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# Multiple Superconducting States Induced by Pressure in $\text{Mo}_3\text{Sb}_7$

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## Abstract:

Tuning competing ordering mechanisms with hydrostatic pressure in the  $4d$  intermetallic compound  $\text{Mo}_3\text{Sb}_7$  reveals an intricate interplay of structure, magnetism, and superconductivity. Synchrotron x-ray diffraction and magnetic susceptibility measurements, both employing diamond anvil cell technologies, link a first-order structural phase transition to a doubling of the superconducting transition temperature. In contrast to the spin-dimer picture for  $\text{Mo}_3\text{Sb}_7$ , we deduce from x-ray absorption near edge structure and dc magnetization measurements at ambient pressure that  $\text{Mo}_3\text{Sb}_7$  should only possess very small, itinerant magnetic moments. The pressure evolution of the superconducting transition temperature strongly suggests its enhancement due to a difference in the phonon density-of-states with changed crystal symmetry.

## I. INTRODUCTION

The interplay of spin, charge, and lattice degrees of freedom in the 4*d* intermetallic compound Mo<sub>3</sub>Sb<sub>7</sub> captures both the excitement and the difficulty of understanding the emergence of collective quantum states. Examples range from metal-insulator transitions [1] to density waves [2] to superconductors [3-8]. In Mo<sub>3</sub>Sb<sub>7</sub> itself, superconductivity emerges below a structural phase transition with claims of accompanying magnetic order and spin dimerization [9-11], potentially placing it in a growing cohort of exotic superconductors with unconventional pairing mechanisms [4, 12-14].

For both phonon and spin-fluctuation driven superconductivity, the charge or spin couplings between itinerant electrons can be described by the susceptibility,  $\chi_{c,m}(\mathbf{q}, \omega)$ , with *c* and *m* referring to the charge and magnetic character, respectively, and the excitation modes characterized by momentum  $\mathbf{q}$  and energy  $\hbar\omega$  [4]. While ferromagnetic spin fluctuations suppress phonon-mediated superconductivity, the relationship between antiferromagnetic spin fluctuations and phonon-mediated superconductivity is less transparent. This relationship is a key aspect of the physics of systems such as the cuprates, heavy fermion materials, iron pnictides, organic superconductors, rare-earth borocarbides, and the 3*d* transition-metal compounds CrAs and MnP [3-7, 15-18]. Tuning system properties with pressure, chemical doping and magnetic field can help parse the competing components of  $\chi_{c,m}(\mathbf{q}, \omega)$ , both in the collective state itself and across a quantum phase transition.

We combine x-ray diffraction and ac magnetic susceptibility measurements up to 17 GPa of applied pressure to examine the nature of the superconductivity in Mo<sub>3</sub>Sb<sub>7</sub>. At ambient pressure, Mo<sub>3</sub>Sb<sub>7</sub> goes superconducting at  $T_c = 2.35$  K, with a structural phase transition from high-temperature cubic symmetry to low-temperature tetragonal symmetry at  $T_s = 53$  K [9-11]. Whether this structural transition is magnetically driven is still an open question [9-11, 19], although no long-range spin order has been observed to date through either neutron or x-ray magnetic diffraction [11]. Magnetic susceptibility

measurements give one  $S=1/2$  local moment per Mo site from fits to a Curie-Weiss law at high temperature [9-11], with spin gap behavior at low temperature that suggests a spin-Peierls transition at  $T_S$  [10,11]. The presence of shortened Mo-Mo bond distances in the tetragonal phase [11] reinforces the idea that 1/3 of the Mo ions form dimers below  $T_S$  [10,11]. A valence bond crystal also has been suggested as a possible ground state amid strong spin frustration [9]. The superconductivity has been claimed to be s-wave at ambient pressure [20-22], but the possibility of unusual magnetic phases at low temperature [9-11,19] have raised the question about the role of spin coupling.

