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Superconducting Properties of Ion Implanted Thin Films

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CHAPTER 6

ION IMPLANTATION IN SUPERCONDUCTORS

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INTRODUCTION

The possibility to introduce controlled amounts of impurities into material with the additional advantage to overcome restrictions due to solubility and diffusibility offers an attractive research tool to study near surface properties of material in a systematic manner. Numerous work has been performed in order to study the influence of implanted ions on the physical properties of material and it is well known that the technique of ion implantation is widely used in semiconductor integrated circuit industry. The main topics of a first international conference on this subject (4,5,11,15 etc.) such as implantation modification of superconducting properties, ion induced surface reactions (corrosion science),(60) alloying and migration in high fluence implants, implanted atom location, ion lattice damage together with ion implanted gas build up and implantation simulation of neutron damage reflect the broad spectrum of applicability of ion implantation and promising progress has been obtained in all these fields.

There has been also considerable interest in the effects of irradiations of superconductors since 1960 and many studies have been concerned with the influence of radiation damage on the superconducting critical current and critical field. Irradiations were performed using neutrons, protons, deuterons and alpha-particles and striking effects were reported for the critical current density, however little influence of radiation damage on the superconducting transition temperature has been observed. A summary of this work up to 1968 is given by Cullen(8).

In the last few years heavy ions have been implanted into superconductors and similar to the experience from ion implantation in semiconductors the influence of radiation damage effects on the superconducting properties has to be separated from the influence due to doping or alloying effects. As the maximum obtainable concentrations by ion implantation is not controlled by equilibrium processes there is a possibility to produce new stable structures as well as metastable phases which may have unexpected superconducting properties. A further possible application of ion implantation is the controlled change of composition in compounds, where it has been demonstrated that the superconducting transition temperature is strongly dependent on composition and density, and these parameters however can not be optimized by conventional techniques.

The purpose of the following contributions is to discuss problems which are connected with the influence of implanted atoms on the superconducting properties and to summarize some work which has been performed in the last few years. For convenience a short introduction to superconductivity is given mainly in order to define the superconducting parameters used in the following sections. The results of damage effects on the superconducting properties are summarized in the next paragraph with emphasize mainly on more recent work performed by heavy ion irradiation. In the last section the influence of metallurgical effects produced by implanted ions on the superconducting properties are discussed. As the superconducting properties strongly depend on the crystal structure of the material it seems reasonable to organize the subsections in this respect.

DEFINITION OF THE SUPERCONDUCTING PARAMETERS

The most obvious property of a superconductor is the total absence of resistance. The transition temperature, T_C, usually defined as the temperature where the resistance R decreases to half of its normal value(Fig.1) is a very specific property of a given element,alloy or compound and is affected by the metallurgical condition of the sample. T_C measurements can therefore provide information about what has happened to the sample and have been used to determine the purity of the sample,the solid solubility level,the composition and phases which are present and the appearance of new phases. A sharp transition width indicates a very pure element or a well annealed alloy,a broad transition width on the other hand reflects inhomogeneities or unusual strain

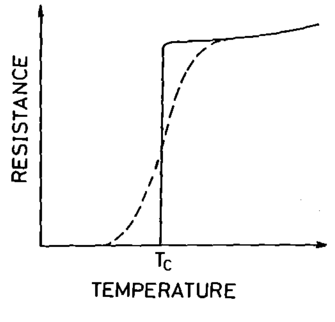

Fig. 1 Schematic diagram showing the decrease of resistance at the superconducting transition temperature T_C.

distributions. Our fundamental understanding of what crystalline properties determine T_c in a particular superconductor is still limited especially as the high T_c-superconductors have complex electronic band structures and even their normal state properties are not well understood. The theory of Bardeen, Cooper and Schrieffer$^{(1)}$ (BCS) shows, that T_c depends sensitively on the product $N(o) \cdot V$, with $T_c = 0.85\ \theta_D \exp - |N(o)\ V|^{-1}$, where $N(o)$ is the density of electronic states at the Fermi surface and V is the electron - electron interaction parameter. This is the difference of two large interactions ($V = V_{Ph} - V_{Coul.}$), the attractive electron-phonon interaction ($V_{Ph} \simeq 1$ eV) and the repulsive Coulomb interaction ($V_{Coul.} \simeq 1$ eV). The Debeye temperature, θ_D, indicates the influence of the phonons and explains the experimentally observed isotope effect (i.e. T_c has been found to be inversely proportional to the square root of the mass of the isotopes for some soft metals). In extension of this theory, Mc Millan$^{(35)}$ derived the following equation, which has found a wide spread use:

$$T_c = 0.69\ \theta_D \exp - (1+\lambda)/(\lambda-\mu^+) \qquad \mu^+ < \lambda \text{ and } \lambda = N(o) I^2/M\theta_D^{\ 2}$$

where I^2 is the electron-phonon interaction constant and M is the mass of the lattice atoms, μ^+ corresponds to the Coulomb interaction and is about 0.1.

Pure soft metals exhibit perfect diamagnetism (Meissner - Ochsenfeld effect) in the superconducting state and exclude an externally applied magnetic field up to some critical field H_c: for higher applied fields the superconductor reverts to the normal conducting state. The dependence of H_c on the temperature is nearly parabolic and can be approximately described by $H_c(T) = H_c(o) \times |1 - T^2/T_c^{\ 2}|$. For a long thin wire parallel to the magnetic field, the magnetization M is proportional to the applied magnetic field until H_c is reached (Fig. 2), where the superconducting state switches to normal. Superconducting materials showing this magnetization behaviour are called type I superconductors. If a current is sent through a type I superconductor, the current flow is restricted to the surface. The maximum current density I_c will be reached if the generated field becomes equal to H_c. (For the above mentioned geometrical conditions I_c is given by $I_c = 2\pi\ RH_c/\mu_o$ with R = radius of the wire and $\mu_o = 4\pi \cdot 10^{-7}$ Vs/Am.)

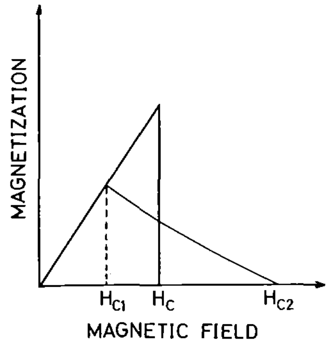

Fig. 2 Schematic drawing of magnetization curves for type I and type II superconductors.

In a type II superconductor the externally applied magnetic field can partly penetrate the superconductor so that in this "mixed state" superconducting and non superconducting regions exist at the same time. This state is also called the Shubnikov-phase. The magnetization curve for a type II superconductor is included in Fig. 2. At H_{c1} the applied magnetic field starts penetrating into the superconductor and forms a regular arrangement of filaments, the so-called flux thread lines. These fluxoids consist of a normal conducting core and a surrounding supercurrent vortex. If a current is sent through a type II superconductor an interaction will occur between the magnetic field of the flux threads and the current (Lorentz-force). The flux threads will move in response to this force, thus producing electrical resistance and losses. Therefore type II superconductors are not appropriate for technical applications in magnets. The flux threads have to be "pinned" and materials which contain pinning centers are called type III superconductors. A great variety of micro-structural features can act as pinning centers such as for example dislocations, grain boundaries, second phase precipitations as well as voids and defect clusters produced by particle irradiation. Both the lower and the upper critical field, H_{c1} and H_{c2} depend on H_c. The BCS theory connect Tc and Hc, and for $T \to 0$ it is: $H_c(0) = T_c \gamma^{0.5}/0.17$, where γ is the coefficient of the specific heat, which is proportional to N(E), the density of electronic states.

There are mainly three structural classes where alloy and compound superconductors with high critical fields have been found and used:

1. Most superconducting magnets have been produced with alloys having the bcc-structure such as NbZr (T_c = 11 K) and NbTi (Tc = 10 K). NbTi is slightly superior to NbZr because of easier fabrication and higher critical fields.
2. Interstitial compounds with NaCl(B) crystal structure are difficult to handle and have not been used. However thin NbN-films (17 K) produced by reactive sputtering have shown rather high current carrying capacities and are found to be rather resistant to radiation as will be shown later.
3. Compounds with the A-15 (ß-tungsten) structure such as Nb_3Sn (18.2 K) V_3Ga (17 K) reveal the best performance in as high field magnets known up to now.

INFLUENCE OF RADIATION DAMAGE ON THE SUPERCONDUCTING PROPERTIES

There are three main reasons which have led to the study of irradiation effects in superconductors:

1. In order to select suitable superconducting material for magnets used in accelerators and possibly in fusion reactors one has to know the influence of radiation damage on I_C, H_C and T_C.
2. The question as to whether irradiation or implantation can provide more effective pinning centers than can be obtained by conventional techniques is still not answered, even if there are some indications in recent work that heavy ion implantation may have some advantage.
3. The study of metallurgical or chemical effects of implanted ions requires a knowledge of possible damage effects.

In the following sections more recent work mainly performed by heavy ion bombardment is discussed.

a) Non Transition Metals

Only small effects of irradiation at 4.2 K on the properties of soft superconductors have been observed, far larger effects have been realized by cold working or in films evaporated on a liquid He cooled substrates (quenched condensed films). Radiation damage effects generally anneal below or at room temperature. This is in agreement with results obtained by Kübler and Meyer(29) for Sn and Pb films bombarded with $5 \cdot 10^{16}$ Ar^+/cm^2 at room temperature, where no influence on T_c has been observed.

