Effect of argon and hydrogen coating on the superconducting transition temperature of granular aluminum

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Superconducting transition temperatures of pure Al, Al-Ar, and Al-H_2 mixtures condensed on substrates at 4.2 °K are measured. A reduction in T_c is observed for the Al-Ar mixture with respect to pure Al ($T_c = 3.46$ °K), and a significant increase in T_c is measured for Al-H_2. These results are discussed following recent observation of (i) T_c depression in films with noble-gas overlayers, and (ii) the formation of Pd-H_2 mixture superconductors.

Recently, the effects of solid-inert-gas absorption on the transition temperatures of superconducting films were studied by Naugle et al.[1] These experiments were aimed primarily to probe the "surface effects" on T_c in the absence of chemical changes on the surface of the metal, such as oxidation or alloying. Coating with molecular solids, such as noble-gas solids, is an ideal test since the chemical bonding with the metal atoms is of the weak van der Waals type. Experiments of this kind have also been reported by Zavaritsky and Yaroshenko[2] and by Felsch and Glover.[3] Characteristic of all those measurements was the systematic decrease in T_c—with respect to the pure T_c of the metal—upon coating; the magnitude was observed to decrease with the decrease of the atomic mass of the inert gas. This trend in T_c is opposite to the common observation of the increase in T_c, in particular for Al with a coating of oxide[4-6] or of semiconductor[7] layers. In this work we present measurements of aluminum grains coated with solid argon and with solid molecular hydrogen produced on a substrate at liquid-helium temperatures. As will be shown, the increase of the surface-to-volume ratio caused by applying the present method of grains indeed enhances, in the case of Ar, the phenomena observed in Refs. 1 and 3 but shows a contradictory trend with H_2 coatings, where T_c dramatically increases as compared with pure Al.

The experiments were performed *in situ* by a four-point resistance measurement on freshly deposited films evaporated on cold substrates at 4.2 °K. Aluminum was evaporated at a rate of 30 Å/sec in an atmosphere of spectroscopically pure Ar or H_2 with a typical pressure of 10^{-4} Torr. Measurements were also performed with the directly evaporated pure Al in a vacuum lower than 10^{-7} Torr. The amount of metal was measured with a quartz-crystal device, and the gas pressure served as a monitor for measuring the amount of solidified gas on the cold substrate. In Fig. 1 we show representative data for the following samples: (i) pure Al ($T_c = 3.46$ °K), (ii) Al with Ar with atomic ratio

of Al/Ar = 1 ($\Delta T_c = -0.13$ °K), and (iii) Al with H_2 with the atomic ratio of Al/H_2 of 0.17 ($\Delta T_c = 1.05$ °K). For samples shown in Fig. 1 the normal-state resistivity at 5 °K was 2.1×10^{-5}, 1.7×10^{-2} and 1.4×10^{-2} Ωcm for pure Al, Al-Ar, and Al-H_2, respectively.

The observation of a finite electrical resistance at $T > T_c$ and a superconducting transition strongly suggests that upon solidification, grains of Al are formed with a respective coating of Ar and H_2. It should be pointed out that upon heating to room temperature, and even at 77 °K, the sample disintegrated, showing no sign of phase stabilization; in particular, no evidence was found for an Al-AlH formation.[8] Measurements were also conducted with different evaporation rates and gas pressure, resulting qualitatively in similar trends—namely, a relatively small decrease in T_c with Al-Ar mixtures and a significant increase in T_c with Al-H_2 mixtures. It should be pointed out that if contaminations such as O_2 had existed, they would have affected the pure Al, our reference, as well as the mixtures.

