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Atomic Ordering and Superconductivity in High-T_c A-15 Compounds*

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Large, reversible changes in the superconducting transition temperature T_c of the Nb-based A-15 compounds Nb_3Al, Nb_3Sn, Nb_3Ga, $Nb_3(Al, Ge)$, and Nb_3Ge are observed when irradiated with high-energy ($E > 1$ MeV) neutrons at 60°C. The transition widths of the irradiated samples are of the same order as the unirradiated samples and the original T_c's are recovered by annealing. The results are discussed in terms of atomic ordering in the A-15 structure.

The effect of high-energy ($E > 1$ MeV) neutron irradiations on the superconducting transition temperature T_c of several A-15 (β-W) compounds was first reported by Swartz, Hart, and Fleischer[1] who observed small depressions, 0.10–0.22°K, for several A-15 compounds when irradiated to a fluence of 1.5×10^{18} neutrons/cm^2. Cooper[2] also observed a slight reduction, 0.16–0.20°K, in T_c for Nb_3Sn for a fluence of 2.7×10^{18} neutrons/cm^2. Recently, Bett[3] has observed large depressions, 1–13°K, of T_c for commercially prepared Nb_3Sn tapes for fluences up to 5×10^{19} neutrons/cm^2. We report here the effect of high-energy ($E > 1$ MeV) neutrons on T_c for the Nb-based A-15 compounds Nb_3Al, Nb_3Sn, Nb_3Ga, Nb_3Ge, and $Nb_3(Al, Ge)$. We observe large depressions, up to 17°K, of T_c for a fluence of 5.0×10^{19} neutrons/cm^2. The transition widths of the irradiated samples are of the same order as the unirradiated samples, and the effect is reversible in that T_c is restored to its unirradiated value by annealing. To the best of our knowledge, these are the largest depressions of T_c reported for the high-T_c A-15 compounds. The results are discussed in terms of atomic ordering in the A-15 structure and a model is developed which relates T_c to the long-range order parameter S.

The samples were prepared in a variety of ways. The preparation of Nb_3Ga,[4] Nb_3Sn,[5,6] and $Nb_3(Al, Ge)$[6] have previously been described. The compositions of the A-15 phase of Nb_3Sn, Nb_3Ga, Nb_3Al, and Nb_3Ge were 75.0, 75.0, 75.5, and 81 at.% Nb, respectively, as deduced from their measured lattice parameters.[4,5,7-9] Details of sample preparation will be presented in a later publication. The irradiations were carried out in the Brookhaven National Laboratory high flux beam reactor (HFBR) where the samples

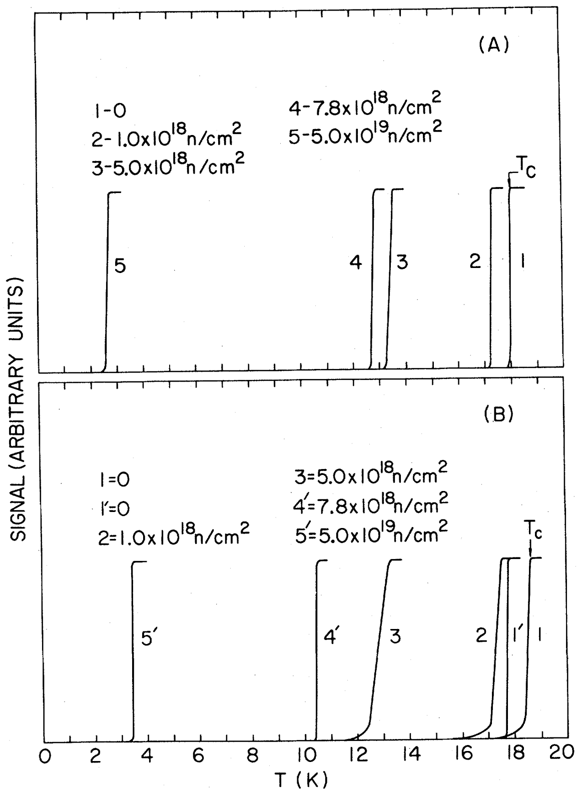

FIG. 1. Superconducting transition curves of (a) Nb_3Sn and (b) Nb_3Al for different fluence values. 90% of the measured transitions are shown. Primed numbers refer to unannealed sample.

