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Disorder in superconductors—a study on $Cu_2Mo_6S_8$

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Abstract. Some of the recent work on disorder-induced changes in T_c is reviewed. Shock-pressures induce a disorder uncomplicated by antisite disorder typical of particle irradiation, and have generated interest because of the shock-synthesis of A-15 Nb_3Si. In this paper we present our results on laser-induced shock-damage, and compare it with the results on V_3Si and the results on particle irradiation of Chevrel phase superconductors.

Keywords. Superconductors; disorder.

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1. Introduction

The effect of disorder on superconductivity has been studied for about a decade now. In addition to affecting the normal state properties, disorder affects the three macroscopic superconducting parameters viz, transition temperature, critical field and critical current. The last two are of interest in view of the large scale applications of superconducting magnets, but in this paper we shall concentrate on the effect of disorder on the transition temperature T_c.

Disorder has been introduced in the past by irradiation with fast neutrons (Sweedler *et al* 1978; Brown *et al* 1977), with protons (Dierker *et al* 1983) and with heavy charged particles (Lehmann *et al* 1981; Adrian *et al* 1981). Some representative results in high T_c materials will be reviewed in the next section. Superconductors have also been prepared in the disordered state by going off-stoichiometry or by quenching. We shall also review in § 2 some theoretical efforts to explain the variation of T_c with disorder in terms of variations caused in relevant microscopic parameters like the electronic density of states $N(E_F)$, the electron-phonon coupling λ, and Coulomb repulsion μ^*. In § 3 we present our results on laser-induced shock damage in $Cu_2Mo_6S_8$ and compare them with other recent results on shock-damaged superconductors. We conclude by comparing our results with earlier studies on neutron irradiated and charged-particle irradiated Chevrel phase superconductors, and present a possible explanation for the apparently conflicting results.

2. Disorder in superconductors—status review

Sweedler *et al* (1978) studied the change in T_c of various A-15 compounds under irradiation with fast neutrons for fluence ($E > 1$ MeV) upto 10^{20} neutrons/cm^2. On plotting T_c/T_{c0} as a function of irradiated fluence they found Nb_3Al, Nb_3Ge, Nb_3Pt, Nb_3Sn, Nb_3Ga and V_3Si to follow a universal curve. T_c dropped to about 20% of its unirradiated value at a fluence of $\approx 4 \times 10^{19}$ neutrons/cm^2 before saturation set in. Sweedler *et al* (1978) explained their data on the basis of antisite defects created by the irradiation. Brown *et al* (1977) studied V_2Hf (C-15 Laves phase), Nb_3Al and $PbMo_6S_7$ and $SnMo_5S_8$ (in Chevrel phase) under fast neutron irradiation going upto a fluence ($E > 0{\cdot}1$ MeV) of $1{\cdot}6 \times 10^{19}$ neutrons/cm^2. They found a decrease of only $\approx 5\%$ in the T_c of V_2Hf, a decrease of $\approx 23\%$ for Nb_3Al, while $PbMo_6S_7$ showed a decrease of $\approx 61\%$ and $SnMo_5S_8$ of $\approx 51\%$ in T_c. They thus found a much larger depression in the T_c of Chevrel phase compounds. Sweedler *et al* (1978) also reported a measurement on $PbMo_6S_8$ where T_c decreased from 12·8 K to below 4·2 K at a fluence ($E > 1$ MeV) of 10^{19} neutrons/cm^2, which is larger than that found by them for the A-15 compounds. They have concluded that the T_c's of the Chevrel phases are "the most sensitive to neutron irradiation of the materials studied to date". They have also reported that elemental Nb shows "little or no change" in T_c under irradiation to high fluences.

V_3Si has also been irradiated with 37 MeV protons to a fluence of $4{\cdot}6 \times 10^{18}$/cm^2, resulting in a drop of T_c from 16·33 K to 5·42 K, with the width of the transition increasing from 0·17 K to 1·31 K (Dierker *et al* 1983). α-particle irradiation on $SmRh_4B_4$ films has recently been reported by Terris *et al* (1984). Irradiation of A-15 compounds with 20 MeV ions of ^{32}S has been reported by Lehmann *et al* (1981) where fluence $> 10^{15}$/cm^2 yields saturation effects in Mo_3Si and Mo_3Ge. Adrian *et al* (1981) irradiated $PbMo_6S_8$ films with 20 MeV ^{32}S ions and found that T_c drops from 12·7 K to $< 1{\cdot}2$ K at a fluence of 10^{14}/cm^2. These results again indicate higher sensitivity of Chevrel phase T_c's to particle irradiation as compared to the A-15 T_c's.

