an improved structural and chemical homogeneity achieved by minimizing carbon deficiency and repeated sintering of compacted pellets.

T_C clearly beyond 10 K was also detected in the dc susceptibility measurements (cf. Fig. 2). As found in a preceding investigation T_C shifts to higher values with increasing pressure. The increase of T_C found in our experiment is also linear with pressure and amounts to 1.3(1) K/GPa, slightly larger than reported before (cf. [10,21]). Up to 1 GPa no pressure hysteresis could be observed.

To establish the equation of state (EOS) neutron powder patterns of a sample of $Y_2C_2I_2$ mixed with about 10 wt% NaCl were collected at seven different pressure values. Apart from reflections related to $Y_2C_2I_2$ and NaCl additional reflections emerging from the pressure cell (WC) and from the Ni gasket could be identified in the powder patterns. Up to a pressure of about 1.7 GPa all reflections attributable to $Y_2C_2I_2$ can be readily indexed on the basis of the spacegroup determined in previous studies [21–23] with pressure-dependent cell parameters and cell volumes as displayed in Fig. 3. At a pressure of about 3 GPa, in addition to reflections from the ambient pressure phase of $Y_2C_2I_2$ the diffraction patterns contain reflections emerging from an apparent new high-pressure phase of $Y_2C_2I_2$. Indication for a structural phase transition in this

---

[1] Tetcon International, 3325 Huxley Drive, Mississauga, Ontario, Canada L5L 4N3.

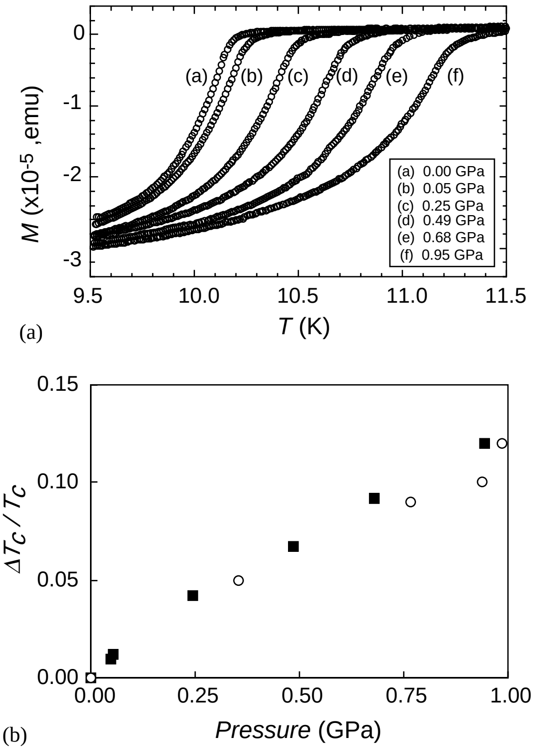

Fig. 2. (a) Meissner fraction of $Y_2C_2I_2$ at various pressures as indicated obtained in a magnetic field of ≈ 0.5 mT. (b) Variation of T_C with pressure (■: present sample; ○: data from Ref. [10]).

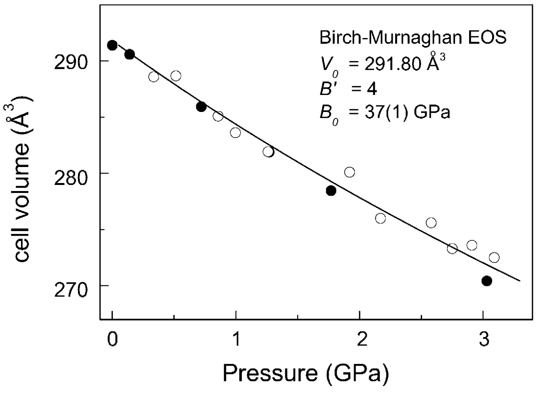

Fig. 3. Birch–Murnaghan fit to the pressure-dependent cell volume data of $Y_2C_2I_2$ (full line). Closed symbols: neutron diffraction data; open symbols: X-ray data.

pressure range was also found in the X-ray diffraction measurements. Details will be given in a forthcoming publication [24]. The compressibilities of $Y_2C_2I_2$ are distinctly anisotropic as may be expected from the layered character of the structure. The largest relative decrease is observed along the c direction with about 4% at 3 GPa while the compressibilities along a and b are more than a factor of two smaller. At small pressure values there is a small but perceptible nonlinearity in the decrease of the lattice parameters b and c.