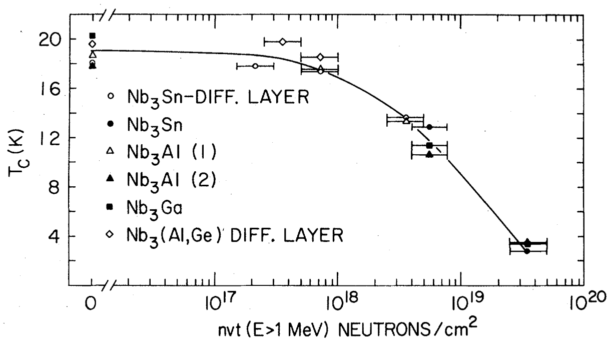

FIG. 2. Superconducting transition temperature T_c against fluence, *nvt* ($E>1$ MeV). Curve is drawn as a visual aide. Fluence values quoted in text and Fig. 1 are the highest values shown in the above figure.

were exposed to the whole spectrum of the reactor.[10] In the following only the fast flux ($E>1$ MeV) will be considered. The calculated temperature of the samples during irradiation was 60 ± 5°C. Superconductivity was detected by a standard mutual-inductance technique operating at 37 Hz, the temperature being determined by a calibrated carbon or Ge thermometer.

The results for Nb_3Sn and Nb_3Al are presented in Fig. 1 where the transitions for different fluence values are shown. It is seen that as T_c is progressively depressed, the transition widths remain constant. In Fig. 2, we have plotted T_c against fluence for all the systems studied. The T_c's are the highest value measured for the particular sample and the error bars for the fluence represent the uncertainty in the flux. It is seen that below a fluence of 1.0×10^{18} neutrons/cm^2, the depression of T_c is quite small, 3.9, 4.9, and 5.8% of the unirradiated value for Nb_3Sn, Nb_3Al, and $Nb_3(Al, Ge)$, respectively. Above 1.0×10^{18} neutrons/cm^2, T_c is rapidly depressed and for a fluence of 5.0×10^{19} neutrons/cm^2, the highest used in these experiments, T_c is reduced by 84.5, 80.8, and 83.3% for Nb_3Sn, Nb_3Al, and Nb_3Ga, respectively. This apparent threshold at $\sim1.0\times10^{18}$ neutrons/cm^2 is explained below. The T_c of arc cast Nb_3Ge was reduced from 6.5 to 4.9°K for a fluence of 7.8×10^{18} neutrons/cm^2, a 24.6% reduction. No evidence of saturation in the depression of T_c is observed, to the highest fluence used, 5.0×10^{19} neutrons/cm^2.

The width of the superconducting transition, ΔT_c, defined as the temperature range over which 90%[11] of the sample is superconducting, was the same for the irradiated and unirradiated samples, ~0.2–2°K. This strongly suggests that neutrons uniformly disorder the samples throughout their entire volume. We have been able to recover the unirradiated value of T_c for Nb_3Sn, Nb_3Ga, and Nb_3Ge by annealing at 750°C. Thus, after a 0.5-h anneal, Nb_3Sn that had been irradiated to 5.0×10^{19} neutrons/cm^2 increased its T_c from 2.8 to 14.3°K. A 5-h anneal yielded a T_c of 18.0°K and a 20.5-h anneal restored T_c to 18.1°K. For Nb_3Ga, irradiated to the same fluence, a 5-min anneal increased T_c from 3.4 to 11.4°K and after 20 min T_c was 19.5°K.[12] Nb_3Ge, irradiated to 7.8×10^{18} neutrons/cm^2, increased its T_c from 4.9 to 6.5°K after a 2-h anneal at 750°C The upper critical field, $H_{c2}(T)$, was also measured for samples irradiated to 5.0×10^{19} neutrons/cm^2 in a manner previously described.[13] $H_{c2}(T)$ was 200 ± 100 G at 2.3°K, 4700 ± 50 G at 1.64°K, and 7700 ± 50 G at 1.49°K for Nb_3Sn, Nb_3Al and Nb_3Ga, respectively. For purposes of comparison H_{c2} at 4.2°K for unirradiated Nb_3Sn, Nb_3Al, and Nb_3Ga is 235, 295, and 340 kG, respectively.[14,15]

There are at least three effects of neutron irradiation: (1) interchange of atoms between sites, (2) creation of interstitial-vacancy pairs, and (3) creation of new elements.[16] The creation of new elements is not important here, as T_c is recovered by annealing and the levels of any new elements would be in the ppm range. As the temperature for migration of interstitials is considerably less than the temperature of the irradiation, 60°C, there should be no free interstitials. The remaining vacancies are estimated to be <1% of the atom replaced.[17] Moreover, the effect of neutron irradiation on the T_c of those superconducting elements and compounds that are not sensitive to atomic order is small.[18]