A slight increase in T_C from 1.20 → 1.21 K of Al films however has been found after implanting high fluences of Ar ions (10^{17} Ar^+/cm^2). In these experiments, the range of the Ar ions was chosen equal to a larger than the film thickness, so that the observed effects are probably due to intrinsic damage. For Sn layers evaporated at room temperature and homogeneously implanted with Cu at 4 K, Buckel and Heim(4) found that the T_C increased by about 0.1 K and that the residual resistance as well as T_C saturated at a concentration of 50 ppm of Cu. In addition it has been found that the resistance of a quenched condensed Sn film (evaporated on a 4 K cold substrate) decreased during implantation of Mn ions in the same concentration region to about the same saturation level and therefore Buckel and Heim(4) supposed that an equilibrium state of radiation damage production and radiation annealing had been reached. For Pb films a small decrease in T_C of about 0.1 K has been observed after implanting Zn^+ ions. These results are in agreement with changes in T_C caused by cold working or by rapid quenching at liquid He temperatures. In contrast to this, earlier measurements by Van Itterbeck et al.(53) on Tl, In and Sn foils irradiated with 5.3 MeV α-particles at 4 K, showed a decrease in T_C of a few tenth of a percent. As the residual resistance ρ had not yet saturated in these experiments and a positive curvature dT_C/dC was indicated, further irradiation may have led to an increase in T_c.

b) Transition Metals

Neutron irradiation of Nb at room temperature have been found to alter the superconducting behaviour (and thus the effects observed are stable at this temperature). Neutron induced flux pinning centers are more effective in Nb than inhomogeneities introduced by mechanical deformation. Tsypkin and Chudnova(53) have bombarded Nb foils of different oxygen content (<2 at %) with 10 - 40 MeV N and O ions at fluences between 10^{12} and 3.10^{15} ions/cm^2 and have observed a significant increase in I_c and a slight increase in H_{c2}, Freyhardt, Loomis and Taylor(15), implanted 3.5 MeV Ni ions in Nb foils at 900°C and found a substantial increase in both I_c and H_{c2}. In both studies it is assumed that the regular arrangement of voids, which has been observed with transmission electron microscopy may be responsible for the observed results, as the superlattice of the voids advantageously fits the flux thread lattice. These results seem to be a first indication that heavy ion irradiation may produce a very effective pinning center arrangement which cannot be obtained by conventional techniques. In the above mentioned experiments T_c is only little affected at fluences which already have large effects on the current carrying properties. Using heavy ions and high fluences and thereby increasing, the energy density deposited in nuclear collisions, Crozat(11) and coworkers found a substantial decrease in T_c for Nb films, and Meyer, Mann and Phrilingos(36) for V, Nb and Ta films. T_c reductions in V layers have been observed by Kübler(28) in dependence on the mass, energy and fluence of the bombarding ions; the results showed that the reductions could be assigned to defects produced in the layers. Kübler(28) further investigated possible impurity effects due to the implanted ions by implanting Ga ions in V layers. By comparing the amount of T_c reductions observed for Ga^+ implantations with those for Kr^+ implantation, no additional effect could be detected up to about 20 at % of Ga atoms homogeneously distributed in the V films.

In a recent more quantitative study by Linker and Meyer(31) the damage production and distribution from Ne ions has been calculated and its influence on the T_c of V, Nb and Ta thin films has been measured. The energy of the Ne ions was chosen such that they penetrated the layers and came to rest in the substrates. In order to obtain a quantitative measure for the distribution and the total energy lost in nuclear collisions by the Ne ions in different layers, the primary energy deposition profile for the projectiles has been calculated from universal $(d\varepsilon/d\rho)_n$ data (ε and ρ are dimensionless range and energy parameters introduced by Lindhard, Scharff and Schiott (LSS)(32) using in the actual computations an analytical expression for $(d\varepsilon/d\rho)_n$ from Winterbon,Sigmund and Sanders(55) which is a good fit to Schiott's data and electronic stopping values from the LSS theory.

Some calculated primary energy deposition profiles for an Ne ion in V, Nb and Ta are given in Fig. 3; the R_p and ΔR_p values from LSS theory have also been included. These profiles are rather homogeneous in layers of about 1000 Å thickness as compared to profiles resulting when particles come to rest in the layer. It should be emphasized however that these are profiles for an average particle, as fluctuations in the range were neglected in the calculations. The influence of fluctuations on primary deposition profiles is evident mainly in the region where the particle come to rest. Similar densities of energies deposited in different materials were obtained by choosing appropriate fluences for the Ne ions.

Relative T_c reductions $\Delta T_c/T_c$ from the work of Linker and Meyer(31) are shown in Fig. 4 as a function of the density of energy deposited in the layers. For energy densities below 10^{18} eV/Åcm^2 the relative reduction increases slightly with increasing energy density and similar values are obtained for V, Nb and Ta. This result is not unreasonable for these groups VB transition metals as they all have the same crystal structure (bcc) and similar electronic density distributions. It is assumed that the heavy ion radiation damage reduces the density of states at the fermi level and/or

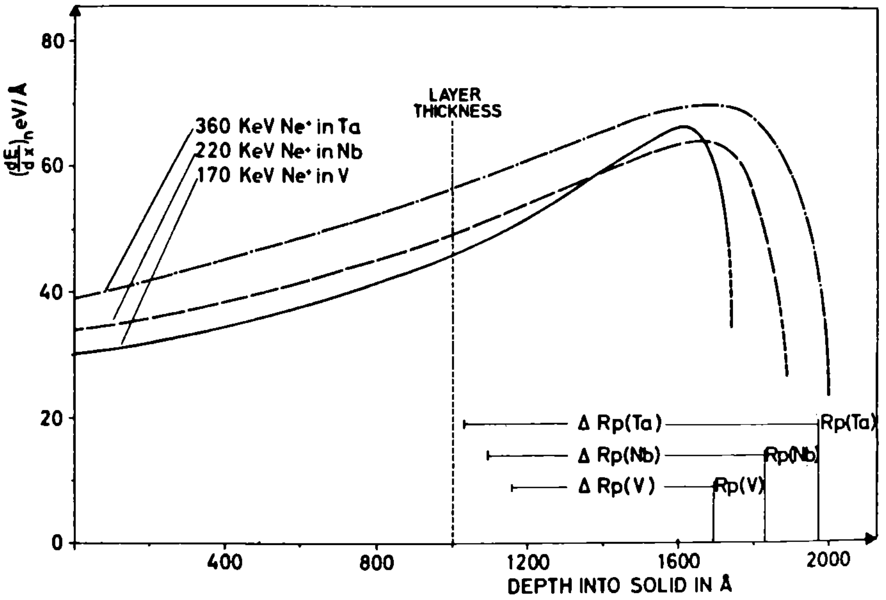

Fig. 3 Calculated primary energy deposition profiles for an average Ne ion in V, Nb and Ta; R_p and ΔR_p values from LSS theory are included in the figure.

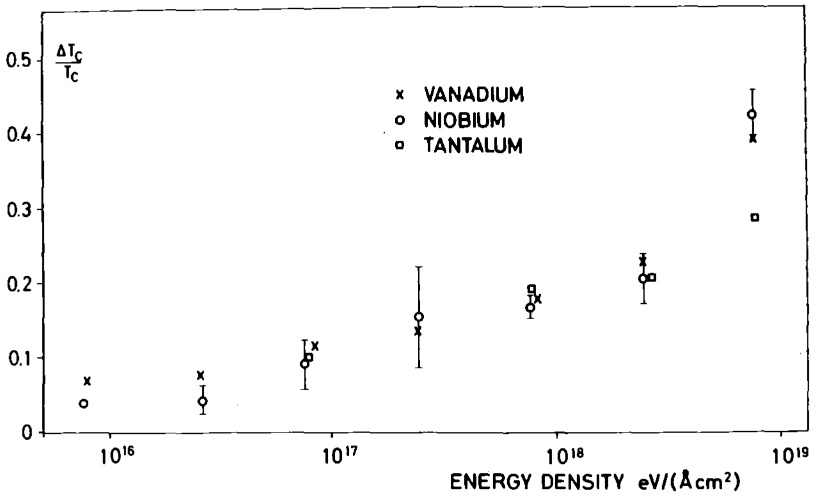

Fig. 4 Relative decrease of the superconducting transition temperature $\Delta T_c/T_c$ as a function of energy density deposited in nuclear collisions (ded).

increases the average phonon frequency as radiation hardening is known to occur in bcc metals. Of course, these are only two possible factors for a microscopic explanation of the T_c-reductions and no solid arguments can be given from the present experiments.

Beyond 10^{18} eV/Å cm^2, corresponding roughly to 50 to 100 dpa (displacements per atom), a pronounced change in slope is observed which indicates a different process influencing the superconducting transition temperature. Backscattering analyses indicated that the layers became slightly porous suggesting discontinuous material removal. In addition, from thin film x-ray analysis of heavily distorted layers only the two strongest reflections were recorded and these showed distinct broadening as compared with the equivalent reflections from unbombarded layers.

Deprez and coworkers(12) determined the low frequency (30 Hz) energy losses in superconducting V before and after implantation of 10^{16} Ga$^+$/cm^2 at 75 keV. They found that the losses for the lower ac amplitudes are about two orders of magnitude smaller in the sample implanted with Ga due to a pronounced increase of the surface shielding capacity.

c) Transition Metal Alloys

For NbZr and NbTi alloys large changes in the superconducting properties have been obtained by mechanical deformation or by introduction of impurities forming a second phase precipitation. Alloys that have been optimized in this way are found to be rather resistant against irradiation with neutrons and light ions. Meyer, Mann and Phrilingos(36) implanted Mo films with C ions up to concentration of about 10 at % and were able to increase the T_c from 1.2 to 7 K. In a second irradiation these layers have been bombarded with Ar ions up to $5 \cdot 10^{16}$ ions/cm^2 at room temperature. Only a small decrease in Tc from 7 to 6.5 K has been observed again indicating that transition metal alloys are rather stable against irradiation.

