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Letters to the Editor

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Superconductivity in Tin-Germanium "Alloys"

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MEASUREMENTS of the variation with temperature of the resistivity in tin-germanium "alloys,"[1] and x-ray investigation,[2] have shown that the major portion of the tin taken up[3] remains free along grain boundaries, forming paths of relatively high electrical conductivity through the bulk germanium. A calculation[4] based on the assumption that veins of free tin were responsible for the observed conductivity gave results in good agreement with experiment.

The transition to the superconducting state has been measured for this material, which becomes effectively a mesh of superconducting filaments and might be expected to show a similar behavior to that observed in alloys. For the latter, the transitions are spread out over a relatively wide range of temperature, the lines of magnetic induction being pushed out of the specimen gradually as the temperature is lowered. The crowding of these lines in other parts of the specimen suppresses the transition there until a lower temperature is reached, where the critical field is correspondingly greater.[5]

The conventional magnetic method was employed, in which the specimen is made the core of a mutual inductance. The secondary coil is connected to a ballistic galvanometer and the throw on reversing the primary current is observed. The apparatus was enclosed in a bath of liquid helium, the specimen being in a small inner vessel also containing liquid helium. The temperature of the latter could be reduced by pumping off the helium vapor and was measured by means of the vapor pressure.

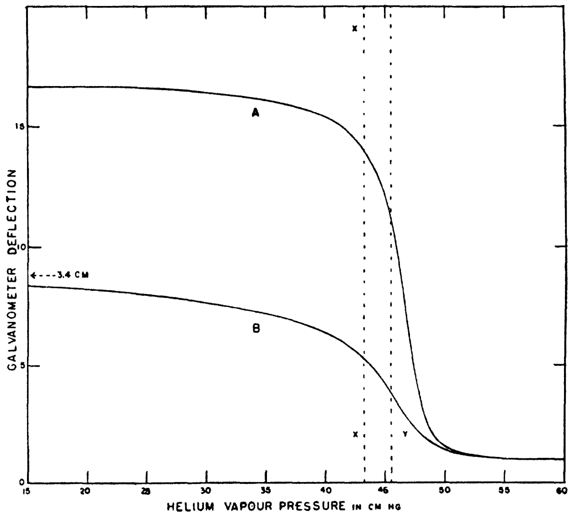

FIG. 1. Superconducting transition curves for tin-germanium "alloys." Measuring field approximately 4 oersted.

Measurements were made on two specimens of practically identical shape and volume, made by rounding off the edges of small rectangular blocks, the one (A) with 9.3 atomic percent of added tin and the other (B) with 2.3 percent. Each in turn was cooled (or allowed to warm up) very slowly through the transition range in the constant magnetic field of the primary coil, which was approximately 4 oersted. The cooling and heating curves coincided when the specimen was just covered by the liquid helium and when the rate of change of temperature was kept small.

Curves for specimens A and B are shown in Fig. 1. The transitions are very much extended and begin at the relatively high temperature of 3.90°, presumably due to strain. Whereas A is completed at 3.05°, curve B does not flatten off until 2.14°.

The total change in the galvanometer deflection indicates that in the case of B, with the smaller tin content, the "superconducting volume" is considerably smaller than the actual volume of the specimen; i.e., even when the transition is complete the magnetic flux is not wholly excluded from the specimen. It seems, therefore, that the "mesh" of tin is able to shield the bulk germanium in the case of A but only partially so in B. (By treating the specimens as ellipsoids of the respective length and diameter, allowance could be made for the demagnetizing effect and the calculations indicate, within the limits of this approximation, that specimen A shows a complete volume participation but B only 50 percent.)

The dotted lines, X, Y indicate, for comparison, the approximate limits of the transition for a sphere of pure, polycrystalline tin. The shift of the transition curves to lower temperatures on using stronger measuring fields was observed to be about the same as that for pure tin.

The investigation was carried out at the suggestion of Dr. K. Lark-Horovitz and was supported by the Signal Corps.

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[1] W. W. Scanlon and K. Lark-Horovitz, Signal Corps Report, Purdue (December 1946), unpublished.

[2] L. Dowell and K. Lark-Horovitz, unpublished.

[3] This was found to be less than the amount of tin added, *viz.* from 25 to 50 percent in different specimens, the remainder presumably being lost by evaporation. The amount taken up into the lattice varied from 0.25 to 0.50 percent.

[4] V. A. Johnson, unpublished.

[5] K. Mendelssohn, Proc. Roy. Soc. **A152**, 34 (1935).

