is small, the dominant contribution is usually given by the states in the vicinity of the gap, and the properties of these states are frequently well known. In the Green's function formalism these dominating states give rise to certain dominating expressions for the zero-magnetic-field density matrix and Green's function.

From the form of Eqs. (6.12) one might expect that for $\omega \to \omega_G$ the leading contribution to the gyration vector comes from (6.12c), but this is not necessarily so. Take, for example, a crystal model as discussed in the last paragraph of Sec. 3. Each one of the two matrix elements in the last cross product in (6.12c) becomes a homogeneous linear function of the components of $\mathbf{k}$ (for $\mathbf{k}$ small) and vanishes, therefore, for $\mathbf{k}=0$. This reduces the singularity of $\mathbf{G}^{(1c)}$ to that of $\mathbf{G}^{(1b)}$, i.e., proportionality to $(\omega_G-\omega)^{-1/2}$ for $(\omega_G-\omega)\to+0$. Actually, it is only the first term in (6.12b) which shows this kind of singularity, while the second term has no infinity in the indicated limit. For the crystal model under discussion, the dominant behavior of the gyration vector for frequencies close to the gap frequency is, therefore, determined by $\mathbf{G}^{(1c)}$ and the first term of $\mathbf{G}^{(1b)}$ in (6.12).

While in the present paper the Green's-function method has been introduced primarily for methodological reasons, Green's functions are of advantage also in the actual calculation of specific problems. In a treatment of magneto-optical effects in insulating crystals with multiple valence and conduction bands at frequencies close to the gap frequency it can be shown, e.g., that the dominating part of the Green's function may be written in a form which is covariant with respect to unitary transformations among the basis functions characterizing the edges of the valence bands or the conduction bands, respectively. This facilitates calculation of the dominating behavior of the gyration vector, and we anticipate reporting about this subject in a later paper.

The model on which our considerations have been based and the results we have derived can easily be extended and generalized. Explicit expressions for effects depending on higher powers of the magnetic field, like diamagnetism or Voigt effect, can readily be derived from our general formalism. An extension of our model to include spin effects is straightforward. Finally, by the very nature of our approach as a Green's-function method, it should lend itself—with appropriate modifications—to take particle interactions into account.

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Superconductivity of Nb_3Ge

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Evidence is presented to show that the maximum transition temperature of compounds with the β-W type structure (*A*15) occurs at the stoichiometric composition A_3B, when B is a nontransition element. The niobium-germanium *A*15-type compound, which normally forms with excess Nb, has a transition temperature of 6.9°K. It has been found that Nb_3Ge compounds prepared by rapid-quench techniques, in the presence of excess germanium, have transition temperatures as high as 17°K. This large increase in transition temperature is attributed to a closer approach to the stoichiometric 3:1 composition.

THIS paper reports experimental results which indicate that the maximum transition temperature of compounds with the β-W type structure (*A*15) generally occurs at the stoichiometric composition, A_3B. In this structure type the A atom is a transition metal of the 4th, 5th, or 6th column of the periodic table and the B atom is either a transition or a nontransition metal. The effect of varying the composition on the transition temperature has been reported for several *A*15-type compounds in which B is a nontransition metal.[1] These include V_3Si, V_3Ga, Nb_3Al, and Nb_3Sn. It is always the stoichiometric compound which has the maximum transition temperature.

In order to illustrate the fact that the maximum T_c occurs at the ideal composition, the *A*15-type compound Nb_3Ge was investigated. This compound is isoelectronic with Nb_3Sn but its transition temperature is considerably lower. Geller[2] pointed out that the lattice constant of 5.168 Å for an Nb_3Ge compound as reported by Carpenter and Searcy[3] was larger than his predicted value of 5.12 Å and suggested that the β-W type phase did not have the correct stoichiometry. Carpenter[4] examined the composition range of Nb_3Ge and found

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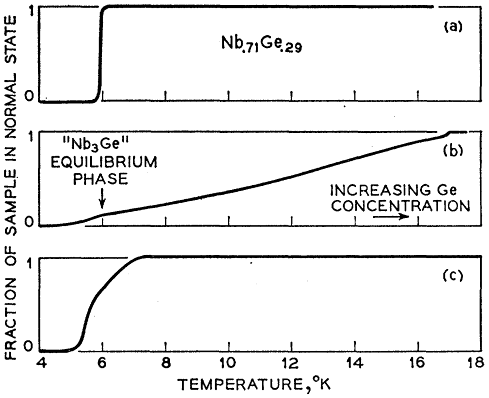