Chang and Rose-Innes(6), altered the composition of a cylindrical $Nb_{77}Mo_{23}$ rod by implanting extra Mo ions into a narrow surface strip parallel to the cylinder axis. This leads to a decrease of T_c where it is not certain if this decrease in T_c is due to a damage or an alloying effect. As T_c decreases rapidly with Mo concentration a local reduction of the surface pinning is observed in the case where the externally applied magnetic field is tangential to the surface strip in one of two possible directions. A reduction of the critical current is observed when the flux threads move towards the implanted surface and are less effectively pinned because superconductivity has been depressed in that region. These results confirmed that the current of a type II superconductor is determined by pinning of flux threads at the surface.

d) Superconductors with A-15 and NaCl-Structure

Numerous studies have been performed in order to investigate the influence of irradiation on the superconducting properties of compounds with the A-15 structure. The results obtained with neutron irradiation of Nb_3Sn have been well documented by Cullen(8). Studies by Wohlleben(56) with protons and deuterons and by Ischenko and coworkers(22) with oxygen ions agree with earlier observations that differences in the effects of irradiation are mainly due to the different microstructures obtained for material produced by different material preparation techniques. In several compounds I_c can be increased by more than an order of magnitude and this enhancement is stable up to annealing temperatures well above room temperature.
Other superconducting properties are less affected; T_c for example was found to decrease only by about 1 % in these experiments. In a more recent work Seibt(45) has studied radiation effects on commercial NbTi and V_3Ga multifilament wires homgeneously irradiated with 50 MeV deuterons up to a fluence of $2.6 \cdot 10^{17}$ ions/cm^2 near liquid He temperature. While irradiation effects on I_c and H_c were found to be negligible for NbTi in agreement with earlier observations, the V_3Ga wires showed a reduction in I_c by about 50 % and T_c decreased from 14.7 to 12.3 K. The influence of the deuteron

fluence on I_c is presented in Fig. 5, I_{co} is the critical current before irradiation. Annealing experiments up to 100°C resulted in a small (15 %) recovery of the superconducting properties of the V_3Ga wire.

Large reductions in T_c of A-15 superconductors have been observed recently in both neutron irradiated and heavy ion irradiated material. Schweitzer and Parkin(44) performed neutron irradiations at ambient temperatures with fluences between 10^{18} and 10^{20} fast neutrons/cm^2 . The A-15 materials Nb_3X, with X = Sn, Al, Ge, Ga and V_3Si showed a rapid monotonic reduction in T_c from about 0.95 T_c to 0.15 T_c of the unirradiated value in the fluence range indicated above. T_c changes for Nb, Nb-Ti and NbN are reported to be about 1 K after exposures of about 10^{20} n/cm^2. Large T_c reductions by thermal neutron irradiation have been observed by Bauer and Saur(2) for Nb_3Sn doped with boron and uranium, due to a large energy density deposited by the reaction products.

The influence of radiation damage produced by Ar ion bombardment with fluences between 10^{13} to 10^{17} ions/cm^2 on the T_c of thin films of various superconducting material observed by Meyer, Mann and Phrilingos(36) is summarized in Fig. 6. The relative decrease

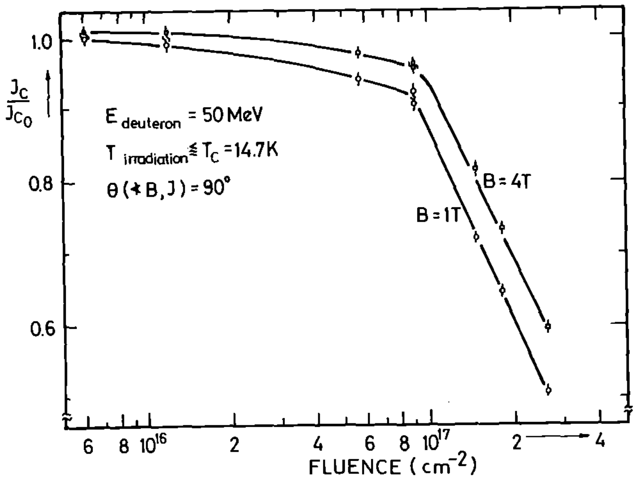

Fig. 5 Critical current ratio I_c/I_{co} versus deuteron fluence for a V_3Ga multicore wire (360 filaments, fil, diam. 10 µm). (from Seibt[45])

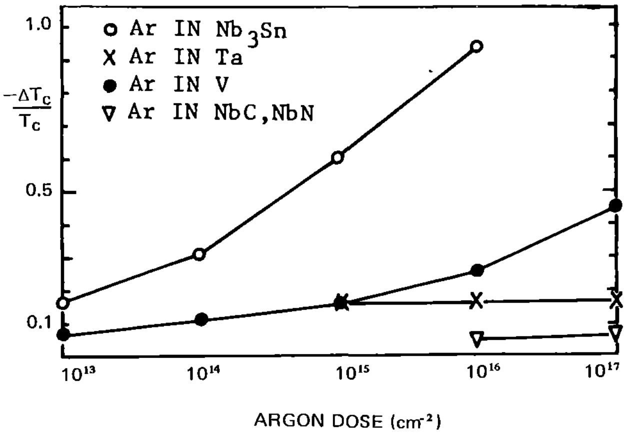

Fig. 6 Decrease of T_c, ΔT_c, normalized to the T_c of the unirradiated layer for V, Ta, NbN, NbC and Nb_3Sn in dependence on the Ar fluence.

in T_c, $\Delta T_c/T_c$, normalized to the corresponding T_c values of the unirradiated films is found to be quite different for Nb_3Sn from what it is for NbN and NbC. In Nb_3Sn layers, for example, the initial T_c of 18.2 K has been reduced to 2 K after implantation of 10^{16} Ar^+/cm^2 whereas for NbN and NbC with the NaCl structure only a slight influence has been found under similar irradiation conditions. In a preliminary experiment Linker and Meyer(31) have reduced the T_c of a Nb_3Ge layer from 20.7 to 7.1 K after irradiation with 10^{17} He^+/cm^2 at 300 keV.

e) Transition Metal Layer Compounds

Tsang and coworkers(57) studied the structural disorder induced by Ar ion bombardment of TaS_2 and $TaSe_2$ at room temperature and observed an increase of T_c to 4,2 K and 2,5 K respectively. Before irradiation the T_c in both cases was below 1,2 K. In NbSe however, T_c did not increase after heavy ion bombardment. This observed increase of T_c, due to inert ion bombardment is far more dramatic than that observed for non transition metals (see chapter Ia).As the crystal bonding in these compounds is predominantly ionic and/or covalent the T_c enhancement is probably due to the fact that in contrast to non transition metals the radiation defects are stable at room temperature. For TaS_2 and $TaSe_2$ as well as for $NbSe_2$ it is thought that the density of states is very high and has a maximum at the Fermi surface. As an increase of T_c has been observed for TaS_2 and $TaSe_2$, a model stating that radiation damage smoothes out sharp anomalies in the density of states which will lead to a decrease in T_c in some cases is probably not appropriate. Tsang et al. associated the changes in T_c in these compounds with the quenching of phase transitions by the introduction of crystal disorder.

f) Quantitative Estimation of Damage in Superconductors

Although numerous papers on the effects of irradiations on the superconducting properties (I_c, H_c, T_c) of elemental and compound superconductors with A-15 and B1-structures have appeared in the last years, only few quantitative connections have been drawn between changes in superconducting parameters and damage generated in the materials by the irradiations. This situation makes it difficult to compare the results obtained by different authors, especially when different particles like n, p, d or heavy ions are used in the irradiation procedures.

Some attempts however were made in this regard and Wohlleben (56), using a Rutherford scattering cross section for the estimation of the density of primary knock on atoms (PKA) produced with p and d irradiations in the MeV range, found that the maximum in the changes of the critical current ΔI_c for Nb_3Sn appeared at the same position on a fluence scale, when a normalized fluence

$$\Phi_n = \Phi \frac{M_1 Z_1^2}{E}$$

(Φ=ions/cm^2, M_1, Z_1,E: mass, charge number, and energy of the incident particles) was used. With this same procedure Ischenko et al.(22) were able to compare their results on the influence of 24 MeV O^{5+} irradiations on the critical current of Nb_3Sn with the findings obtained with proton and deuteron irradiations. Further Freyhart, Loomis and Taylor(15) converted the irradiation fluence of 3.5 MeV Ni^+ ions in Nb to a number of atom displacements per atom (dpa) whereas Crozat et al.(11) set the number of defects produced in Nb by Nb^{++}, $oxygen^+$and Er^+bombardment with energies of 130 keV, 15 and 40 keV and 50, 110 and 260 keV respectively, proportional to the ions energy. Linker and Meyer(31) recently compared the influence of heavy ion radiation damage produced with Ne^+ ions on the superconducting transition temperature T_c of V, Nb and Ta layers with the total energy density deposited in nuclear collisions (s. chapter I_b).

In principle, just as damage production rates and deposition profiles have been calculated by several authors for neutron and ion bombardment of solids (especially reactor materials) these procedures can also be applied to damage produced in superconductors. In the slowing down process of a particle, damage is generated mainly by nuclear stopping and, for a quantitative estimation, the appropriate cross section σ for nuclear stopping, for the ion-target systems and the ion energies under consideration, must be known for a calculation of the amount of energy deposited into nuclear collisions, and a reasonable displacement production function ν must be used to estimate the number of displaced atoms. If a damage density as a function of depth is desired the depth dependence of these functions must also be known.

