Unconventional superconductivity in weakly correlated, non-centrosymmetric \( \text{Mo}_3\text{Al}_2\text{C} \)

E. Bauer, G. Rogl, Xing-Qiu Chen, R.T. Khan, H. Michor, G. Hilscher, E. Royanian, K. Kumagai, D.Z. Li, Y.Y. Li, R. Podloucky, and P. Rogl

1 Institute of Solid State Physics, Vienna University of Technology, A-1040 Wien, Austria
2 Institute of Physical Chemistry, University of Vienna, A-1090 Wien, Austria
3 Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China
4 Division of Physics, Graduate School of Science, Hokkaido University, Sapporo, 060-0810, Japan

(Dated: July 5, 2010)

Electrical resistivity, specific heat and NMR measurements classify non-centrosymmetric \( \text{Mo}_3\text{Al}_2\text{C} \) (\( \beta\)-Mn type, space group \( P4_32 \)) as a strong-coupled superconductor with \( T_c = 9\) K deviating notably from BCS-like behaviour. The absence of a Hebel-Slichter peak, a power law behaviour of the spin-lattice relaxation rate (from \( ^{27}\text{Al} \) NMR), a \( T^4 \) temperature dependence of the specific heat and a pressure enhanced \( T_c \) suggest unconventional superconductivity with a nodal structure of the superconducting gap. Relativistic DFT calculations reveal a splitting of degenerate electronic bands due to the asymmetric spin-orbit coupling, favouring a mix of spin-singlet and spin triplet components in the superconducting condensate, in absence of strong correlations among electrons.

PACS numbers: 74.25.Bt, 74.70.Ad, 72.15.Eb

Carbides based on Mo comprise a large body of refractory compounds, where carbon atoms (in trigonal prismatic or octahedral \( \text{Mo}_6\text{C} \) subunits) occupy a fraction of the interstitial sites either in an ordered or in a random manner. Among Mo-based carbides for which superconductivity (SC) was reported (\( \alpha \text{MoC} \) at \( T_c = 9.95\) K, \( \eta \text{MoC} \) at 7.57 K, \( \text{Mo}_2\text{BC} \) at 6.33 K and \( \text{Mo}_3\text{Al}_2\text{C} \) at 9.05 K) the crystal structure of \( \text{Mo}_3\text{Al}_2\text{C} \) is outstanding, since the respective \( \beta\)-Mn type does not possess a center of inversion \( \beta \). The missing inversion symmetry might initiate a mixture of spin-singlet and spin-triplet pairs in the SC condensate \( \eta \) as was recently proposed to explain SC in \( \text{CePt}_3\text{Si} \), \( \text{UIr} \), \( \text{CeRhSi}_3 \), and \( \text{CeIrSi}_3 \). Non-centrosymmetry (NCS) of the crystal structure introduces an electrical field gradient and, thereby, creates a Rashba-type antisymmetric spin-orbit coupling \( \alpha \).

The Ce and U-based SCs indicated above are characterised by heavy fermion behaviour at low temperatures provoked by Kondo interaction. NCS in such systems can lead to new anomalous spin fluctuations, stabilizing triplet pairing, in addition to the singlet part \( \alpha \). On the other hand, a variety of SCs has been identified, which lacks strong electron correlations as well as a centre of inversion. For a recent listing of these systems see Ref. \( \beta \). Except Li\(_2\)Pt\(_3\)B \( \gamma \), all yet studied NCS SCs without strong correlations among electrons are typical \( s\) wave fully gapped BCS SC either weakly or strongly coupled.

In order to shed light onto the primary mechanism activating unconventional SC, we are searching for systems where SC occurs in absence of inversion symmetry, and also in absence of strong electron correlations. Revisiting \( \text{Mo}_3\text{Al}_2\text{C} \) (\( \beta\)-Mn structure), we aim to extend research done in the 1960’s \( \delta \), providing insight into microscopic features and the electronic structure.

For the preparation of \( \text{Mo}_3\text{Al}_2\text{C} \) an elemental powder mixture (purity > 99.9 mass\%, about 5 g) was cold compacted, reacted in a high vacuum furnace for 24 hrs at 1500°C with one intermediate grinding and compacting step. Afterwards the material was ball milled and hot pressed at 1250°C at 56 MPa. Refinement of the crystal structures was performed with the program Fullprof \( \epsilon \). Measurements of physical properties were carried out with standard techniques \( \zeta \). The density functional theory (DFT) calculations were performed with the Vienna ab initio Simulation Package (VASP) \( \eta \). For details see our recent paper on NCS \( \text{BaPtSi}_3 \).