The pressure-dependent cell volume was fitted to a Birch–Murnaghan EOS [25,26]:

$$P = \tfrac{3}{2} B_0 (v^{7/3} - v^{5/3})[1 + \tfrac{3}{4}(B' - 4)(v^{2/3} - 1)] \tag{1}$$

with P being the pressure, B_0 the bulk modulus at $P = 0$, $v = V_0/V(P)$ with V_0 and $V(P)$ the volume of the unit cell at $P = 0$ and at pressure P, respectively. B' is the derivative of B with respect to P. V_0 was fixed to 291.80(9) Å as obtained from laboratory based X-ray and neutron powder diffraction [21]. Initially the fits converged to $B' \approx 4$. Consequently, because of the limited number of data points we fixed B' to 4 in the final refinement in which satisfactory convergence was achieved with $B_0 = 37(1)$ GPa.

For the quantitative discussion of the pressure dependence of T_C we start from the Allen–Dynes modification of the McMillan equation [27,28]

$$T_C = \frac{\langle \omega_{\log} \rangle}{1.2} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1 + 0.62\,\lambda)} \right), \tag{2}$$

where λ is the electron-phonon coupling constant defined as

$$\lambda = \frac{N(E_F)\,\langle I^2 \rangle}{m \langle \omega^2 \rangle}. \tag{3}$$

$\langle I^2 \rangle$ is the square of the matrix element of the electron–phonon interaction averaged over the Fermi surface, m the atomic mass, μ^* the Morel–Anderson effective Coulomb pseudopotential [29], and $\langle \omega_{\log} \rangle$ and $\langle \omega^2 \rangle$ are averages over the phonon spectrum defined explicitly in Ref. [27]. The pressure dependence of T_C therefore arises from the pressure dependence of the electron–phonon coupling constant for which the pressure dependencies of the electronic density of states $N(E_F)$ and of the averaged phonon frequency $\langle \omega^2 \rangle$ in the denominator largely dominate the pressure dependence of the interaction matrix element $\langle I^2 \rangle$ in the numerator [28].

The pressure dependence of T_C can be expressed via the total differential as

$$\frac{\mathrm{d}\ln T_c}{\mathrm{d}P} = \frac{\partial \ln T_C}{\partial \lambda}\frac{\mathrm{d}\lambda}{\mathrm{d}P} + \frac{\partial \ln T_C}{\partial \langle \omega_{\log} \rangle}\frac{\mathrm{d}\langle \omega_{\log} \rangle}{\mathrm{d}P}. \tag{4}$$

Neglecting any pressure dependence of μ^* and following approximations suggested by Loa et al. [30] one arrives at

$$\frac{\mathrm{d}\ln T_c}{\mathrm{d}P} \approx C \frac{\mathrm{d}\ln N(E_F)}{\mathrm{d}P} + (1 - 2C)\frac{\gamma}{B_0} \tag{5}$$

with $C = (1.04 + 0.4\mu^*)\lambda/(\lambda - \mu^*(1 + 0.62\lambda))^2$.

With $\lambda \approx 1$ as estimated by Henn et al. from heat capacity measurements [19], $\mu^* \approx 0.1$, assuming a mode Grüneisen parameter $\gamma \approx 1$ and using the results for the bulk modulus $B_0 = 37(1)$ GPa and $1/T_C(0)\,\mathrm{d}T_C/\mathrm{d}P = 0.13(1)$ from Eq. (5) we obtain an increase of the electronic density of states with pressure, $1/N(E_F)\,\mathrm{d}N(E_F)/\mathrm{d}P$, of 0.12 states/eV GPa for $Y_2C_2I_2$. Without this increase of $N(E_F)$ with pressure T_C would decrease by an amount of $1/T_C \, dT_C/dP \approx -6\%$ which is in fact very close to the results found for $Y_2C_2Br_2$ and $Y_2C_2Br_{0.5}I_{1.5}$ due to pressure-induced lattice stiffening [10].

In summary, the presented results support the suggestion that the significant pressure-induced increase of T_C in the layered carbide halide superconductors $Y_2C_2I_2$ and $La_2C_2Br_2$ is due to a significant increase of the electronic density of states at E_F. The electronic states at E_F have $C_2\pi^*$ and also essential rare-earth d orbital character and reflect the backbonding of the carbon to the d orbitals which gives rise to the metallic character of the rare-earth carbide halides [9]. According to this pressure study the carbon–metal orbital overlap appears to be very sensitive to subtle structural changes. The associated electronic bands have low dispersion essentially due to the anisotropic nature of the crystal structure [12]. Mild variations of the crystal structure therefore may lead to significant changes in the electronic density of states. A more detailed analysis of the structural changes and particularly the atomic positions with pressure as well as electronic structure calculations using the atomic parameters of the compressed crystal structure are underway to understand the present results more quantitatively.