The atomic concentration of displaced atoms C_d for monoenergetic ions may then be expressed by the following formula according to e.g. Thompson(51):

$$C_d = \Phi \int_{T_{min}}^{T_{max}} \nu(T) \frac{d\sigma}{dT} (E,T)\, dT$$

The symbols in this formula are:

Φ	total fluence
T	energy transferred to a target atom in a recoil with $T = 4\, M_1 M_2/(M_1+M_2)^2\, E \sin^2 \Theta/2 = \Lambda \cdot E \cdot \sin^2 \Theta/2$
E	energy of the incident particles
Θ	scattering angle in the center of mass system
M_2	mass of the target atoms
T_{max}	ΛE, maximum possible energy transfer to a struck atom
T_{min}	threshold energy for displacement production

For neutrons a similar general formula may be used e.g. Köhler and Schilling(24), Kulcinski et al.(27) and the concentration of displaced atoms is given by:

$$C_d = \Phi \cdot N \iint \rho(E) \sigma(E,T)\, \nu(T) dE\, dT$$

with

N	number of scattering centers per cm^3
$\rho(E)dE$	neutron fluence in energy range, E, $E + dE$
$\sigma(E,T)dE$	cross section for a neutron with energy E to produce a PKA in energy range T, $T + dT$

In these general formulas for the displacement production function $\nu(T)$, a simple KINCHIN-PEASE(23) model with $\nu(T) = T/2E_d$ (E_d-displacement threshold energy) may be used whereas for the differential cross section $d\sigma/dT$ a form suitable for the particle, energy and target-system under consideration depending on an appropriate interaction potential must be applied.
For light ions like p or d with energies in the MeV range a Rutherford scattering cross section ($d\sigma/dT \simeq 1/ET^2$) can be used; for heavy ions a differential cross section given by Lindhard,

Nielsen and Scharff(59) based on a Thomas-Fermi interaction potential which also covers the Rutherford cross section range is most suitable.
This scattering cross section is given by:

$$d\sigma = \pi a^2 f(t^{1/2})\ dt/2t^{2/3}$$

where
$t = \varepsilon^2 \sin^2 \Theta/2$
$a = 0.8853\ a_o(Z_1^{2/3} + Z_2^{2/3})^{-1/2}$
a_o = Bohr radius
ε = reduced energy parameter
Θ = scattering angle in the center of mass system.

$f(t^{1/2})$ is a function given in numerical form. A good analytical approximation for this function has been published by Winterbon, Sigmund and Sanders (55). Sophisticated calculations on damage distributions have been performed by Brice(3), who was able to include the energy transport of recoiling target atoms into the energy deposition distribution calculations.

INFLUENCE OF IMPLANTED IONS ON THE SUPERCONDUCTING TRANSITION TEMPERATURE

A continuous aim in the field of superconductivity is the search for material with large T_c values and this search has led to the observation, that material showing structured instabilities exhibit the best results in this respect. Instabilities in compounds or alloys occur at compositions close to phase transition regions and also in metastable compounds produced by non equilibrium processes such as splat cooling, evaporation and sputtering. The most obvious example for this is Nb_3Ge which has the highest known T_c of 23 K and which has been produced by all these techniques.

Ion implantation as a nonequilibrium technique is thought to be of interest in this respect because of its inherent possibility to increase solubility levels above thermal equilibrium values and to produce metastable alloys. A further possible application of this technique is the use of ion implantation in order to compensate deviations from stoichiometry and also to fill vacancies in sublattices of compounds which cannot correctly be formed by conventional techniques. A first indication that this might be possible has been obtained by Meyer and Hofmann(38), who implanted N ions in $NbC_{0.95}$ at room temperature and observed an increase in T_c from 9 to 11 K. The metallurgical nature of an ion implanted layer is known to be very complex as radiation damage and associated effects such as radiation enhanced diffusion and precipitate growing during implantation can significantly modify the metallurgical conditions. Therefore T_c measurements besides X-ray diffraction technique and transmission electron microscopy etc. can be used as an additional simple means to obtain information on the fate of the implanted ion. In the last few years ion implantation has been used by several groups in order to study the effect of implanted ions on T_c and their results will be summarized in the following chapters.

a) Magnetic Impurities in Non Transition Metals

The interaction of paramagnetic impurities in a metal with electrons in the normal as well as in the superconducting state will change the resistance and will lead to a decrease in T_c. With conventional techniques the preparation of interesting alloys is often limited because of very low solubility levels. Geerk, Heim and Kessler(18), and also Buckel and Heim(4) have produced such alloys by ion implantation near liquid He-temperature in order to prevent diffusion and precipitation of the implanted ions and to obtain metastable alloys beyond the solubility limit. On the other hand, very small concentrations were needed in order to avoid interaction among impurities. Ion implantation is known to provide small concentrations in the ppm range with the same relative accuracy as at very high concentrations. Results of this group(4) are presented in Fig. 7 where it can be seen that small concentrations of Mn cause a strong depression of the T_c of homogeneously doped Hg, Pb and Sn-films. The slope of the curves is approximately constant at concentrations above 100 ppm in agreement with theoretical calculations. At concentrations below 100 ppm a curvature in the T_c curves can be seen, being positive for the system Mn in Sn and negative for Mn in Pb and in Hg. These deviations from the linear dependence are thought to be due to lattice defects. In order to verify this assumption Buckel and Heim(4) implanted the nonmagnetic ions Cu and Zn which are close to Mn in the periodic system,into Sn and Pb layers respectively. The observed changes in T_c are also included in Fig. 7 and they explain the observed deviations at concentrations below 100 ppm. In several implanted dilute magnetic alloys a resistance minimum had been found at low temperatures. The observed logarithmic increase of the resistivity towards low temperatures indicates that the Kondo(26) effect is present in these alloys. In the theoretical work of Kondo this behaviour is explained by a negative exchange interaction between the spin of the conduction electrons and the localized spins of the magnetic impurities.

b) Pd-, Pd-Noble Metal Alloy, -Hydrogen System

A further excellent example of the usefulness of ion implantation has been demonstrated by Buckel and Stritzker(5), who succeeded in preparing superconducting Pd-H alloys by means of H im-

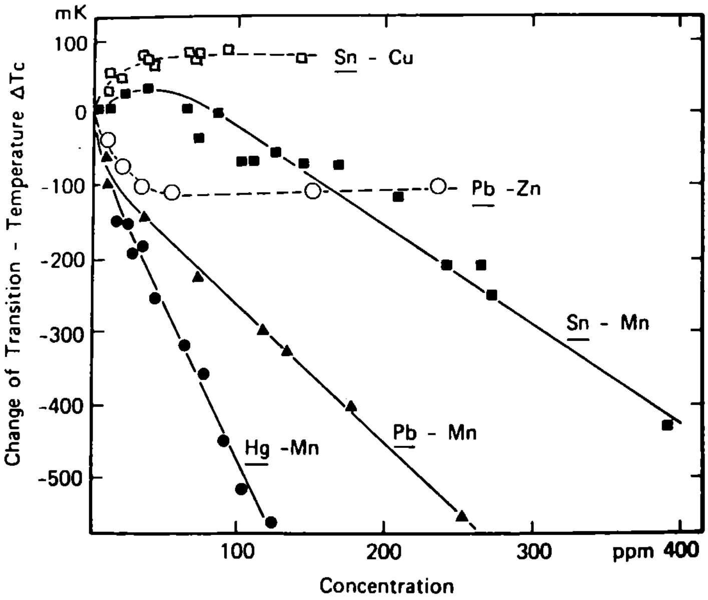

Fig. 7 Change of transition temperature ΔT_c for superconducting films of Pb, Sn, and Hg, as caused by implantation of Mn, Cu and Zn ions. (from Buckel[4])

plantation at liquid He temperature. They found a maximum in T_c with increasing fluence of H and D ions of almost 9 K for the Pd-H system and of 11 K for the Pd-D system. These maximum T_c values were estimated for a H/Pd ratio of about 1, which is not easily obtainable by other techniques. One of the main reasons for this T_c increase is thought to be due to the supression of the spin-fluctuations of the Pd as it is known, that the system becomes diamagnetic at a H/Pd ratio of about 0.7. In an extension of this work Stritzker(17) implanted H in Pd-noble metal alloys which are known to become diamagnetic if the noble metal concentration exceeds 60 at %. These Pd-noble metal alloys however do not show superconductivity above 10 mK. After implantation of H or D high T_c values have been measured which are probably due to a different T_c-enhancement mechanism. Foils with different noble metal concentrations for the three systems Pd-Cu, Pd-Ag and Pd-Au have been implanted with H ions and the fluence has been increased until T_c passed the maxi-

mum. These maximum T_c values are shown in Fig. 8 in dependence on the noble metal concentration. In the system Pd-Cu-H the highest T_c of 16.6 K has been observed.
With increasing noble metal concentration a decreasing H content is necessary to obtain the optimal T_c values. By further increasing the H concentration Buckel and Stritzker observed an irreversible change to the normal state. The resistance of the layers dropped and no superconductivity was found above 1 K. It is believed that this result is due to a phase transition from a lattice instability to a non superconducting phase with lower resistivity. Therefore it is assumed that the main precondition for the superconductivity in these systems is the suppression of the spin fluctuations, but that in addition, a peculiar phase transition indicates that weak phonon modes might be responsible for the high T_c values.

c) Ion Implanted Transition Metal Systems

Enhancements of T_c in various ion implanted transition metal systems based on Mo, W, Re and Ti have been reported(36). In a systematic study Phrilingos(42) tried to find out the physical reason for this T_c enhancement of implanted system produced at room temperature in comparison with the dependence of T_c on impurity concentration observed for solid solutions produced by conventional melting techniques.

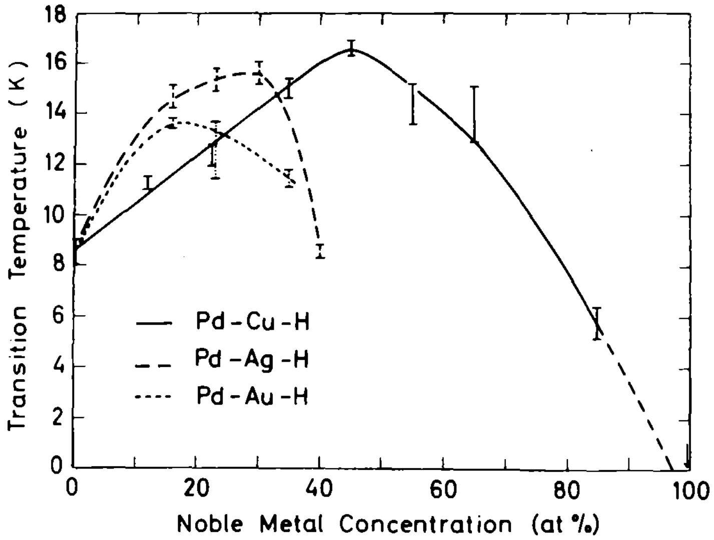

Fig. 8 Maximum T_c values after H implantation versus noble metal concentration in the systems Pd(Cu, Ag, Au)H. (Stritzker[47])

The superconducting transition temperature, T_c of transition metal alloys is known to vary strongly with the variation of the number of electrons per atom, e/a. Matthias(34) has formulated useful empirical rules for the T_c behaviour in transition metal alloys, suggesting that T_c depends on the e/a-ratio and maxima in T_c should occur at an average e/a near 4.8 and 6.8 (the number of e is set equal to the group number). In a theoretical work by McMillan(35) on transition metal alloys the rigid band model is assumed to hold for alloys of metals which are neighbours in the periodic table. Miedema(40) assumed that the two metals in the solution contribute individually to the density of states at the Fermi energy and he predicted a linear relation between the change of T_c with concentration, dT/dC, and the electron transfer which is proportional to the electronegativity difference.