Thus, in this case, the principal result of neutron irradiation is the exchange of atoms between sites. We can describe the positions of the atoms in the unit cell by the Bragg-Williams long-range-order parameter $S \equiv (P-r)/(1-r)$, where $0 \leqslant S \leqslant 1$, P is the probability of an A site being occupied by an A atom, and r is the fraction of A atoms in the binary alloy. Aronin[19] derived a relationship between S and the fluence n, which he has successfully used to describe results of neutron-induced order-disorder transformations in Ni_3Mn and Cu_3Au. His expression is $S = S_0 e^{-kn}$, where S_0 is the value of S before irradiation, n the fluence, and k is a proportionality constant. Aronin assumed k to be the same for both A and B atoms, a procedure criticized by Damask,[20] but we feel that is justified in the case of Nb_3Sn as the elastic cross section for neutrons, σ, for Nb and Sn at 1 MeV are equal and the masses are not too dissimilar. If a value of k could be obtained, it would be possible to relate S to T_c via the fluence n.

Aronin also noted that the number of atoms exchanged dQ per primary knock-on dc in a fast flux dn is given by k/σ. We have used the model of Kinchin and Pease[16,21] to calculate dQ/dc, and hence k, for the case of Nb_3Sn. The model neglects all irradiation effects except replacement collisions and, as the masses of Nb and Sn are relatively heavy, we assume both atoms lose energy to the lattice by atomic collisions and neglect any energy loss due to ionization effects. Assuming a monoenergetic beam of 1-MeV neutrons we obtain a value of 1501 ± 450 atoms replaced per primary knock-on, the error, indi ing the accuracy of the calculation, being abou 30%.[22] The value of σ for Nb and Sn is 6.1×10^{-24} cm^2,[23] yielding a value of $k = (0.9 \pm 0.3) \times 10^{-20}$ cm^2/neutron. We can now compare T_c directly with

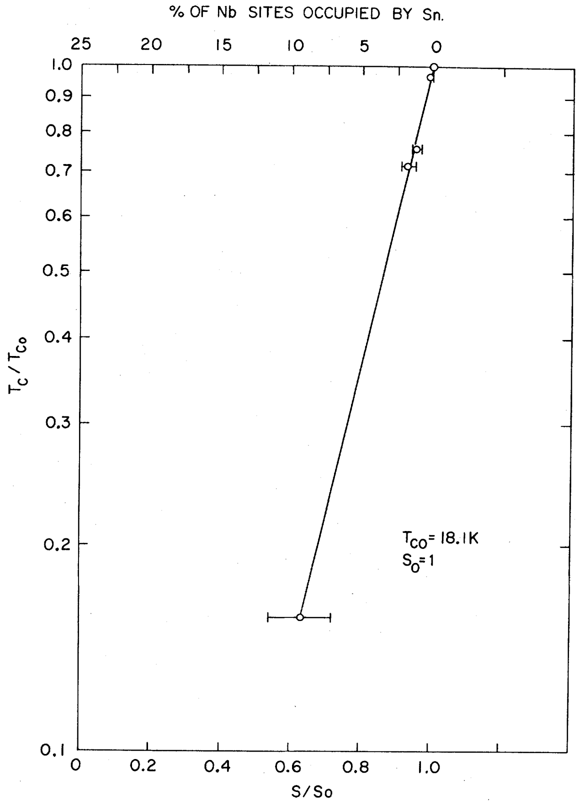

FIG. 3. Reduced transition temperature, T_c/T_{c0}, against reduced long-range-order parameter, S/S_0, for neutron irradiated Nb_3Sn. Also shown is the percentage of Nb sites occupied by Sn.

S through the fluence n. The results are shown in Fig. 3 where we have plotted the reduced transition temperature, T_c/T_{c0}, against the reduced order parameter, S/S_0. We find that T_c depends exponentially on S and is given by $T_c = T_{c0} \exp[-\alpha \times (1 - S/S_0)]$, where $\alpha = 5.0 \pm 1.5$, $T_{c0} = 18.1$°K, and we have used $S_0 = 1$, complete order, at $T_c = T_{c0}$. The exponential dependence of T_c on S, and of S on the fluence n, explains the apparent threshold in the depression of T_c at $n \sim 1.0 \times 10^{18}$ neutrons/cm^2. At this fluence S has changed by only 1% and T_c by 5.5%. However, by a fluence of 5×10^{18}, S has changed by 4.5% and T_c by 20%, and for $n = 5 \times 10^{19}$, S has changed by 37% and T_c by 85%, in good agreement with the observed T_c's.

Depressions of T_c for sintered and chemically-vapor-deposited Nb_3Sn have previously been observed.[24-27] These authors could not unambiguously ascribe the changes in T_c as due to disorder since the composition of the samples had to be varied in order to vary T_c. In our experiment, however, the depression of T_c is clearly due to disorder as the composition of the alloy is unaffected by irradiation and T_c is recovered by annealing. Splat-cooled Nb_3Sn displays a broad superconducting transition from 16.7 to 4°K indicating an inhomogenous disordering process due to the nonuniform cooling rate.[28] The measured average long-range-order parameter of 0.2 ± 0.15 in that case and our deduced values are not in good agreement, a fact which we hope to resolve by measuring the order parameters for our samples.