Before proceeding to theoretical efforts we shall point out that inelastic neutron scattering measurements (Cox and Tarvin 1978) and sound velocity measurements (Guha *et al* 1978) on neutron-irradiated V_3Si have shown that the softening of the transverse acoustic mode is absent in the irradiated compound indicating that the phonon properties, and possibly the electron-phonon coupling constant, are modified by irradiation. Dierker *et al* (1983) have done Raman scattering on the proton irradiated V_3Si mentioned above. By studying the temperature variation of the linewidth of the E_g phonon in irradiated and unirradiated samples they conclude that the electron-phonon coupling is reduced in the irradiated sample. It should be mentioned that they believe this reduction to be due to the broadening of the peak at $N(E_F)$.

Based on electron-microscopic observations of the disorder caused in their samples, Pande (1977, 1978) proposed a model based on proximity effect to explain the decrease of T_c with disorder. Farrell and Chandrasekhar (1977) proposed that disorder decreases gap anisotropy and reduces T_c. These two models required an excessive volume fraction of disordered regions, and an excessive gap anisotropy respectively, and have not been pursued much (Dierker *et al* 1983). Other microscopic models discuss the variation of the microscopic parameters $N(E_F)$, λ and μ^* with disorder. Appel (1976) related T_c of the A-15's to the long-range order parameters S using McMillan's equation with both λ and $N(E_F)$ being functions of S. The drawback is that a critical component of the theory, the variation of $N(E_F)$ with S, must be independently determined. Testardi and Mattheiss (1978) treat the effect of the disorder via electron-lifetime broadened density of states. The electrical resistivity of the disordered sample is used to determine the life-time, and an effective $N(E_F)$ is obtained. Assuming λ to be proportional to $N(E_F)$ averaged over an energy equal to the Debye energy, they also related T_c to the resistivity of the disordered sample. With these assumptions, they obtained a reasonable agreement with data for V_3Si except in the low resistivity region. Anderson *et al* (1983) were the first to consider the effect of disorder on T_c via its effect on μ^*. They noted that the normalized T_c of many high temperature superconductors decreases similarly with increasing resistivity and took this to be the single parameter specifying disorder. They further stated that since the electron-phonon coupling is strong in these materials, a one-electron description (which is the basis of the models discussing the variation of $N(E_F)$ with disorder) is unrealistic. They proposed that Anderson localization in extremely disordered systems provides an explanation for the degradation of T_c. They showed that μ^* increases with increasing resistivity and using McMillan's formula

$$T_c = \frac{\omega_D}{1{\cdot}45} \exp\left[-\frac{1{\cdot}04(1+\lambda')}{\lambda' - \mu^*(1+0{\cdot}62\lambda')}\right]; \quad \lambda' = N(E_F)\lambda,$$

obtained the degradation of T_c with increasing resistivity. They have obtained good agreement with the experimental data for Nb_3Ge, V_3Si and $LuRh_4B_4$. They need, however, a low value of the critical resistivity ($\rho_c \approx 0{\cdot}04\rho_c^f$, the free electron gas estimate) to obtain this agreement. There are two viewpoints contradicting this model. Leavens (1985) claims that a detailed solution of the Eliashberg-gap equations, with $\rho_c \approx 0{\cdot}04\rho_c^f$, actually results in T_c increasing with increasing disorder due to the dominant effect of the renormalization function $Z(\omega)$. He believes that though the effect considered by Anderson *et al* is correct, it is not the primary cause of the degradation of T_c and the extremely low ρ_c used by Anderson *et al* is not justified.

Following the proposal of Anderson *et al* (1983), two-electron tunneling measurements on Nb_3Sn have reported μ^* for samples with differing Sn concentration and differing T_c. Geerk *et al* (1984) have made measurements for Sn concentration 25, 23, 20 and 19 at.%, while Rudman and Beasley (1984) had Sn concentration varying from 22·4 to 26·7 at.%. While T_c vs resistivity follows the universal behaviour, μ^* shows no measurable variation with resistivity, in contrast to large variation predicted by Anderson *et al.*

To sum up the present status, there does not exist a generally accepted understanding of the degradation of T_c with disorder. The model of Pande (1977, 1978) and the work of Appel (1976) corresponds to different ideas about the effect of the disorder on microscopic structure. The concept of antisite defects proposed by Sweedler *et al* (1978) and by Appel (1976) is relevant to damage by particle bombardment but perhaps not to compositionally disordered samples. Similarly, shock-generated disorder yields defects which are dominantly dislocation lines for shock pressures above ≈100 kbar. In the next section we shall report our studies (Chaddah *et al* 1986) on $Cu_2Mo_6S_8$ samples disordered by laser-induced shock. Shock-induced disorder has also been studied in V_3Si (Stewart *et al* 1985) and in Nb (Nellis *et al* 1985) and these will be discussed below.