Numerous work has been performed in order to study the influence of alloying on T_c of transition metals. For Mo it has been reported(19) that T_c is raised when the elements Tc, Re, Ru, Os, Rh, Ir, Pd and Pt, which have larger e/a ratios than Mo are dissolved in it. On the other hand, transition metals with smaller e/a ratios as for example V, Nb, Ta, Ti, Zr and Hf are known to decrease T_c upon alloying with Mo. The increase in T_c of Mo based alloys have been explained by Miedema (40) by a charge transfer from Mo to the more electronegative metals.

Ion implantation at room temperature has been used in order to introduce ions from all groups of the periodic system over a wide range of concentrations into the near surface region of molybdenum. This method has the advantage to overcome restrictions due to the solubility limit, as the solubility in a solid solution of elements with large differences in electronegativity are strongly restricted by the formation of stable intermediate compounds during recrystallization from melt.

In a systematic study Phrilingos tried to find out if the concept of charge transfer is a more general concept that will also hold for non transition metals in molybdenum. Ion species with different electronegativities and with concentrations of about 5, 10 and 15 at % in the peak maximum of the distribution of the implanted ions for each system have been used in this systematic study. The T_c-values of the implanted systems have been recorded and the results have been summarized in Fig. 9. This plot, as proposed by Darken and Gurry(14), combines the electronegativity and the atomic radii, the most important parameters involved in the Hume-Rothery rules(21) for the alloying behaviour of metals. In this plot Goldschmidt's(21) atomic radii for the coordination number 12 and Pauling's(41) values for the electronegativity have been used. The square in Fig. 9. around Mo, indicates the region where, concerning to the Hume-Rothery rules, elements have a high probability

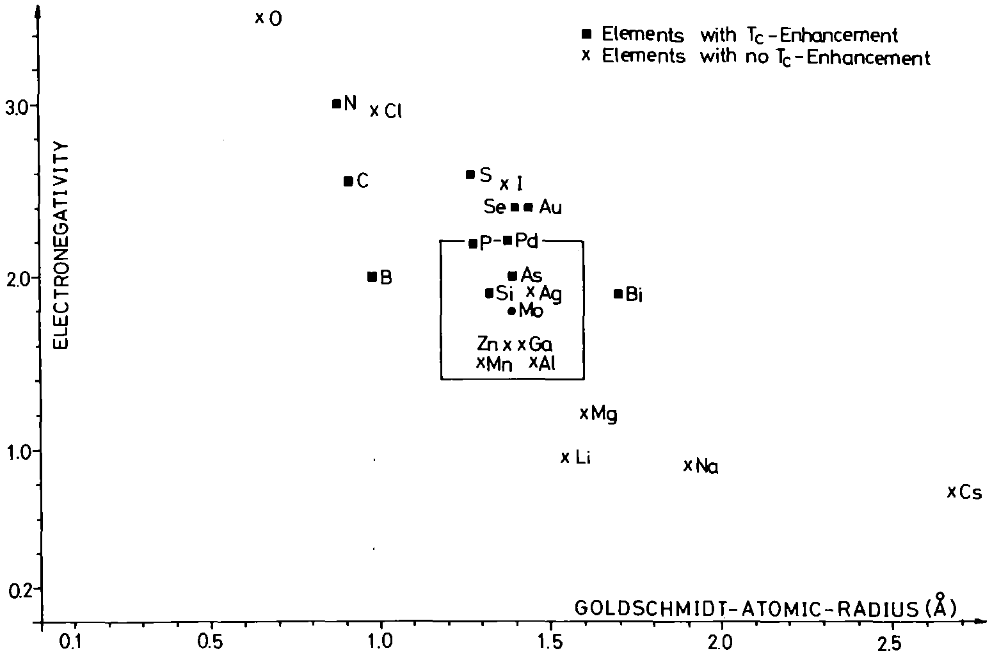

Fig. 9 Darken-Gurry Plot of ion implanted Mo-based systems summarizing the results of T_c measurements.

of forming a substitutional alloy with Mo. For the elements located in the square Ag, Zn, Ga, Mn and Al do not show any T_c enhancement, whereas for Pd (in agreement with conventionally prepared alloys), P, As and Si a T_c increase above 1.2 K has been observed. T_c enhancement is also found for elements located outside the square and therefore it is concluded that the formation of substitutional alloys is not of primary importance for the T_c enhancement mechanism. The results indicate that electronegativity is more important as for elements being more electronegative than Mo, an increase of T_c usually is observed.

The increase of T_c in dependence of the ion fluence has been measured for the systems Mo-C, Mo-N, Mo-S, Mo-Si, Mo-Au, Mo-As, Mo-B, Mo-Se, Mo-P, Mo-Pd and Mo-Re. The slopes $dT_c/\partial C$ of the last two transition metal systems were found to agree with those of

Mo-Pd and Mo-Re alloys prepared by conventional techniques. However the maximum observed T_c value of 10.5 K for ion implanted Mo-Re alloys was found to be smaller than T_c (max) of 12 K determined for conventionally prepared Mo-Re alloys.

The increase of T_c versus atom concentration is shown in Fig. 10 for Mo layers implanted with the non transition metals C, N, S and Si. After a sharp rise in T_c with concentration a saturation level is observed with a small decrease for high ion fluences. The slopes dT_c/dc were found to depend on the difference in electronegativity $\Delta\chi$.

The result that $\Delta\chi$ is the most important factor is further supported by the observation that for the Mo-Ag system with $\Delta\chi \simeq 0.1$ no T_c increase has been found whereas for the same group element Au with $\Delta\chi$ (Mo-Au) = 0.6 dT_c/dc is found to be about 0.2 K/at %.

In order to study the stability of the ion implanted Mo-based alloys the influence of isochronal annealing processes on the T_c of the ion implanted systems Mo-N, Mo-C and Mo-S have been studied and the results are given in Fig. 11. It can be seen that the T_c-

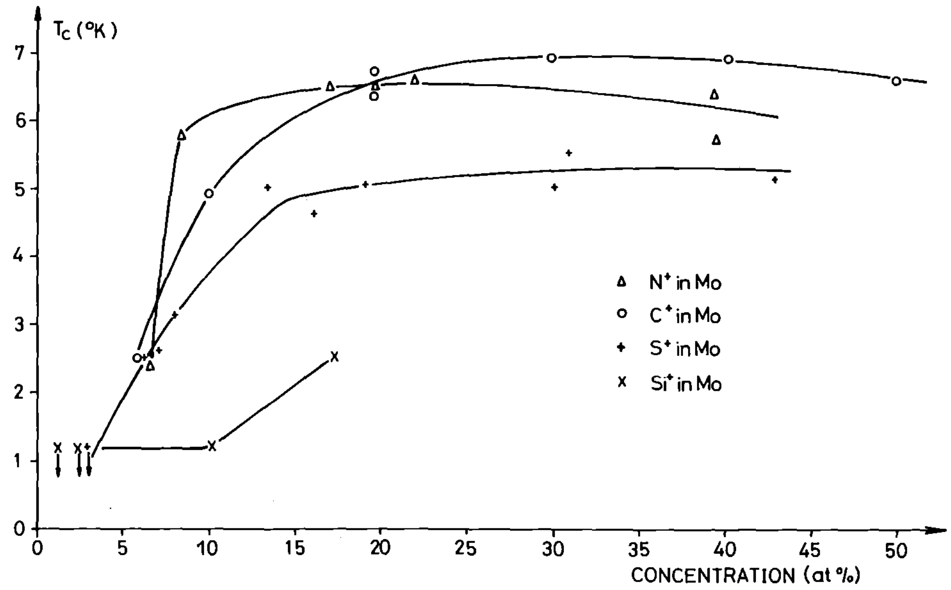

Fig. 10 Increase of the T_c of Mo layers after implantation of Si, S, C and N ions in dependence on impurity concentration.

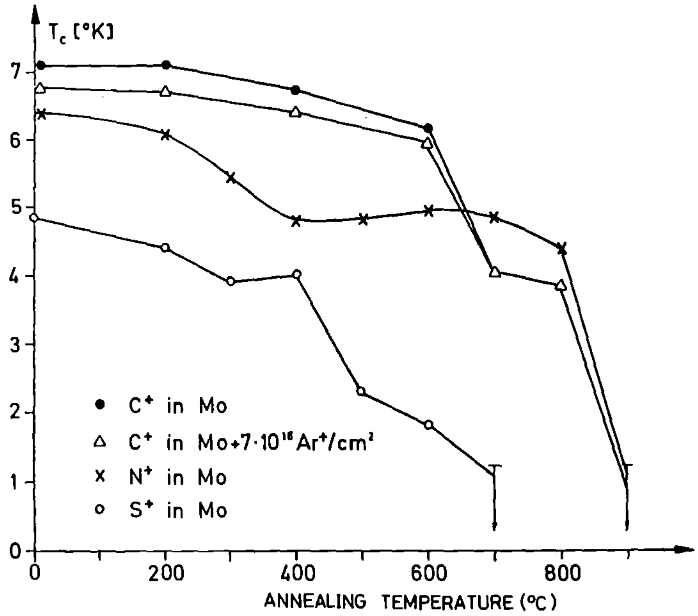

Fig. 11 Influence of an isochronal anneal process on the T_c of implanted Mo layers.

enhancement of this alloys is stable for annealing temperatures up to 400°C in the system Mo-S and up to 800°C in the systems Mo-N and Mo-C.