X-ray Rietveld refinement confirmed a cubic, non-centrosymmetric structure (space group \( P4_32 \)), isotypic to the \( \beta\)-Mn type; see Fig. \( 1 \).

Measurements of the temperature dependent electrical resistivity \( \rho \) of \( \text{Mo}_3\text{Al}_2\text{C} \) clearly evidences metallic be-

![FIG. 1: Rietveld refinement (Guinier-Huber image plate system, CuK\(_{\alpha1}\)) and crystallographic data of \( \text{Mo}_3\text{Al}_2\text{C} \). The inset shows a 3-dimensional view of the crystal structure. Traces of \( \text{Mo}_2\text{C} \) are indicated by vertical bars.](image-url)
haviour and indicate a SC phase transition at $T_c = 9$ K (see Fig. 2), in agreement with the data reported by Johnston et al. 18. SC with almost 100% volume fraction is revealed from magnetic susceptibility measurements as well. Since the absolute resistivity values are large, the parallel resistance model (compare e.g., Ref. 18) can be used to describe $\rho(T)$, where the ideal resistivity follows from the Bloch-Gruneisen model. A fit employing this model is shown in Fig. 2 as a solid line, revealing a Debye temperature $\theta_D = 286$ K and a saturation value $\rho_{sat} = 350 \mu\Omega cm$. An estimation of the electron-phonon interaction strength $\lambda_{e,ph}$ is possible in terms of the McMillan formula 17. Applying this model, and taking the repulsive screened Coulomb part $\mu^* \approx 0.13$, yields $\lambda_{e,ph} \approx 0.8$; this characterizes Mo$_3$Al$_2$C as a SC well beyond the weak coupling limit.

The pressure dependence of $T_c$ of Mo$_3$Al$_2$C is displayed in the inset of Fig. 2. Obviously, $T_c(p)$ increases, but tends to saturate for high pressures. An increase of $T_c$ is rarely found in a simple materials; rather, such a behaviour frequently occurs in unconventional SCs like in high temperature SCs, in various pyrochlores, in some Fe-pnictides or heavy fermion materials. Bogolyubov et al. 18 demonstrated that there are two principal parameters determining $T_c$: $\theta_D$ and the electronic density of states at the Fermi energy, $N(E_F)$. Since the application of pressure hardly modifies $\rho(T, p)$ in the normal state region (not shown here), $\theta_D(p)$ remains unchanged. Thus, a slight increase of $N(E_F)$ is concluded, enhancing $T_c$ on pressurizing Mo$_3$Al$_2$C.

Fig. 3 shows the temperature dependent specific heat $C_p$ of Mo$_3$Al$_2$C taken at 0 T and plotted as $C_p/T$ vs. $T^2$. Bulk SC is evidenced from a distinct anomaly at 9 K, rendering the onset of the SC phase transition. A closer inspection of the data gives evidence of various non-BCS like features: i) The jump of the specific heat at $T_c$, $\Delta C_p/(\gamma T_c) \approx 2.28$, is well above the value expected for an s-wave BCS SC with $\Delta C_p/(\gamma T_c) \approx 1.43$. This clearly evidences strong-coupling SC. ii) The temperature dependent heat capacity below $T_c$ significantly deviates from the universal BCS dependence as indicated by the solid line. Rather, a power law with $C_p(T < T_c) \propto T^3$ is obvious from the experimental data (compare Fig. 3), which is sketched by the dashed line as well. Such a temperature dependence excludes a fully gapped SC state; instead, a nodal structure is likely, where the SC gap vanishes along points.