3. Details of our measurement

We have studied the effect of laser-induced shock on $Cu_2Mo_6S_8$ (Chaddah *et al* 1986) as a representative compound of the high-T_c Chevrel phase compounds. The sample preparation procedure (Gopalakrishnan *et al* 1984) is outlined below. The sample was obtained in powder form, which was pelletized for our measurements. $Cu_2Mo_6S_8$ was prepared by direct reaction of molybdenum (99·9%), copper (99·99%) and sulphur (99·99%) powders in vacuum. Appropriate mixtures were pelletized and sealed under vacuum in quartz tubes after flushing with pure argon for 30 minutes. These were heated at 300°C for 3 hr, 400°C for 5 hr, 550°C for 16 hr and 850°C for 24 hr and furnace-cooled. The quartz ampules were then vigorously shaken and reheated at 900°C for 24 hr. The product was subsequently ground, pelletized, sealed again under vacuum and re-sintered at 1250°C for 4 hr. X-ray diffraction showed only single-phase $Cu_2Mo_6S_8$ with no detectable contamination of MoS_2 or any other impurity phases. The hexagonal lattice parameters of this sample are $a = 9{\cdot}60$ Å and $C = 10{\cdot}24$ Å.

The T_c was measured by the a.c.-inductive technique. The primary coil was wound of Cu-clad Nb-Zr and the secondary was wound using a copper wire. The sample, the standard (lead was used) and the thermometer and the heater were mounted on a 5N-pure Cu rod, and the sample volume used was ≈ 1 mm^3. The change in inductance was monitored using a PAR 124A lock-in amplifier, and the frequency was 31 Hz.

The shock was generated using a Nd-glass laser having a wavelength of 1·06 μm. The pulse width was 5 nsec and the laser power used was 4·5 Joules and 7·8 Joules. The laser pulse was focused to 270 μm diameter on the sample surface, the sample being maintained in vacuum. The power density on the sample surface, was thus $1{\cdot}46 \times 10^{12}$ W/cm^2 and $2{\cdot}53 \times 10^{12}$ W/cm^2 respectively. To estimate the shock pressures generated, we have modelled the shock propagation using a one-dimensional hydrodynamic code. Among the input physical parameters of $Cu_2Mo_6S_8$ required were the sound velocity, the thermal expansion coefficient and the specific heat, all above room temperature. For the specific heat we extended the fit of Lachal *et al* (1984), while the sound velocity for the polycrystalline pellet was estimated from the phonon distribution curves (Bader *et al* 1982). Thermal expansion data were not available, and we have used the triclinic cell parameters (Baillif *et al* 1979) to provide an estimate. The pressures indicated in table 1 correspond to pressures obtained by using these estimates of input physical parameters.

Figure 1 shows the results of our measurement in the neighbourhood of the $Cu_2Mo_6S_8$ transition. Table 1 gives the values of T_c and ΔT_c obtained for the unshocked and the shocked samples. We note that the broadening of the transition is slight (ΔT_c goes up from 0·42 to upto 0·66), while the depression in T_c is as large as 0·45 K. The only other reported T_c measurements on shock-disordered samples (though these do not use laser driven shocks) are on V_3Si (Stewart *et al* 1985) and on Nb (Nellis *et al* 1985). In the case of Nb the maximum depression in T_c was 0·035 K while in the case of V_3Si the depression was $\approx 1{\cdot}8$ K but the transition width broadened from ≈ 1 K to $\approx 3{\cdot}5$ K. The results for Nb are not surprising since, as mentioned earlier, it shows no change in T_c under neutron irradiation. Nb_3Si has been synthesized in the A-15 phase (Olinger and Newkirk 1981) using a shock compression, but shows a transition width of only $\approx 0{\cdot}7$ K. The electronic specific heat coefficient γ in shocked Nb_3Si is 24 ± 6 mJ/mol against 45 ± 2 mJ/mol in shocked V_3Si ($\gamma = 58 \pm 2$ mJ/mol in their unshocked V_3Si sample) and Stewart *et al* (1985) explain the increased ΔT_c for V_3Si (under shock conditions similar to that of Nb_3Si) as due to the higher $N(E_F)$ in V_3Si. The value of $N(E_F)$ for $Cu_2Mo_6S_8$ is $N_{bs}(0) = 0{\cdot}35$ states/eV-atom-spin (Fischer 1978), while $N_{bs}(0)$ for V_3Si is $> 1{\cdot}24$ states/eV-atom-spin (Junod *et al* 1983) and thus the small depression in T_c seen by us appears to be in accordance with Stewart's