FIG. 1. Superconducting transitions of a melt of composition $Nb_{0.71}Ge_{0.29}$: Curve (a) as prepared in the arc, curve (b) after rapid quench and subsequent annealing up to 1000°C, curve (c) after annealing at 1100°C for three days.

a solid-solution range at 1600°C extending from 15 to 22±1 at.% Ge. The lattice constant varied from 5.177±2 to 5.167±2 Å, decreasing with increasing germanium content. Plotting Carpenter's data, and neglecting one experimental result which deviates considerably from limits of error which are quoted, the extrapolated lattice parameter for stoichiometric Nb_3Ge is 5.15±0.01 Å. The transition temperature of "Nb_3Ge" with a lattice constant of 5.166 Å was 6.90°K.[5] According to Reed, Gatos, La Fleur, and Roddy,[6] the transition temperature of an *A*15-type compound containing 14 at.% Ge was 4.9°K and for 18 at.%, it was 5.5°K.

Since it has not been possible to prepare the stoichiometric Nb_3Ge compound by conventional arc melting and annealing techniques, rapid quenching from the molten state[7] was attempted. Previous experiments have shown that one of the features of this quenching method, in which cooling rates in excess of 2×10^6 deg/sec have been achieved, was to increase the solubility of elements in each other. Two modifications of the quenching technique were used; one employed arc-melting and the other will be described by R. H. Willens in a later publication. In the arc-furnace method a small copper tube is connected by means of a quick-opening valve to a 30-cc pressure chamber of argon at 1000-lb pressure and is aimed at the ingot. When the ingot is molten, the valve is opened and the melt is thereby spattered against a massive copper shield on the far side of the arc furnace.

The transition temperatures of the samples were measured using the resonant-frequency shift circuit of Schawlow and Devlin[8] and a measuring frequency of 16 kc/sec. A series of samples was prepared with nominal compositions from 25 to 29 at.% Ge. All had rather sharp transitions at about 6°K as indicated for the $Nb_{0.71}Ge_{0.29}$ sample in Fig. 1(a). When these alloys were rapidly quenched from the liquid state the superconducting transition was raised as shown in Fig. 1(b). A few of the quenched samples also had an additional transition below 4°K, presumably from a very small quantity of a second phase in the sample. No effort was made to identify the phase belonging to this transition. The start of the high-temperature transition was pronounced and increased with increasing quenching speeds to above 17°K. The maximum transition temperatures were reached near compositions described above. Higher and lower germanium concentrations would lower the transition temperature. The quenched state was remarkably stable; the transitions were not due to any effects that could be annealed out at temperatures where one would expect to relieve strain. In fact, curve (b) of Fig. 1 was reproduced by the sample after various annealings up to and including 850°C for 3 days and subsequently 16 h at 1000°C. Finally after annealing at 1100°C for 4 days the original 6° transition was again approached as shown in Fig. 1(c).

By rapid quenching from the melt, it has been possible to achieve a more stoichiometric Nb_3Ge β-W phase. However, although this quenching method tends to increase the solubility of one element in another, there is also the possibility of producing disorder. Previous investigations[6] have shown the equilibrium β-W alloy to be ordered to the extent that all Ge atoms are on their correct sites. The x-ray patterns of the quenched Nb-Ge alloys are almost completely β-W with a few faint lines at low angles which could not be identified. The lattice parameter of a nominal 29 at.% Ge alloy is 5.149±5 which corresponds, within the limits of accuracy, to a stoichiometric alloy as determined from Carpenter's corrected data. (Using Carpenter's data directly, this lattice parameter would correspond to a β-W phase with 36 at.% Ge!) The ordering of the alloy has been investigated by comparing the integrated intensities of the (210) and (211) reflections on a Debye-Scherrer pattern. For a perfectly ordered alloy the intensity ratio of the (211) to the (210) reflection, with copper $K\alpha$ radiation, is 0.58. For a completely disordered alloy this ratio is 0.76. The measured intensity ratio is is 0.68. Assuming the germanium sites have equal probability (actually the site on the cube corner is different from that in the center), the intensity ratio is related to the long-range order parameter by the expression

$$I_{211}/I_{210}\approx0.756(1-0.259S+0.033S^2-0.003S^3+\cdots).$$

Using the measured intensity ratio, the average long-range ordering parameter is 0.41±0.15. This implies that about half (actually 0.45) of the germanium atoms are on a wrong site. The long-range order parameter as determined by x-ray diffraction is an average parameter.