The decrease in T_c for the Al-Ar mixture is consistent both in trend and in magnitude with the results obtained by Naugle et al.[1] with Ar coating of thin Al films. The result for Al-H_2, however, is surprising. According to the interpretation given by Naugle et al., the role of the noble-gas layer is to modify the surface vibrational modes of the metal. This should apply for molecular hydrogen as well; namely, one would expect a negative ΔT_c, smaller in magnitude than the ΔT_c of Al-Ar, following the trend of Al-Ne. Solid H_2, as far as bonding character and lattice dynamics properties are concerned, is similar to the solid inert gas. This van der Waals crystal has a low Debye temperature $\theta_D = 117$ °K at 4.2 °K (Ref. 9) which is similar to θ_D of Ar (85 °K) and to θ_D of Ne (74.4 °K). Despite the somewhat higher vibrational frequencies due to the small mass of H_2, one cannot account for a *positive* ΔT_c by using arguments of Ref. 1, which successfully accounts for the trends observed
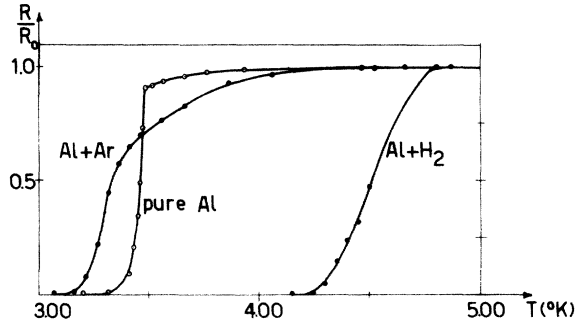
FIG. 1. Typical transition curves for pure Al and Al mixtures with Ar and H_2 condensed on a 4.2 °K substrate. The pure Al is 350 Å thick. The Al/Ar and Al/H_2 atomic ratios are 1 and 0.17, respectively. The T_c referred to in the text is taken at $R/R_0 = 1/2$, a convenient choice for the case where transitions are broadened by fluctuation effects (e.g., Ref. 6).

in Al—noble-gas layers.

In fact, the observation of the increase in T_c in granular Al is very common. The present results of the high T_c of amorphous Al as compared with the bulk ($T_c = 1.2$ °K) is an example. The enhancement of the transition temperature in granular Al-Al_2O_3 and Al-Ge was explained by Deutscher et al.[6] and Fontaine and Meunier[7] on the basis of Hurault's model.[10] According to Hurault, the critical temperature depends on the electron-phonon mechanism, on the excitonic mechanism induced by the dielectric layer, and on the properties of metal itself, namely,

$$T_c = \theta_D \exp - [N(0)V + N(0)W_1 + N(0)W_2]^{-1} . \quad (1)$$

The first term in the square brackets as well as θ_D is characteristic of the bulk material, the second term results from electrophonon interactions and depends on the surface-to-volume ratio of the granule (S/V), and the third term is proportional to $(S/V)^2 F(\epsilon)$, where $F(\epsilon)$ is a function of the dielectric constant ϵ of the coating material. The effect of the last term, namely, the dielectric properties of H_2, could not account for the significant increase in T_c. The dielectric constant of H_2 is rather small ($\epsilon = 1.15$) as compared with that of Ge ($\epsilon = 16$) and even smaller than that of Ar ($\epsilon = 1.65$). Thus the mechanism invoked by Ref. 7 to justify the high T_c of the Al-Ge mixture cannot apply to our case. The effect of the second term should be similar for both molecular hydrogen and argon therefore should result in a negative ΔT_c.

Following the above arguments, based on Hurault's model, as well as the arguments of Naugle et al. based primarily on McMillan's[11] theory, we come to the conclusion that there must be additional mechanisms present in the Al-H_2 mixture and absent in the Al—noble-gas mixtures that are responsible for the increase in T_c. Recently, Sansores and Glover[12] discovered that a mixture of Pd-H_2 produced in similar conditions to our Al-H_2 mixture is a superconductor with T_c depending on the H_2 concentration. They explain the occurrence of superconductivity on a possible formation of hydrides of Pd, thus exhibiting properties of Pd-PdH as reported by Skoskiewicz.[13] It seems to us very improbable that a chemical reaction takes place at these low temperatures to produce hydrides of Al. Nevertheless, the same mechanism that induced superconductivity in the Pd-H_2 mixture could be the one that enhances T_c in the Al-H_2 mixture despite competing mechanisms present in the Al—noble-gas mixtures that tend to decrease T_c.

Further experiments are now being conducted to elucidate the role of molecular hydrogen in superconducting transitions of Al as well as in other weak and strong coupling superconductors.

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