The influence of lattice disorder as discussed in chapter Ic is included in Fig. 11. Backscattering spectra from N^+ implanted Mo layers have shown that at 800°C the N has moved throughout the Mo layer and that at 900°C annealing temperature, additional oxygen had been incorporated. The sulphur profile however had not been found to change in the temperature range between 400 and 600°C.

Chu, McMillan and Luo(7) observed that the T_c of Re always increased by adding small amounts of transition metal impurities. As the density of states for Re sharply increases just below the Fermi level this authors believed that the observed increase of T_c is due to impurity scattering of electrons smearing out the density of states and thus leading to an increase of the density of states at the Fermi energy. The increase in T_C should be larger for Re samples doped with impurities having smaller e/a ratios than Re. In terms of Miedema's theory however, it is expected that impurities with an electronegativity smaller (larger) than that of Re will increase (decrease) T_C.

In order to test these predictions the author performed a preliminary study and the results are presented in Fig. 12 for Zr, N and S ions implanted in Re. A sharp increase of T_C for the Zr^+ implanted Re layers is found and the observed slope follows the results of Chu, McMillan and Luo for the W-Re-system. A relatively small increase in T_C is found for the N and S implanted Re layers

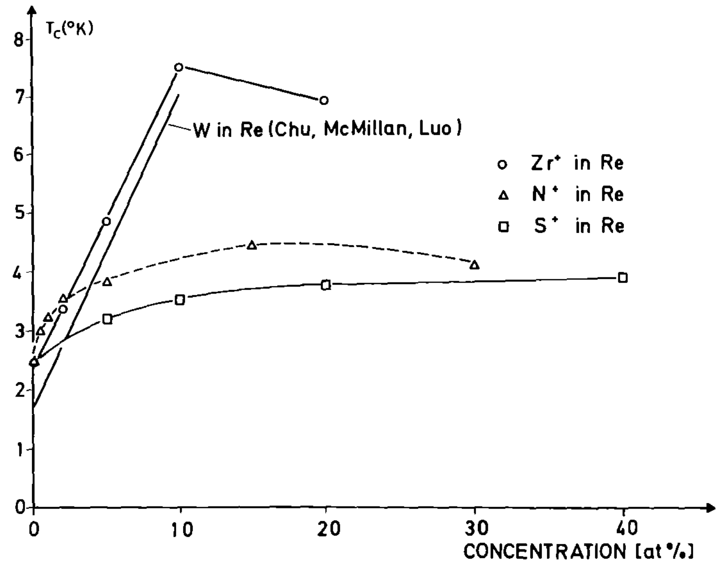

Fig. 12 Increase of the T_C of Re layers after implantation of Zr, N and S ions in dependence on impurity concentration; the T_c values of the W-Re alloys versus W concentration produced by Chu, McMillan and Luo are included for comparison.

which is consistent with the impurity scattering model discussed above. Further experiments are in progress in order to test if the charge transfer mechanism is also a useful concept for Re as it was for Mo.

d) Aluminum Based Ion Implanted Systems

In contrast to transition metals, alloying of the simple (sp) metal elements is nearly ineffective in enhancing T_c (alloys with transition metals are excluded) and usually the solid solubility level is very limited. In a preliminary study the author$^{(37)}$ used the simple metal Al as a target material mainly because numerous studies had been performed on the influence of impurities, pressure, strain and damage on T_c. In addition Thackery and Nelson $^{(50)}$ as well as Thomas and Picraux$^{(51)}$ have already performed studies on ion implantation in Al and information on radiation damage and precipitate growing during bombardment is available. Therefore it was hoped that T_c measurements would provide new information about the metallurgical nature of ion implanted Al layers.

In order to compare T_c-values measured for Al based alloys produced by conventional alloying and produced by ion implantation at room temperature, the elements Ge, Zn and Mg have been implanted. The solid solubility levels for these elements in Al are rather high (Ge 2 at %, Zn 25 at %, Mg 15 at %) and the influence of these impurities in Al samples produced by conventional alloying techniques on T_c has been studied by Chanin, Synton and Serin $^{(19)}$. They found that at low concentration (<0.1 at %) these impurities produced a decrease of a few percent in the T_c of Al, independent of the nature (electronegativity, valence, atomic size) of the dopant. This decrease in T_c is explained by Markowitz and Kadanoff$^{(33)}$ to be due to the removal of the anisotropy effect. A further increase in concentration C, yields a positive curvature in dT_c/dC, and the magnitude of this curvature seems to depend on the valence of the solute.

Seraphim, Chiou and Quinn$^{(46)}$ extended the experiments to higher (>1 at %) dopant concentrations and described the T_c dependence on the concentration by a single equation: $T_c = C(k_1+k_2 \ln C)$ where the parameters k_1 and k_2 seem to depend on the valence of the dopant and also on the mean free path of the electrons. They believe that clustering will effectively remove the dopant from the solution.

In Fig. 13 the results on T_c of Chanin et al. and Seraphim et al. are presented together with results observed for ion-implanted systems (Ge, Zn, Mg in Al) produced at room temperature. For Ge and Zn implants an increase ΔT_c is observed in the concentration region between 0.001 and 0.01 at %. The slope dT_c/dC decrea-

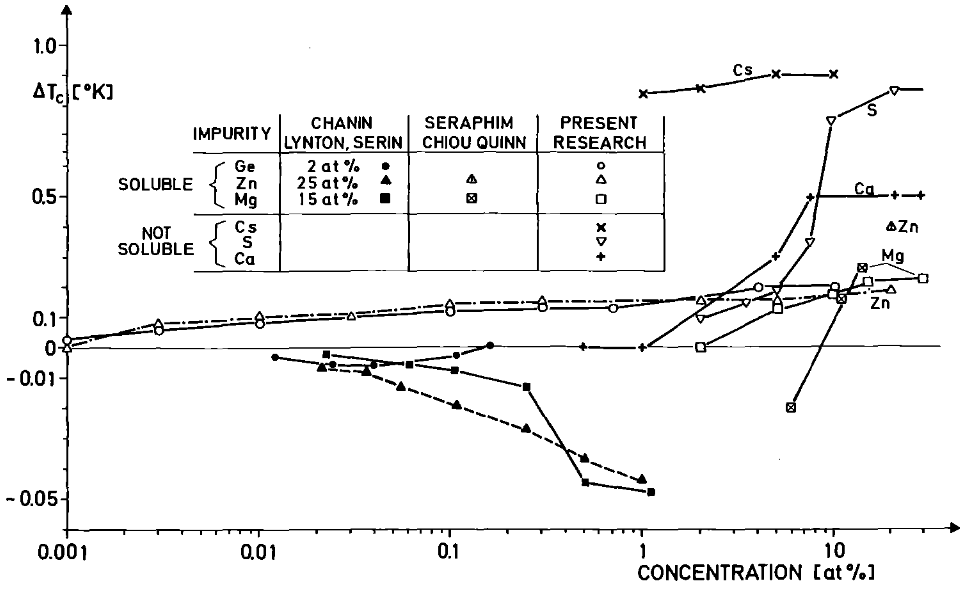

Fig. 13 Changes of the superconducting transition temperature ΔT_c in Al layers after implantation of different ions as a function of concentration compared with results obtained with conventional alloying techniques from other authors.

ses and is found to be nearly constant between 0.1 and 20 at %. The T_c value given for the system Al-Zn (20 at %) is found to be larger than the corresponding value for an implanted system. For Mg on the other hand an increase in T_c is observed for concentrations above 2 at % and a saturation level in T_c, T_c(max) is found for concentrations above 20 at %. In this case the behaviour of the ion implanted alloy is not too different from results obtained for conventional alloys although the different slope and the increase in T_c at smaller concentrations indicate that additional effects may influence the increase in T_c in implanted alloys.

It is obvious from the figure that the results obtained for as implanted samples cannot be described by the equation given by Seraphim, Chiou and Quinn(46) and one may conclude, that valence effects and the influence of impurities as scattering centers for electrons on the mean free path are not important. The results on the influence of pressure and strain as mentioned in the introduction lead to the hypotheses that localized strain fields associated with the impurity ions may be responsible for the observed increase in T_c. The possibility that local strain fields of the impurity atoms could influence the energy gap of superconducting Al-based alloys has already been treated by Claiborne(10).

In order to test the assumption that strain fields connected to the impurity atom or to an impurity-defect complex may cause the T_c-enhancement, ions, known to exhibit large size effects in Al have been implanted. The size mismatch between solvent and solute atoms results in a deviation from Vegard's law(21) and is proportional to the elastic strain energy as has been shown for example by Friedel(16). The size factor Ω_{sf} is defined by $(\Omega^x-\Omega_{Al})/\Omega_{Al}$, where Ω_{Al} is the atomic volume of Al and Ω^x is the value of the volume for a 100 at % impurity concentration extrapolated from the slope of the lattice parameter versus concentration obtained at low impurity concentrations. Table 1 shows the results for such impurities in Al, where the size factors are known and have been summarized by King(25):

Dopant	Ca	Mg	Ge	Ga	Ag	Zn	Cu	Pb
Ω_{sf}	+177	+ 41	+ 13	+ 5	+ 0.12	-5.7	-38	-53
$T_c^{(max)}$	+ 0.5	+0.23	+ 0.2	+0.22	+ 0.1	+0.13	0	+0.2

Table 1: Size factor and T_c(max) in ion implanted Al based systems.

In the limited number of Al based alloys for which size factors are available, Ca undoubtely has the biggest value and this value correlates with the largest value of T_c(max) in this special selection of elements. As an example the dependence of T_c for Ca on the concentration is also included in Fig. 13. For the other elements the correlation is not obvious and Cu, for example, which has a negative size factor does not show any increase in T_c at all. This observation may indicate that Cu completely precipitates during implantation at room temperature. The strain fields connected to the precipitates are believed to have no influence on T_c otherwise such influence should have been observed in conventional alloys with high impurity concentration levels.