Chemical doping has been exploited previously to study superconductivity in  $\text{Mo}_3\text{Sb}_7$  [19, 23]. We show here that hydrostatic pressure is a particularly effective tuning mechanism, and we find a second superconducting state with a factor of two greater  $T_c$  following a pressure-induced first-order phase transition to a higher structural symmetry phase (Fig. 1a). The high-pressure phase is cubic and continuously connects to the ambient-pressure, high-temperature paramagnetic phase. By contrast to previous suggestions of spin-dimer magnetic order in a local spin picture [9], we argue that spins in  $\text{Mo}_3\text{Sb}_7$  should be considered as both highly itinerant and small in magnitude. The link of  $T_c$  to structure suggests that spin fluctuations are not a dominant coupling mechanism in this system, while the abrupt variation in  $T_c$  points to a symmetry-related difference in the phonon density-of-states.

## II. EXPERIMENTAL METHODS AND RESULTS

$\text{Mo}_3\text{Sb}_7$  single crystals of several mm size were grown using a Sb self-flux technique [11]. Single crystals were polished down to plates of 20-30  $\mu\text{m}$  thickness with a surface norm of (1,0,0), and broken into small shards ( $120 \times 120 \times 20 \mu\text{m}^3$ ) to be loaded into the diamond anvil cell. AC magnetic susceptibility measurements at a probe field of 0.5 Oe were carried out using a diamond anvil cell designed for rapidly exploring  $H$ - $P$ - $T$  parameter space [24]. Sapphire seats and thermally-hardened BeCu or MP35N gaskets were used to avoid any ferromagnetic background disturbance to the superconducting transition [24, 25]. Four different crystals were studied in a Methanol:Ethanol 4:1

hydrostatic pressure medium. Pressure was monitored by ruby fluorescence *in situ* at low temperature [26].

X-ray absorption and high-pressure diffraction measurements were carried out at Sector 4-ID-D of the Advanced Photon Source. X-ray absorption was performed at ambient pressure and temperature, using single crystal  $\text{Mo}_3\text{Sb}_7$  along with annealed Mo metal foil, and  $\text{MoO}_2$  and  $\text{MoO}_3$  powders. For diffraction, 19.950 keV x-rays were used in order to avoid the Mo K-edge fluorescence. The Methanol:Ethanol 4:1 mixture was used as the pressure medium and a piece of polycrystalline silver foil was included as a manometer at low temperature [26]. The ambient-pressure magnetization was measured using a SQUID magnetometer (Quantum Design MPMS) on a cubic shaped single crystal of 0.0138 g along the (100) direction and at both  $T = 60$  and 6 K, bracketing the phase transition at  $T_S$ .

The pressure evolution of superconductivity in  $\text{Mo}_3\text{Sb}_7$  was measured using ac magnetic susceptibility (Fig. 2). From 0 to 10 GPa,  $T_c$  slowly increases from 2.3 to 3 K with increasing  $P$ . Starting at 10 GPa, a new superconducting phase was observed with  $T_c \sim 6$  K, a jump of a factor of two. This quantum phase transition between two superconducting states is clearly first order, with susceptibility manifesting two superconducting steps as a sign of phase coexistence over a wide pressure region (Fig. 2a). As expected, an external magnetic field suppresses the superconducting transitions (Fig. 2b).

Turning to structural information, the phase boundary  $T_S(P)$  was tracked by macroscopic probes such as the electrical resistivity [27], where  $T_S(P)$  is suppressed by increasing pressure (Figs. 1), but only slowly ( $\sim 2.5\text{K/GPa}$ ), remaining well above zero out to 12 GPa. We performed a set of x-ray diffraction measurements to specify the evolution with  $P$  of the microscopic structure and associated lattice symmetries, Longitudinal diffraction line scans of various lattice orders such as (4,0,0), (4,4,0), and (4,4,4) at  $T = 4$  K (Fig. 3a) indicate a lattice symmetry change from tetragonal at low pressure to cubic at high pressure. We examine in Fig. 3b the relationship between this