The $1/T_1$ $^{27}$Al relaxation rate, taken at $\mu_0 H = 1.24$ T and partially at 6.95 T is plotted in Fig. 3(b) on a double logarithmic scale. A Hebel-Slichter peak right at $T_c$ is absent. This is compatible with a partial disappearance of the SC gap at the Fermi energy, in line with non-s-wave

TABLE I: Normal state and SC properties of Mo$_3$Al$_2$C.

| Crystal structure | Space group | Lattice parameter |
|-------------------|-------------|-------------------|
| Cubic, $\beta$-Mn type | $P4_132$ | $a = 0.68630$ nm |
| Sommerfeld value | $\gamma_n \approx 17.8$ mJ/molK$^2$ | $\theta_D = 315$ K |
| Debye temperature | |
| Transport mean free path | $\lambda_{e,ph} \approx 0.8$ | $\lambda_{e,ph} \approx 1.8$ |
| Upper critical field slope | $\mu_0 H_{c2}(0) \approx 15.7$ T | $\mu_0 H_{c2} \approx 3$ T/K |
| Thermodynamic critical field correlation length | $\mu_0 H_{c1}(0) \approx 0.146$ T | $\xi \approx 4.6$ nm |
| Ginzburg-Landau parameter | $\kappa_{GL} \approx 76$ | $\kappa_{GL} \approx 76$ |
| London penetration depth | $\lambda \approx 380$ nm | $\lambda \approx 380$ nm |
| Nodal structure | Point-nodes | Point-nodes |
paramagnetism and spin-orbit scattering. Two parameters, the Maki parameter $\alpha$ (Pauli paramagnetic limitation) $^{24}$ and spin-orbit scattering $\lambda_{so}$ specify this model. While an increase of $\alpha$ decrements the upper critical field, an increase of $\lambda_{so}$ compensates the former, restoring for $\lambda_{so} \rightarrow \infty$ a maximum field constrained from orbital pair breaking only. In a first approximation, the Maki parameter $\alpha$ can be derived from $\gamma$ and $\mu_0 H_{c2}^{\prime}$, resulting in $\alpha = 1.32$. Alternatively, $\alpha$ can be estimated from $\mu_0 H_{c2}^{*}$ $^{24}$, revealing $\alpha^* = 1.6$. The sizable Maki parameter of both approximations is an indication that Pauli limiting is non-negligible in Mo$_3$Al$_2$C.

Using $\alpha = 1.32$ ($\alpha^* = 1.6$) and $\mu_0 H_{c2}^{*} = -3$ T/K yields $\mu_0 H_{c2}(T)$ as displayed as solid and dashed lines in Fig. 4(b) for $\lambda_{so} = 1.4$ and $\lambda_{so} = 2.5$, respectively, with $\mu_0 H_{c2}(0) \approx 15.7$ T. The Pauli limiting field follows from $\mu_0 H_{p}(0) = \sqrt{2}\mu_0 H^{*}(0)/\alpha$, where $\mu_0 H^{*}(0) = 18.72$ T, is the WHH result for $\alpha = 0$, i.e., the orbital limit. Thus, $\mu_0 H_{p}(0) = 20$ T for the former and 16.5 T for the latter value of $\alpha$. These values are in line with $\mu_0 H_{p}(1.2 \text{ K}) = 15.6$ T reported by Fink et al. $^{23}$. In the case of strong coupling superconductivity, these values are further en-

![Image 1](https://via.placeholder.com/150)

FIG. 4: (Color online) (a) Temperature and field dependent specific heat $C_p$ of Mo$_3$Al$_2$C. (b) Temperature dependent upper critical field $\mu_0 H_{c2}$ and thermodynamic critical field $\mu_0 H_c$ as obtained from specific heat measurements. The solid and the long-dashed lines are fits according to the WHH model for different values of the Maki parameter. The horizontal bar indicates the upper critical field $\mu_0 H^{*}(0)$ in absence of Pauli-limiting. The dashed-dotted line is an extrapolation of the thermodynamic critical field towards zero.

![Image 2](https://via.placeholder.com/150)

FIG. 5: (Color online) (Upper panel) Section of relativistic total and atom-projected densities of states (DOS) in states eV$^{-1}$ for Mo$_3$Al$_2$C summed over all three Mo atoms for the energy range $\pm 1$ around the Fermi energy $E_F$. (Lower panel): Relativistic electronic band structure along high symmetry directions for Mo$_3$Al$_2$C in the energy range $\pm 1$. eV around the Fermi energy $E_F$. SC. Below $T_c$, a non-exponential but rather a $T^n$ temperature dependence hints towards a nodal structure, closing partially the SC gap at the Fermi surface. We note that a $1/T_1 \propto T$ component, expected as a signature of a finite impurity density of states, is clearly absent in our low temperature data. Volovik and Gorkov $^{20}$ have shown that a proportionality of the density of states according to $N(E) \propto E^m$ results in a NMR relaxation rate $1/T_1 \propto T^{2n+1}$. Thus, an anisotropic gap with nodal structures yields, in general, a $T^n$ power law of $1/T_1$ with $n = 3$ for line nodes and $n = 5$ for point nodes. Intersecting nodes, however, might modify such simple temperature dependencies. $^{21}$ Furthermore, Hayashi et al. $^{22}$ demonstrated that NCS SCs with mixed spin singlet and triplet states infer a rather unconventional $1/T_1$ relaxation rate.