In a further study, ions of different electronegativity, χ have been selected in order to see if the chemical nature of the element is important for T_c enhancement.

In Table 2 the results from this systematic study are summarized:

Dopant	Cs	K	Ba	La	In	Pb	Sb	B	Au	C	S	N
χ	0.7	0.8	0.9	1.2	1.7	1.8	1.9	2	2.4	2.55	2.58	3
T_c(max)	+0.9	0	+0.25	+0.1	+0.2	+0.2	+0.25	+1.1	0	+0.6	+0.9	+0.65

Table 2: Electronegativity and ΔT_c(max) in ion implanted Al based systems.

The T_c-enhancements seem to be pronounced for elements with large electronegativity values but there are two important exceptions: Au has a large electronegativity value but it does not show any T_c enhancement; this is similar to the result obtained for Cu. Cs has a very low electronegativity value but a large increase in T_c is observed. Here it is believed that, similar to the results obtained for Ca, a large size mismatch is responsible for this observation. From this study on electronegativity one may conclude that the chemical behaviour of the implanted ion itself does not play a major role for the T_c-enhancements observed in ion implanted Al base alloys produced at room temperature.
Large electronegativity values on the other hand may reduce the migration probability and prevent precipitation. The T_c dependence on the concentration of implanted S and Cs ions are also included in Fig. 13. It is assumed that a density effect is responsible for the observed results. A lowering of the density can lead to a reduction of the bonding forces between the Al atoms in the disturbed lattice and this in turn will reduce the average frequency of the lattice vibration and will increase the electron-phonon coupling strength in Al. This explanation is supported by several experiments which are summarized as follows: Hauser(20), studied mixtures of Al and 3.6 at % Ge sputtered at room temperature and observed a maximum T_c of 2.5 K. He explained his results by an observed 5-10 % increase in volume. This explanation is in accordance with a possible negative pressure effect, as Levy and Olsen(30) found that hydrostatic pressure p applied to Al decreased T_c. At low pressures dT_c/dp shows a linear variation for $p \to 0$, indicating that a negative pressure effect (decrease in density) may result in an increase in T_c. This assumption is supported by Notary's(39) observation of T_c-enhancement obtained by applying tensile strain on Al films evaporated on mylar.

APPLICATION TO SUPERCONDUCTING DEVICES

One of the first attempts to use ion implantation as a tool in the production of superconducting devices and integrated circuits has been performed by Harris(58), who implanted patterns of N and S ions into Mo films making use of the results already described in chapter III b. Harris successfully produced Josephson weak link structures in which two heavily doped Mo regions with relatively high transition temperature (T_c=4 K) are separated by a short (1 μm long) lightly doped Mo region with much lower transition temperature (T_c'=1.5 to 2 K). Near T_c' the lightly doped region acts as a weak link between the heavily doped regions and passes a supercurrent having an oscillatory diffraction pattern dependence on the magnetic field similar to that of Josephson tunnel junctions. A common feature of all weak link structures is the abrupt spatial variation of the superconducting properties and ion implantation may provide a technique to control the superconducting properties on a microdimensional scale and to produce very abrupt boundaries between implanted and unimplanted regions avoiding unwanted edge effects.

CONCLUSIONS

Numerous work has already been performed in order to study the influence of radiation damage on the superconducting properties as material has to be selected for superconducting magnets used in radiation environment and similar to reactor material, neutron radiation damage can quickly be simulated by heavy ion bombardment. The results of such work indicate whether the current carrying capacity of the material has been optimized or not and the irradiation equipment can therefore be used as a material test facility. It is not certain however if pinning centers or special arrangements of these centers produced by ion implantation will have some principle advantage as compared to pinning centers produced by metallurgical techniques; more work has to be done with heavy ion implantation.

Ion implanted systems have shown promising effects as far as the superconducting transition temperature is concerned and these results are mainly based on the fact that ion implantation is a versatile nonequilibrium technique. Figures of merit in this respect are the possibility to form metastable structures and the enhancement of solubility as has been shown for the Pd-H system and for non transition metals implanted into Mo and Re films, further advantage is the exact control of composition and stoichiometry. As the metallurgical state of an ion implanted system is difficult to analyze a detailed understanding requires more intensive work and it is believed that the determination of the superconducting properties of implanted systems together with the large experience from metallurgical superconductivity will provide further insight in these problems. The implantation technique itself has the advantage that systematic studies can be performed rather quickly and the optimized conditions for various parameters of a promising system under consideration such as atomic species, concentration, reaction temperature etc. can be determined in a reasonable time. Based on these data a special production procedure may be found which is not necessarily ion implantation.

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SUPERCONDUCTING PROPERTIES AND STRUCTURAL TRANSFORMATIONS OF NITROGEN IMPLANTED MOLYBDENUM FILMS

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Evaporated Mo-layers have been implanted with nitrogen ions to maximum fluences corresponding to a concentration of 33 at.%. The implantations lead to an enhancement of the superconducting transition temperature T_c up to 9.2 K and to structural transformations. Both effects are attributed to radiation induced disorder stabilized by the implanted impurity atoms; in particular the increase of T_c is thought to be due to the formation of impurity-defect complexes; channelling experiments support the idea of locally stabilized complexes.

1. INTRODUCTION

BULK MOLYBDENUM has a b.c.c. structure and is a superconductor with a transition temperature of 0.92 K. It has been found,[1–4] however that thin films of the element exhibit different structural and superconducting properties to the bulk material. For example vapor-quenched films show a high degree of disorder and have high transition temperatures T_c.[1,2] Chopra *et al.*[3] observed a f.c.c.-phase in evaporated and sputtered Mo-films; this phase has been found to be superconducting at a transition temperature of about 6.2 K and was interpreted as a polymorphous modification of molybdenum. F.c.c.-phases in sputtered Mo-films were also reported by Nagata and Shoji[4] but in contrast to Chopra *et al.* these phases were explained by the formation of γ-Mo_2N. An increase in T_c up to 7.2 K of Mo-layers sputtered with various noble gases has been observed by Schmidt *et al.*;[5] this increase was accompanied by a sizable lattice expansion but no additional phases were detected. Structural transformations in Mo from b.c.c. to f.c.c. lattice resulting from argon and nitrogen ion bombardment have been described by Pavlov *et al.*[6] and by Bykov *et al.*[7] and an increase of T_c in Mo-layers implanted with different ions has been reported for room temperature and low temperature implantations by Meyer *et al.*[8] and Meyer.[9]

In this present paper the influence of nitrogen implantations on both the transition temperature and structural transformations in Mo-layers is examined. Particularly it is investigated how the observed increase of T_c is correlated with radiation induced disorder and with structural transformations. The implantation process yields a dotation of the layers, in addition however in the energy loss process of the ions, target atoms are removed from their original lattice positions. This removal produces considerable lattice disorder and leads possibly to structural transformations; both these alterations of the host lattice (disorder and transformation) may be stabilized by the implanted impurity atoms.

2. EXPERIMENTAL

The Mo-layers were deposited onto heated (~ 900°C) quartz substrates by electron beam evaporation at a rate of about 100 Å/sec and a vacuum of 10^{-7} torr was maintained during evaporation; these deposition conditions were necessary to produce high purity layers. Layer thicknesses, which were monitored during evaporation with a quartz oscillator, were typically 1500–3000 Å.

Implantations were performed at room temperature and into liquid helium cooled layers to maximum fluences corresponding to 33 at.% nitrogen. In order to obtain a constant concentration of nitrogen over the range of interest several different ion energies were used; the fluences for each energy were determined by the calculation of added depth distributions using values of projected and straggling in projected range from Johnson and Gibbons.[10] The actual nitrogen distribution, layer thickness and purity have been analyzed by Rutherford backscattering[11] of 2 MeV $^4He^+$ ions while structural information has been obtained by diffraction measurements with a thin film X-ray camera. The superconducting transition temperatures were determined resistively using a standard four point probe arrangement. The lowest temperature attainable in our cryostat was 1.2 K.

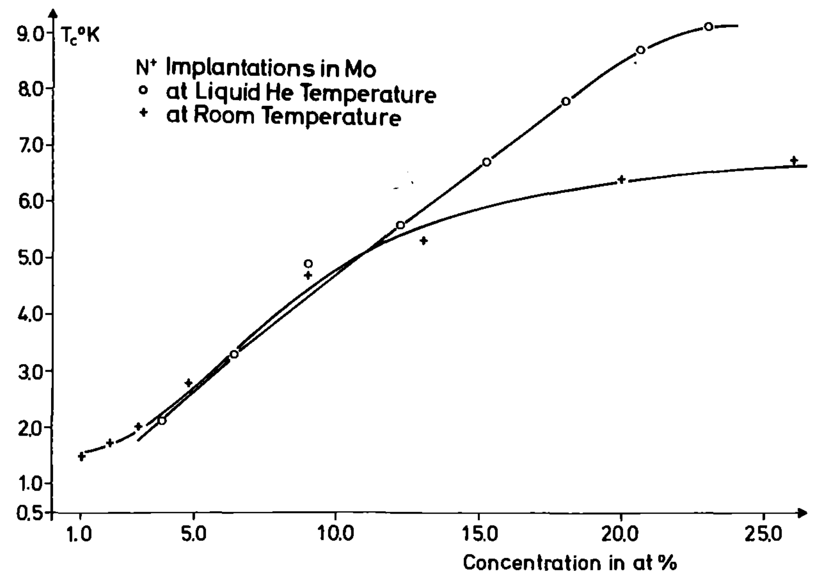

Fig. 1. Increase of the superconducting transition temperature T_c as a function of implanted nitrogen concentration at liquid He and room temperature implantations. Maximum observed T_c-values were 9.2 and 7.0 K for these temperatures, respectively.