high-pressure, low-temperature cubic phase and the ambient pressure, high-temperature cubic paramagnetic phase by traversing the  $P$ - $T$  phase diagram for  $T > T_S$  out to  $P = 17.1$  GPa. The lattice constants of both  $\text{Mo}_3\text{Sb}_7$  and the silver manometer were measured at various  $(P, T)$  points along the path, and then compared to each other. We find that  $a_{\text{Mo}_3\text{Sb}_7}(P, T)$  vs.  $a_{\text{Ag}}(P, T)$  collapses onto a straight line throughout the trajectory. Hence the cubic phase of  $\text{Mo}_3\text{Sb}_7$  at high  $P$  and low  $T$  and the cubic phase at  $P = 0$  and  $T > T_S$  are continuous, ruling out the separation that would result from a sudden unit cell collapse in an isostructural phase transition.

Given the continuous evolution of the ambient pressure paramagnet above  $T_S = 53$  K to high pressure and low temperature, we might expect the spins in the high-pressure cubic phase of  $\text{Mo}_3\text{Sb}_7$  to remain disordered. Spin fluctuations in  $\text{Mo}_3\text{Sb}_7$  have been discussed in the literature based on the assumption of one  $S=1/2$  local moment per Mo site [10,11]. However, the existence of magnetic moments in Mo compounds strongly depends on its ionic state and local symmetry. For example,  $\text{Mo}^{4+}$  carries a moment of  $S=1$  in  $1T$ - $\text{MoS}_2$  but no moment in  $2H$ - $\text{MoS}_2$  due to a different splitting of the  $4d$ -orbitals by local symmetries [29]. In  $\text{Ba}_2\text{YMoO}_6$  [30], a  $\text{Mo}^{5+}$  state leads to a localized  $S=1/2$  moment, which also was assumed for  $\text{Mo}_3\text{Sb}_7$  [9]. The ionic state of Mo in  $\text{Mo}_3\text{Sb}_7$  can be determined by x-ray absorption near-edge structure (XANES) measurements [31]. In the cubic phase of paramagnetic  $\text{Mo}_3\text{Sb}_7$ , there is only one unique Mo site in the unit cell [11], and the measured XANES K-edge of  $\text{Mo}_3\text{Sb}_7$  is very similar to that of pure Mo metal (Fig. 4a), lying 10-15 eV away from the K-edge of both  $\text{Mo}^{4+}$  in  $\text{MoO}_2$  and  $\text{Mo}^{6+}$  in  $\text{MoO}_3$ . This suggests that the Mo ions in  $\text{Mo}_3\text{Sb}_7$  are close to charge neutral. They are also unlikely to have valence fluctuations like those displayed by highly ionized  $\text{Re}^{5+}$  ions in  $\text{Cd}_2\text{Re}_2\text{O}_7$  [32].

We plot in Fig. 4b the dc magnetization,  $M(H)$ , at ambient pressure. It is linear and non-saturating at both  $T = 60$  and 6 K, above and below  $T_S$ , without hysteresis for applied fields between  $\pm 7$  T. Since  $\text{Mo}_3\text{Sb}_7$  is cubic in the paramagnetic phase, no strong anisotropy of  $M(H)$  is expected along the major crystalline axes. Here the non-saturating  $M(H)$  of  $\text{Mo}_3\text{Sb}_7$  differs from the isothermal magnetization behavior of many magnetic