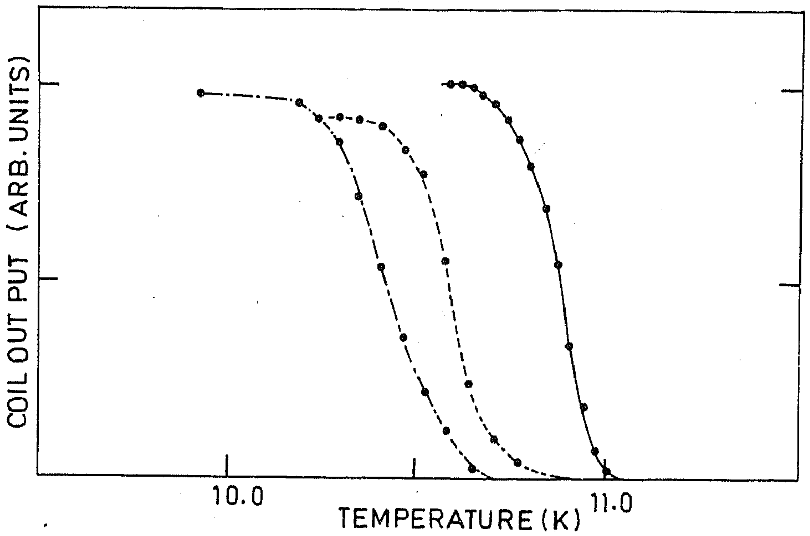

Figure 1. Results of our T_c measurements. The full line corresponds to sample I, the dashed line to sample II, and the dot-dashed line to sample III.

Table 1. Various parameters for the $Cu_2Mo_6S_8$ samples are listed. ΔT corresponds to 10% to 90% of the transition.

Sample	Laser power density (W/cm^2) ($\times 10^{12}$)	Peak pressure (kbar)	T_c (mid-pt) (K)	ΔT (K)
I	—	—	10·88	0·42
II	1·46	950	10·60	0·48
III	2·53	1200	10·43	0·66

explanation that a higher $N(E_F)$ is more depressed by disorder. This does not however explain why $PbMo_6S_8$ ($N_{bs}(0) = 0{\cdot}67$) and other Chevrel compounds show such a large depression of T_c under particle irradiation. We believe that one must also consider the effect of disorder on the electron-phonon coupling, and this is described below.

4. Discussion

The electron-phonon interaction in Chevrel phase compounds is discussed in detail by Pobell *et al* (1982). It is believed that since the peak in $N(E_F)$ is due to the Mo 4*d* electrons, the electron-phonon coupling of the conduction electrons is dominantly to internal deformations of a Mo_6S_8 cluster, while phonons involving intercluster coupling do not play a major role in superconductivity. The displacements of the copper atoms as well as those of rigid Mo_6S_8 clusters may contribute to superconductivity only to the extent that these modes are hybridized with internal modes of the Mo_6S_8 cluster. This viewpoint has received a lot of support from the isotope effect measurements (Pobell 1981) which show that the vibrations of the 6 Mo and 8 Se atoms (in Mo_6Se_8) contribute almost equally to the transition temperature, while those of the Sn atom (in $SnMo_6Se_8$) do not contribute. We thus assert that $N(E_F)$ is dominated by the Mo 4*d* electrons, and λ by the internal deformations of the Mo_6S_8 cluster.

We now point out Sweedler's results which attribute the degradation in T_c to anti-site defects. Generation of such defects is common to particle-irradiation where the impinging particle displaces an atom in the lattice by a knock-on scattering while for shock pressures greater than 100 kbar dislocations are believed to be the major defects. Available estimates (Morosin and Graham 1983) on shock-induced dislocation densities are in the region of $10^{11}/cm^2$. Thus undamaged regions of dimensions ≈ 100 Å can be expected. Since the phonons of interest in $Cu_2Mo_6S_8$ are intra-cluster phonons, shock-induced disorder should not affect the phonon spectrum in the region of interest and the electron-phonon coupling λ is unaffected. Shock-induced-disorder will thus affect T_c of Chevrel phase superconductors only because of changes caused in $N(E_F)$. Since $N(E_F)$ in $Cu_2Mo_6S_8$ is not very high, the net effect of shock-induced disorder is small. Neutron or heavy ion irradiation causes knock-on reactions and the intra-cluster phonons are directly affected. Thus both $N(E_F)$ and λ are reduced and the large depression in T_c (even in comparison to A-15 compounds) can be understood. This distinction will be characteristic of compounds where dominant electron-phonon coupling is with localized phonon modes. Since such localized modes do not occur in A-15 compounds T_c depression will not be dependent on the type of disorder caused. If our understanding is correct, the type of disorder caused will be of major importance for Chevrel phase compounds and a single parameter fit for the degradation of T_c (as done by Anderson *et al* for A-15's) will not be possible.

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