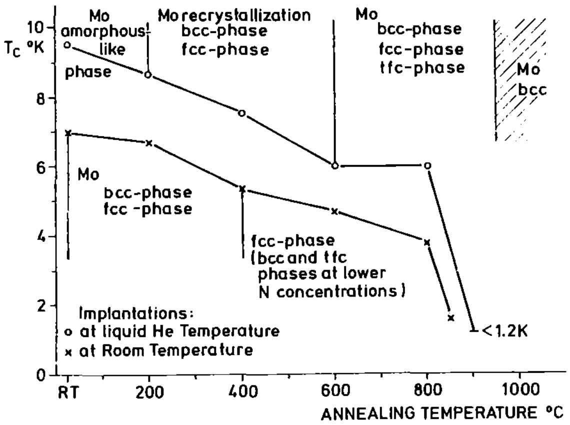

Fig. 2. Decrease of the superconducting transition temperature T_c and structural transformations as a function of temperature in an isochronal (1 *h*) annealing process. Samples were implanted till T_c-saturation at liquid He temperature and with 33 at.% nitrogen at room temperature respectively.

3. RESULTS AND DISCUSSION

All the as-evaporated Mo-layers had the b.c.c. structure. A residual resistance ratio of 4 or better was found for all layers and has been considered as a measure of the layer purity.

The nitrogen implantations lead to an enhancement of the transition temperature of the layers. This enhancement is shown in Fig. 1 where T_c values are plotted as a function of nitrogen concentration for both room temperature and low temperature implantations. For both sets of implantation conditions an increase of T_c with increasing nitrogen concentration is observed until saturation occurs at about 20 at.% nitrogen. The curves show a similar shape up to a dose of 12 at.% nitrogen, at which point the saturation region starts for the room temperature implants. An additional T_c-increase is observed for the low temperature implantations between 12–20 at.% nitrogen. The maximum detected T_c-values were 7.0 and 9.2 K for the room and low temperature implantations respectively. Synchronously with the observed T_c-increase the residual resistivity ratio of the implanted Mo-layers decreases.

Parallel to changes in the superconducting transition temperature and film resistance the nitrogen implantations caused modifications of the crystallographic structure in the evaporated layers. These modifications depended on the nitrogen concentration, on the implantation temperature and on the temperature in a subsequent annealing procedure.

Room temperature implantations with small nitrogen concentrations (up to 5%) lead only to a line broadening of the reflections from the b.c.c.-Mo phase. Above a dose of 10% at nitrogen, however, additional lines attributable to a f.c.c. Mo phase were detected in the diffraction patterns. With increasing nitrogen concentration not only does the number of lines from this f.c.c.-phase increase but also the lattice parameter expands from 4.15 Å (10 at.%) to 4.21 Å (33 at.% nitrogen). Structural investigations for layers implanted at liquid He temperature were restricted to concentrations where T_c-saturation had been achieved and were performed for samples already annealed to room temperature. Here only the strongest Mo-b.c.c. line (110)

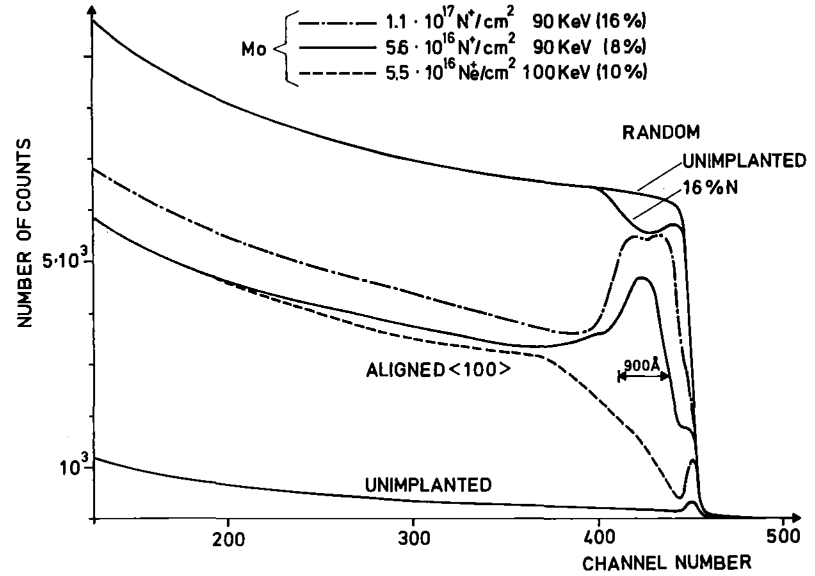

Fig. 3. Backscattering spectra with 2 MeV $^4He^+$ ions from aligned and randomly oriented Mo single crystals; the aligned spectra from nitrogen and neon implanted samples clearly reveal the different dechannelling behaviour in the region of the implanted ions. Spectra from an unimplanted crystal are included for comparison.

has been observed. This line exhibits considerable broadening when compared with the equivalent line from an unbombarded layer; a result which indicates that highly disordered, amorphous-like structures stable up to room temperature are produced at the low temperature bombardments.

Annealing of the implanted samples effects the transition temperature and the structure of the layers. Some representative results are illustrated in Fig. 2 where the T_c-values as a function of annealing temperature are shown in an isochronal annealing process (the structural alterations are included in a parametric presentation). The results stem from two samples, one implanted at liquid He temperature until T_c-saturation was reached and the other at room temperature with 33 at.% nitrogen. For both samples T_c decreases continuously as a function of annealing temperature up to about 900°C where a rapid reduction to below 1.2 K is observed.

The amorphous-like structure generated at low implantation temperature is conserved up to room temperature. It recrystallizes between 200 and 600°C whereby lines from b.c.c. Mo and f.c.c.-phases emerge in the diffraction patterns. Above 600°C the b.c.c.-phase is recrystallized and a weakening of the f.c.c.-lines is observed, however some additional lines attributed to a molybdenum face centered tetragonal (f.c.t.) phase are detected. Above 1000°C only b.c.c.-Mo is observed. The disappearance of the face centered phases above 1000°C is related to nitrogen outdiffusion off the samples; an effect that has been detected from backscattering measurements. For room temperature implantations b.c.c.- and f.c.c.-phases are present simultaneously in the as-implanted layers. In the sample shown in Fig. 2 above 400°C only reflections of a pure f.c.c-phase are observed; for samples with lower nitrogen content than that presented, above 400°C similar to the results described for the liquid He implanted layers also b.c.c. and depending on concentration, f.c.t.-lines are observed. Above about 1000°C again the face centered phases disappear together with nitrogen loss from the samples.

From the results described above we conclude that the T_c-enhancement in the nitrogen implanted Mo-layers is due to a disordered Mo phase, this phase being stabilized by the chemically active nitrogen possibly by the formation of Mo–N complexes. An indication that such a formation of complexes occurs has been already found in oxygen contaminated Mo-layers where a T_c increase has been observed by noble gas ion bombardment at low temperatures.[9] In layers having a small amount of contamination (< 0.5%) however the generation of pure defects by either implanting noble gas atoms or by bombarding through the layers did not increase the T_c above 1.2 K. Also no structural transformations were observed in these experiments with Ne or Ar irradiation, a result which is not in agreement with the observations of Pavlov.[6]

Channelling experiments performed on nitrogen and neon implanted Mo single crystals support the idea of a characteristic lattice distortion closely related to the chemically active dopant. The results from these measurements are illustrated in Fig. 3. Here backscattering spectra of a pure Mo-crystal aligned in [100]-direction and randomly oriented are shown together with spectra of aligned crystals implanted with nitrogen and neon ions. The spectrum from the Ne implanted sample shows an almost linear increase of dechannelling in the range of the implanted ions indicating the presence of long range order distortions like e.g. dislocations. The spectra from the nitrogen implanted samples however reveal well resolved disorder peaks originating from direct backscattering of He ions from displaced Mo-atoms probably bound to the displaced position by the nitrogen through complex formation. This disorder peaks anneal out between 800 and 900°C coinciding with the T_c decrease below 1.2 K in the implanted layers. The structure of these complexes is as yet not known especially as structural transformations at nitrogen concentrations above 10 at.% complicate the interpretation.

Finally the question arises as to what extent nitride phases determine or modify the superconducting properties of the layers. This question is important as for example γ-Mo_2N is a superconductor with a T_c of about 5 K and has a lattice constant in the range observed for the f.c.c.-phases in our experiments. Several arguments can be advanced to support the idea that nitride formation is not the primary reason for the T_c-enhancement. The highest T_c-values were observed at low temperature implantations and were correlated with a highly disordered b.c.c.-Mo phase; such disorder phases have also been activated by ion irradiation of oxygen, nitrogen or carbon contaminated Mo films and may be present also in films prepared by other techniques where energy loss processes in the keV range are involved (sputtering, ion beam deposition etc.). Further Mo_2N has a very narrow range of composition near 33 at.% nitrogen, whereas f.c.c. lines are observed at doses as low as 10 at.% nitrogen in the present investigation. Though nitrogen diffusion together with formation of islands of Mo_2N cannot be excluded with our analyzing techniques, this process seems improbable at room temperature. Implantations with 33 at.% nitrogen of course fulfill the conditions of Mo_2N formation and in the annealing experiments above 400°C only lines from a f.c.c. phase are observed, however also in these samples T_c decreases continuously as a function of annealing temperature while the f.c.c. phase emerges more distinctly in the X-ray patterns. Finally T_c decreases below 1.2 K while the f.c.c. phase is still present.

The results from nitrogen implanted Mo layers may be summarized as follows: the implantations lead to a T_c enhancement up to a maximum value of 9.2 K and to structural transformations with the occurrence of f.c.c. and f.c.t. crystallographic structures. Both these observations can be ascribed to radiation effects whereby disorder – and new phases are stabilized by the chemically active impurity atoms as no such effects are observed with the bombardment or implantation of noble gas ions. Similar results to those reported here for Mo have been observed in group Vb transition elements, although further investigation must be made before a detailed behaviour pattern can be assessed.

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