Mo compounds. For ferromagnetic and paramagnetic  $\text{MoS}_2$  [29,33] and ferromagnetic  $\text{GaMo}_4\text{S}_8$  and  $\text{GaMo}_4\text{Se}_8$  [34, 35],  $M(H)$  would saturate at relatively low fields, typically  $< 3$  T. At  $H = 7$  T there is no saturation and the measured moment is extremely small:  $2 \times 10^{-3} \mu_B/\text{Mo}$ . This small and unsaturated moment of  $\text{Mo}_3\text{Sb}_7$  derived from  $M(H)$  contrasts sharply from the magnetic moment deduced from the paramagnetic susceptibility,  $\chi'(T)$ . Fitting to a Curie-Weiss law for  $230 \text{ K} < T < 700 \text{ K}$  yields a local moment of  $1.56 \pm 0.10 \mu_B/\text{Mo}$ , consistent with a  $S=1/2$  moment per Mo site [10,11]. The discrepancy between the values of the magnetic moment following from the magnetization at 7 T and fits to the magnetic susceptibility gives a Rhodes-Wohlfarth ratio  $\sim 500$ . This indicates that the Curie-Weiss behavior is due to band structure effects rather than localized spins [36]. Indeed the shortest Mo-Mo distance in  $\text{Mo}_3\text{Sb}_7$  is  $2.98 \text{ \AA}$  [11], a distance similar to the value of  $2.73\text{-}2.9 \text{ \AA}$  in elemental Mo and ferromagnetic  $\text{GaMo}_4\text{S}_8$  and  $\text{GaMo}_4\text{Se}_8$  [34], where the overlap of  $4d$  orbitals results in the electrons being considered as itinerant [34,35,37]. The combination of the valence state (Fig. 4a) and magnetization (Fig. 4b) measurements therefore permits us to conclude that the spins in  $\text{Mo}_3\text{Sb}_7$  are highly itinerant and very small in magnitude. The magnetic nature of the tetragonal phase in  $\text{Mo}_3\text{Sb}_7$  is consistent with paramagnetism (Fig. 4b); the temperature dependence of the magnetic susceptibility at ambient pressure [10,11] could be due to a structural phase transition with no magnetic correlation, similar to that in  $\text{Cd}_2\text{Re}_2\text{O}_7$  [32]. Hence we do not expect that the localized spin-dimer picture should be applicable to either phase of  $\text{Mo}_3\text{Sb}_7$ .

### III. DISCUSSION

The superconducting transition in  $\text{Mo}_3\text{Sb}_7$  lacks significant pressure dependence in either the tetragonal or cubic phase, leading to an abrupt doubling of the transition temperature at the phase boundary (Fig. 1). While the connection between superconductivity and structural symmetry is particularly prominent, the crystal symmetry dependence of superconductivity is opposite to the typical expectation for spin-fluctuation-mediated superconductivity, which is believed to benefit more from a tetragonal structure than a higher-symmetry cubic phase [4]. An increasing tetragonal

distortion drives the system closer to the two-dimensional limit and hence enhances spin fluctuations via a diverging  $\chi_m(\mathbf{q}, \omega)$ . This trend has been observed in heavy fermion superconductors; for example,  $T_c$  is significantly larger in tetragonal CeRhIn<sub>5</sub> than in cubic CeIn<sub>3</sub> [4]. Here in Mo<sub>3</sub>Sb<sub>7</sub>,  $T_c$  in the high-symmetry cubic phase doubles that in the low-symmetry tetragonal phase, while both structures are stable ground states. Symmetry considerations thus favor phonon-mediated superconductivity in Mo<sub>3</sub>Sb<sub>7</sub> at high pressure.

Analogous to the original BCS formula in the weak coupling limit,  $T_c$  is expressed in McMillan's formula for intermediate phonon-coupling strength [22,38,39] as:

$$T_c = \frac{\Theta}{1.45} \exp \left( -\frac{1.04 (1+\lambda)}{\lambda - \mu^* (1+0.62\lambda)} \right), \quad (1)$$

with the Debye temperature,  $\Theta$ , dimensionless electron-phonon coupling constant,  $\lambda$ , and screened Coulomb potential,  $\mu^*$ . While all three could potentially vary under pressure to account for the  $T_c$  evolution, both the constancy of the superconducting transition within each structural phase and its discontinuous nature in the phase coexistence region strongly suggest that the cause can be identified by comparing two structural phases of different symmetries at the same pressure. From calculations at ambient pressure [38], it is reasonable to assume that both  $\Theta$  and  $\mu^*$  are nearly identical in the tetragonal and cubic phases at the same pressure in the phase coexistence region. We therefore believe that the main influence on  $T_c$  should come from the electron-phonon coupling constant  $\lambda$ , with  $\lambda$  dependent on both electronic structure and the phonon dispersion spectrum [39]. The smoothly varying resistivity under pressure [27] indicates a continuously evolving electronic structure, consistent with estimated small difference between the tetragonal and cubic structures by theoretical calculation at ambient pressure [38]. Hence the origin of the doubled  $T_c$  most likely arises from details of the symmetry-dependent phonon dispersion [39]. This causes  $\lambda$  to grow from 0.55 at ambient pressure [22,38] to 0.75 in the cubic phase.