Summarized in Fig. 4(a) is the field and temperature dependent heat capacity of Mo$_3$Al$_2$C, highlighting the suppression of SC upon the application of a magnetic field. The fact that even fields of 11 T do not suppress superconductivity evidences a large upper critical field $\mu_0 H_{c2}$ as well as a large initial slope $\mu_0 H_{c2}^{\prime}$. The extension of the normal state behaviour towards lower temperatures with rising magnetic fields allows to obtain in a standard manner the Sommerfeld value $\gamma = 17.8$ mJ/molK$^2$ and $\theta_D \approx 315$ K (compare Fig. 4(a), inset). The accurate determination of $\gamma$ and of $T_c(\mu_0 H)$ was accomplished by idealizing the heat capacity anomaly under the constraint of entropy balance between the superconducting and the normal state. $T_c(\mu_0 H)$ obtained from Fig. 4(a) is plotted in Fig. 4(b).

The temperature dependency of $\mu_0 H_{c2}$ is described following the model of Werthammer et al. $^{23}$, incorporating orbital pair-breaking, the effect of Pauli spin
hanced according to $H^{	ext{str}}(\epsilon) = H_p(\epsilon)(1 + \lambda_{\text{ph}})^{\epsilon}$ with $\epsilon = 0.5$ or 1.0 [26, 27]. Hence, Pauli limiting is not the principal mechanism restricting the upper critical field in Mo$_3$Al$_2$C, but is present in a relevant size.

The thermodynamic critical field $\mu_0 H_c(T)$ derived from heat capacity data (compare e.g. Ref. [8]) is shown in Fig. 4(b) by open squares; an extrapolation to $T \to 0$ (dashed-dotted line) yields $\mu_0 H_c(0) \approx 0.146$ T.

SC and normal state parameters of Mo$_3$Al$_2$C can be assessed from $\gamma$, $\mu_0 H_{c2}$, $\mu_0 H_{c2}(0)$ and $\rho_0$ [24, 28]. From the Ginzburg Landau theory with the thermodynamic critical field as primary input, the coherence length, the Ginzburg Landau parameter and the London penetration depth are calculated. Parameters are summarized in Table I. Based on the estimate $\Delta T/\xi \approx 0.66$ we classify Mo$_3$Al$_2$C as a superconductor in the dirty limit; $\kappa_{GL} \approx 76$ refers to a type II superconductor.

A section of the calculated electronic density of states (DOS) of Mo$_3$Al$_2$C is shown in Fig. 3 for a relativistic calculation including spin orbit coupling (upper panel). The DOS around the Fermi energy stems primarily from Mo-4$d$ states, whilst the contribution of Al and C is almost negligible. The low partial Al DOS calculated at $E_F$ corresponds well to the NMR Korringa constant, $T_K = 11$ sK ($1/T_K \propto N(E_F)^2$). A comparison with Al metal ($T_K = 1.8$ sK) reveals a local Al DOS in Mo$_3$Al$_2$C of about 3% with respect to the total DFT DOS.

The Fermi energy $E_F$ of Mo$_3$Al$_2$C is located in a local maximum of the DOS; its large value favours SC. Employing the Sommerfeld expansion, $N(E_F) = 5.48$ states/eV corresponds to $\gamma_F = 12.9$ mJ/molK$^2$, in fair agreement with $\gamma_F = 12.9$ mJ/molK$^2$.

The lower panel of Fig. 3 displays the DFT electronic band structures along high symmetry directions for Mo$_3$Al$_2$C. With respect to a non-relativistic calculation (not shown here), the degenerate bands become split due to the lack of inversion symmetry in Mo$_3$Al$_2$C.