Acknowledgments

Useful discussions with O. Dolgov, J. Köhler, J. Kortus, I. Loa and K. Syassen are gratefully acknowledged. We thank E. Brücher, H. Eckstein, M. Hanfland, S. Höhn and G. Siegle for technical assistance.

References

[1] V.L. Ginzburg, D.A. Kirzhnits, Sov. Phys. JETP 19 (1964) 269.

[2] V.L. Ginzburg, D.A. Kirzhnits (Eds.), High-Temperature Superconductivity, Consultant Bureau, Plenum, New York, 1982.

[3] T.H. Geballe, in: S. Maekawa, M. Sato (Eds.), Physics of High-Temperature Superconductors, Springer Series in Solid-State Sciences, No. 106, Springer, Berlin, 1992, p. 339; T.H. Geballe, Science 259 (1993) 1550.

[4] J. Akimitsu, Symposium on Transition Metal Oxides, Sendai, January 2001; J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature 410 (2001) 63.

[5] L. Gao, Y.Y. Xue, F. Chen, Q. Xiong, R.L. Meng, D. Ramirez, C.W. Chu, J.H. Eggert, H.K. Mao, Phys. Rev. B 50 (1994) 4260.

[6] A. Simon, Hj. Mattausch, R. Eger, R.K. Kremer, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook of the Physics and Chemistry of Rare Earths, Vol. 15, Elsevier Science Publ., Amsterdam, 1991, p. 191.

[7] U. Schwanitz-Schüller, A. Simon, Z. Naturforsch. B 40 (1985) 710.

[8] Hj. Mattausch, R.K. Kremer, R. Eger, A. Simon, Z. Anorg. Allg. Chem. 609 (1992) 7.

[9] A. Simon, A. Yoshiasa, M. Bäcker, R.W. Henn, C. Felser, R.K. Kremer, Hj. Mattausch, Z. Anorg. Allg. Chem. 622 (1996) 123.

[10] R.W. Henn, K. Ahn, H.-A. Krug von Nidda, R.K. Kremer, A. Simon, Physica C 341–348 (2000) 719.

[11] J.S. Schilling, S. Klotz, in: D.M. Ginsberg (Ed.), Physical Properties of High Temperature Superconductors III, World Scientific, Singapore, 1992, and references cited therein.

[12] K. Ahn, B.J. Gibson, R.K. Kremer, Hj. Mattausch, A. Stolovits, A. Simon, J. Phys. Chem. B 103 (1999) 5446.

[13] K. Ahn, et al., A carbon deficiency of about 3% is sufficient to decrease T_C to ≈ 5 K, to be published.

[14] W. Gerhardt, Diploma Thesis, University Bochum, 1981, unpublished.

[15] A. Eiling, J.S. Schilling, J. Phys. F: Metal Phys. 11 (1981) 623.

[16] D.L. Decker, J. Appl. Phys. 42 (1971) 3239.

[17] A.P. Hammersley, S.O. Svensson, M. Hanfland, A.N. Fitch, D. Häusermann, High Pressure Res. 14 (1996) 235.

[18] H.K. Mao, J. Xu, P.M. Bell, J. Geophys. Res. 91 (1986) 4673.

[19] R.W. Henn, W. Schnelle, R.K. Kremer, A. Simon, Phys. Rev. Lett. 77 (1996) 374.

[20] W. Schnelle, R.W. Henn, Th. Gulden, R.K. Kremer, A. Simon, J. Appl. Phys. 83 (1998) 7321.

[21] R.W. Henn, Ph.D. Thesis, University Karlsruhe (TH), 1996.

[22] Hj. Mattausch, H. Borrmann, A. Simon, Z. Krist. 209 (1994) 281.

[23] R.W. Henn, T. Strach, R.K. Kremer, A. Simon, Phys. Rev. B 58 (1998) 14 364.

[24] K. Ahn, R.K. Kremer, A. Simon, W.G. Marshall, P. Puschnig, C. Ambrosch-Draxl, in preparation.

[25] F. Birch, J. Geophys. Res. 83 (1978) 1257.

[26] F.D. Murnaghan, Proc. Natl. Acad. Sci. USA 50 (1944) 244.

[27] P.B. Allen, R.C. Dynes, Phys. Rev. B 12 (1975) 905.

[28] W.L. McMillan, Phys. Rev. 167 (1968) 331.

[29] P. Morel, P.W. Anderson, Phys. Rev. 125 (1962) 1263.

[30] I. Loa, K. Syassen, Solid State Comm. 118 (2001) 279.