Spin fluctuations in general would disrupt a phonon-coupled superconductor by suppressing the value of  $\lambda$  [22] and thereby  $T_c$ . All suggested forms of singlet magnetic



correlations (either long range antiferromagnetic order or spin-dimer pairs) in the tetragonal phase would introduce *reduced* singlet-type spin fluctuations as compared to fluctuations in the spin-disordered, high-pressure phase. This dearth of spin fluctuations in the tetragonal phase is consistent with the fact that  $\rho(T)$  does not manifest  $T^{3/2}$  behavior at ambient pressure [10, 11, 28]. If spin fluctuations would affect the phonon-mediated superconducting state in  $\text{Mo}_3\text{Sb}_7$  [28], then  $T_c(P)$  should be suppressed in the spin-disordered cubic high pressure phase, while the experiments demonstrate the opposite.

#### IV. CONCLUSIONS

In summary, pressure enhances the superconducting transition temperature in  $\text{Mo}_3\text{Sb}_7$  by a factor of two, accompanied by a first order phase transition from tetragonal to cubic lattice symmetry at low temperature. Direct x-ray diffraction results reveal that the high-pressure cubic phase continuously evolves from the paramagnetic phase at ambient pressure and is expected to be spin disordered. However, given the relatively small itinerant moments and weak spin fluctuation effects, we attribute the increase of  $T_c$  to a modified phonon density-of-states in the high-symmetry cubic structure. We are able to draw this conclusion because of the combination of magnetic, electronic, and structural measurements and the ability to tune different lattice symmetries with pressure. This general approach is necessary to parse the competition between different pairing mechanisms in materials with tendencies towards both magnetic and superconducting order.

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### Figure Captions:

FIG. 1.  $P$ - $T$  phase diagram of  $\text{Mo}_3\text{Sb}_7$ . Red squares mark the phase boundary between tetragonal and cubic structures at  $T_S(P)$  as determined from electrical resistivity [27]. Superconducting transitions (dark and light blue circles) in both crystal structures are demarcated by characteristic signatures of the magnetic susceptibility. The shaded area marks the phase coexistence region.

FIG. 2. (a) AC magnetic susceptibility at the superconducting transition at a series of pressures  $P$  in  $\text{Mo}_3\text{Sb}_7$ . The two-step transitions indicate phase coexistence. (b) An applied magnetic field suppresses the superconductivity.

FIG. 3. Lattice symmetry and phase continuity. (a) Longitudinal ( $\theta/2\theta$ ) scans of three lattice orders of  $\text{Mo}_3\text{Sb}_7$ , measured for various pressures (in units of GPa) at  $T = 80\text{K}$  (red) or  $T < 4.3\text{K}$  (blue). All scans are plotted on a logarithmic scale in order to both show the symmetry state and rule out the presence of minor phases. (b)  $\text{Mo}_3\text{Sb}_7$  lattice constant vs. Ag lattice constant at each  $(P, T)$  point along the specified path in the inset. (Inset) Trajectory in  $P$ - $T$  phase space for x-ray measurements.  $\text{Mo}_3\text{Sb}_7$  remains in the same cubic phase throughout. The bulk modulus at 80 K is  $B_0 = 111.5 \pm 0.8$  GPa.

FIG. 4. Chemical and magnetic characteristics of  $\text{Mo}_3\text{Sb}_7$ . (a) X-ray absorption near edge

spectroscopy at ambient conditions for a comparison between four different Mo compounds of various valence conditions. (b) Magnetization measurements  $M(H)$  at  $T = 60$  K and 6 K, bracketing  $T_S$  at  $P = 0$ , indicate no magnetic hysteresis and no saturation up to  $H = 7$  T.