Specifically, for all bands crossing the Fermi energy the degeneracy is lifted, separating spin-up and spin-down electrons. This provides conditions for the occurrence of spin-singlet and spin-triplet Cooper pairs, leading to two gap functions, where each gap is defined on one of the two bands formed by degeneracy lifting. Superposition of these gaps is presumed to constitute a nodal structure of the resulting SC gap as corroborated from the present experimental data.

In conclusion, electrical resistivity, specific heat and NMR measurements classify non-centrosymmetric Mo$_3$Al$_2$C as a strong-coupled SC with $T_c = 9$ K. The temperature dependent specific heat and the $1/T_1$ NMR relaxation rate deviate from BCS predictions, thus referring to a nodal structure of the superconducting gap even though SC of Mo$_3$Al$_2$C occurs in the dirty limit. This manifests a robustness of the unconventional order parameter of the NCS superconductor. Moreover, unconventional pairing is in line with the splitting of electronic bands due to the asymmetric spin-orbit coupling as revealed from relativistic DFT calculations. These split bands might be the cause of a mixing of spin-singlet and spin-triplet Cooper pairs, which otherwise are distinguished by parity [2], making a nodal structure likely [23, 24]. Whilst this proposition has been corroborated for SCs with strong correlations among electrons, specific heat data unambiguously disprove a strongly correlated electronic state in Mo$_3$Al$_2$C. In spite of a lack of correlations, unconventional SC seems to arise from a substantial band splitting and the fact that inversion symmetry is missing in all crystallographic directions. In these respects, Mo$_3$Al$_2$C is the only example besides isomorphous Li$_2$Pt$_3$B [9].

Work supported by the Austrian Science Foundation FWF P22295. X.-Q.C acknowledges the support from the “Hundred Talents Project” of CAS.

[1] L.E. Toth and J. Zbasnik, Acta Met., 16, 1177 (1968).
[2] L.P. Gor’kov and E.I. Rashba, Phys. Rev. Lett. 87, 037004 (2001).
[3] E. Bauer et al., Rev. Lett., 92, 027003 (2004).
[4] T. Akazawa et al., J. Phys.: Cond. Mat. 16, L29 (2004).
[5] N. Kimura et al., Phys. Rev. Lett. 95, 247004 (2005).
[6] I. Sugitani et al., J. Phys. Soc. Japan 75, 043703 (2006).
[7] T. Takimoto and P. Thalmeier, J. Phys. Soc. Japan, 78, 103703 (2009).
[8] E. Bauer et al., Phys. Rev. B, 80, 064504 (2009).
[9] H. Q. Yuan et al., Phys. Rev. Lett. 97, 017006 (2006).
[10] L. E. Toth, in Transition Metal Carbides and Nitrides, Refractory Materials, Vol. 7, A Series of Monographs, Ed. J.L. Margrave, Acad Press Inc., NY & London, 1971.
[11] J. Rodriguez-Carvajal, Physica B 192, 55 (1993).
[12] E. Bauer et al., Phys. Rev. B 66, 214421 (2002).
[13] E. Bauer et al., Phys. Rev. B 76, 014528 (2007).
[14] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996); G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1996).
[15] J. Johnston et al., Solid State Commun., 2, 123 (1964).
[16] O. Gunnarsson et al., Rev. Mod. Phys. 75, 1085 (2003).
[17] W. L. McMillan, Phys. Rev. 167, 331 (1968).
[18] N.N. Bogoliubov et al., Fortschr. Physik 6, (1958) 605.
[19] B. Mülhschlegel, Z. f. Physik 155, 313 (1959).
[20] G.E. Volovik and L.P. Gor’kov, Sov. Phys.-JETP 61, 843 (1985).
[21] Y. Hasegawa, J. Phys. Soc. Japan, 65, 3131 (1996).
[22] N. Hayashi et al., Phys. Rev. B 73, 092508 (2006).
[23] N.R. Werthamer et al., Phys. Rev. 147, 295 (1966).
[24] K. Maki, Phys. Rev. 148, 392 (1966).
[25] H.J. Fink et al., Phys. Rev. 138, A1710 (1965).
[26] T.P. Orlando et al., Phys. Rev. B 19, 4545 (1979).
[27] M. Schossmann and J.P. Carbotte, Phys. Rev. B 39, 4210 (1989).
[28] See, for example M. Tinkham, Introduction to Superconductivity, McGraw-Hill, New York, 1975.
[29] P. A. Frigeri et al., Phys. Rev. Lett. 92, 097001 (2004).