It is not possible to determine whether A- or B-site disorder is more important in the depression of T_c from an experiment of the type described here. However, available models[29-31] used to describe the properties of A-15 compounds have invoked the concept of "A chain integrity," i.e., A sites occupied by A atoms, as being important in determining the properties of these materials. Assuming this to be the case we can relate the depression of T_c to the replacement of Nb (A) atoms by Sn (B) atoms in Nb_3Sn. In Fig. 3 the percentage of Nb sites occupied by Sn for stoichiometric Nb_3Sn is also shown. At $T_c = T_{c0}$ a replacement of 1% Nb by Sn results in a T_c depression of 3.3°K and, when 9% of the Nb has been replaced by Sn, T_c has fallen to 2.8°K.

The results reported here indicate that high-energy neutron irradiation of superconductors can be a useful technique in the study of order-disorder effects, especially in the case where homogeneous disorder is difficult or impossible to induce by conventional means. Experiments are underway to measure S directly by x-ray and neutron diffraction techniques in the irradiated samples and to see the effect of disorder on the martensitic phase transition.

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Magnetic Interference Function of Amorphous Cobalt-Phosphorus Alloys

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A magnetic interference function has been observed for an amorphous ferromagnetic cobalt-phosphorus alloy by unpolarized-neutron diffraction. The distribution of the magnetic moments of cobalt is analyzed in terms of a partial pair-correlation function. Comparison with x-ray results gives good agreement.

The measurements of Rhyne, Pickart, and Alperin[1] on Tb-Fe alloys showed that the magnetic structure of amorphous alloys can be elucidated in the same way as magnetic structures of crystallized substances by unpolarized-neutron experiments. In such a study one has to make two essential choices: the nature of the alloy and the experimental method. We chose the cobalt-phosphorus system because in this alloy there is only one kind of magnetic atom, namely cobalt. Therefore, one can give an interpretation of the measurements in terms of a single pair-correlation function $G_{\text{Co-Co}}$. As pointed out by Rhyne, Pickart, and Alperin[1] such an interpretation is impossible if both constituents carry moments, as in Tb-Fe alloys, since in that case three pair-correlation functions have to be introduced.

In order to separate the magnetic scattering, one of two experimental methods can be used. Rhyne, Pickart, and Alperin obtained the magnetic contribution by subtracting two scattering patterns, one taken at a temperature above and one below the Curie temperature T_c of the sample. In Co-P alloys, however, complete crystallization has been reported to take place in the sample when heated to about 100°C[2] above T_c, the necessary temperature to obtain a perfectly disordered paramagnetic state. Therefore we chose to extract the magnetic signal by making difference measurements with a magnetic field applied successively parallel and perpendicular to the scattering vector and keeping the sample well below T_c (at room temperature).

Amorphous platelets of Co-P of five different concentrations around the eutectic composition (19 at.%) were prepared by electrodeposition from baths analogous to those described by Brenner, Couch, and Williams.[3] The platelets were 50 mm ×10 mm large and about 0.5 min thick. Their amorphous structure was carefully checked by x ray.

Neutron experiments were performed on the D2 diffractometer at the Institut Laue-Langevin. The neutron flux on the sample was 3×10^7 neutrons/cm^2 sec with horizontal collimations of 60′ in the pile, 60′ between the monochromator and the sample, and 20′ in front of the counter. The instrumental resolution over the whole κ range, $\Delta\kappa/\kappa$, was better than 5%[4] and no resolution corrections were necessary.

Two wavelengths λ were used: 0.94 Å reflected from a copper monochromator ($\lambda/2$ contamination less than 0.5%), and 1.92 Å reflected from a germanium monochromator ($\lambda/3$ contamination less than 0.8%). This permitted the recording of diffraction patterns between $\kappa_1 = 1$ Å^{-1} and $\kappa_2 = 7$ Å^{-1}, where $\kappa = (4\pi/\lambda)\sin\theta$. Measurements below κ_1 have to be performed on a small-angle-scattering apparatus. Beyond κ_2, measurements are practically impossible since the magnetic signal is roughly proportional to the square of the form factor of crystalline cobalt, which drops down to 1% of its initial value near $\kappa = 7.5$ Å^{-1}.[5]

A magnetic field of 15 000 G was used to magnetize the sample up to saturation. During the experiments the sample platelet was oriented so that its normal was always perpendicular to the scattering vector (Fig. 1).