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There are probably wide fluctuations about this value due to the nonuniform very fast cooling rate. These fluctuations in ordering over the dimension of a coherence length are probably the reason for the broad superconducting transition temperature. Heat treatment at elevated temperatures would not be expected to improve the ordering since the metastable stoichiometric alloy would decompose to a composition having a lower superconducting transition temperature.

The validity of the above model was investigated by quenching the homologous alloy Nb_3Sn. The observed superconducting transition was very similar to Nb_3Ge: a broad transition extending over a temperature range from 16.7 to 4°K. The initial transition temperature was also lowered 1.25° for the quenched alloy as compared to equilibrium alloy. The Debye-Scherrer x-ray diffraction pattern revealed a very sharp β-W pattern (resolution of the copper $K\alpha_1$ and $K\alpha_2$ reflection at high diffraction angles). The equilibrium alloy has been shown to be perfectly ordered[9]; however, examination of the intensities of the x-ray diffraction lines of the quenched alloy revealed that it was disordered. Applying the same analysis as that used for Nb_3Ge, the average long-range order parameter was 0.2 ± 0.15.

CONCLUSIONS

The transition temperature of stoichiometric, partially disordered Nb_3Ge which is produced by rapid-quench techniques is taken to be the rather reproducible start of the high-temperature transition, namely 17°K. The breadth of the transition is probably due to variations in order. Owing to the fact that Nb_3Sn when quenched has had its transition lowered by 1.25°, it is likely that stoichiometric-ordered Nb_3Ge would have a transition of at least 18°K.

The results tend to support our hypothesis that in β-W type compounds formed by transition and nontransition elements, the maximum superconducting transition temperature occurs at the stoichiometric composition; for it is at this composition that the atoms of the compound are probably completely ordered with respect to the A and B sites. The effect of disorder on the transition temperature is shown quite clearly when solid solutions are formed between two A15-type compounds such as V_3Si and V_3Ga or Nb_3Sn and Nb_3Al. Previous investigations have shown[5] that generally the transition temperature of the resulting ternary solid solution is lower than that of at least one of the stoichiometric compounds. The possibility of achieving local order, such as $ABABAB$ for example, over a coherence length for a system with only two components is, of course, vastly greater than that of achieving similar order for a three-component system, such as $ABCABC$. We had previously observed (unpublished) that even in solid solutions of two elements in one another the maximum transition temperature of the binary system could usually not be duplicated by any combination of three elements. This depression for ternary systems with identical number of valence electrons first showed the negative effect of local disorder, regardless of whether the rigid band model was valid or not.[10]

However, our hypothesis is not always valid if the B element is a transition metal. To date the exceptions are V_3Ir,[5] Cr_3Ir,[11] and the Mo-Tc compound containing 60 at.% Tc.[12] The V_3Ir compound is not superconducting above 0.35°K whereas $(V_{2.67}Ir_{0.33})Ir$ becomes superconducting at 1.39°K. The reason for this is not understood at present but it is not due to a more favorable valence-electron concentration for $(V_{2.67}Ir_{0.33})Ir$ (6.33 valence electrons). This is illustrated by the effect of varying the composition, and therefore the number of valence electrons, on the transition temperature of the A15-type V-Pt compound, which is quite similar to V_3Ir. The stoichiometric compound V_3Pt (6.25 valence electrons) has a transition temperature of 2.83°K; the nonstoichiometric compounds $V_{2.5}Pt$ (6.43 valence electrons) and $V_{3.5}Pt$ (6.11 valence electrons) are superconducting at 1.36°K and 1.26°K, respectively. Since as of today there is no explanation for the high transition temperatures of the ideal β-W compounds it seems rather futile at present to indulge in speculations on the nonideal ones. High-temperature superconductors are very rare. No new ones have been reported during the last five years. Nb_3Ge is particularly remarkable since a small variation of external parameters raises the temperature by 10 deg.

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