Radiofrequency Spectrum of H_2 in a Magnetic Field*

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THE radiofrequency spectrum of H_2 in a magnetic field has been studied with a new molecular beam apparatus of high resolution. This apparatus is similar to that used by Kellogg, Rabi, Ramsey, and Zacharias[1-3] in the original study of the r-f spectra of the hydrogen molecules. In order that much narrower resonances might be obtained, the effective length of the homogeneous field region was increased from the 13.5 cm of the original studies to 149 cm. As a result, the total length of the beam was increased from 77 cm to 269 cm. The separated oscillating field method suggested by Ramsey[4] was used to increase the sharpness of the resonances and to average out the inhomogeneities which are almost unavoidable with such a long iron magnet. The beam was detected with a Stern-Pirani detector of improved design.

Figure 1 shows graphically the difference in results between using a single r-f field along the *C*-magnet and using the two separated fields. Somewhat more than optimum r-f current was used in each case to gain greater total intensity. For the single field case this results in a broadening of the peaks, whereas in the separated oscillating field method, the peaks have approximately the same width for all r-f currents.

It was found that the end sections of the *C*-magnet, where the r-f is applied in the separated field method, did not have quite the same average value of magnetic field as did the center section.

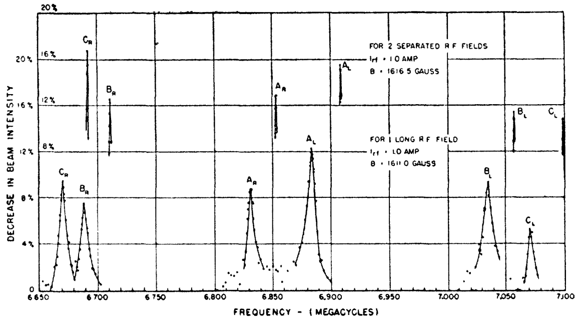

FIG. 1. Radiofrequency spectrum of ortho-H_2 for transitions with $\Delta m_I=\pm 1$ and $\Delta m_J=0$. Lower curve is with the conventional technique while the upper is with separated oscillating field method.

They were brought into agreement by passing appropriate small currents through two extra coils wrapped around the end sections of the *C*-magnet.

The r-f spectrum obtained with this apparatus for nuclear transitions of the first rotational state of ortho-H_2 in a magnetic field of about 1600 gauss is shown in Fig. 1. The half-widths of the sharp resonances are 0.7 kc, in contrast to the half-widths of 13 kc obtained in the previous studies of ortho-H_2. From these data the values for H′, the magnetic field at the position of the protons caused by the rotation of the molecule in its first rotational state, and H″, the field at one proton due to the magnetic moment of the other, are:

$$H'=26.74\pm 0.05 \text{ gauss},$$
$$H''=33.85\pm 0.09 \text{ gauss}.$$

This work is continuing and a more complete report will be made later.

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* This work was assisted by the joint program of the ONR and AEC.
† AEC Fellow.
‡ NRC Fellow.
[1] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **56**, 728 (1939).
[2] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **57**, 677 (1940).
[3] N. F. Ramsey, Phys. Rev. **58**, 226 (1940).
[4] N. F. Ramsey, Phys. Rev. **76**, 996 (1949); Phys. Rev. **78**, 695 (1950).

The Zero-Point Energy of Helium

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THE basic problems in the behavior of helium at low temperatures are to explain (a) why of all substances helium alone remains liquid down to absolute zero, for pressures below 25 atmos.; (b) why its molar volume at 0°K of 27.6 cc is about three times greater than the volume which a classical crystal would assume under the known forces acting between helium atoms; (c) why it has an energy at 0°K of −14.2 gram calories per mole, as compared with a value of about −150 for the classical crystal. It was Simon[1] who first proposed that these are quantum-mechanical effects stemming from the large zero-point energy of helium, which compensates most of the negative potential energy, and also "blows" it up. *If* these are quantum-mechanical effects, then the first problem can be explained. It was pointed out by J. De Boer[2] that the quantum effects depend on the magnitude and range of inter-atomic forces through the parameter $\Lambda^*=h/(\sigma^2 m\epsilon)^{\frac{1}{2}}$, where m denotes the atomic mass and ϵ and σ are the parameters in the Lennard-Jones type expression for the potential $\varphi(r)$ between a pair of atoms:

$$\varphi(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]. \tag{1}$$

ϵ and σ have been determined from the second virial coefficient (and in some cases also theoretically), and De Boer finds that for He, H_2, D_2, Ne, Λ^* has the values 2.64, 1.73, 1.22 and 0.591, respectively. F. London[3] estimated the zero-point energy of helium by adopting as a model a gas of rigid spheres. Since the latter quantum-mechanical problem has been solved only for the limiting case of low densities, he had to make an extrapolation to high densities. By choosing the best-fitting value for the molecular diameter, he showed that under these approximations problems (b) and (c) can be explained. In this theory the zero-point energy is taken to be independent of the structure of the liquid.

We have determined the zero-point energy of liquid helium on the basis of the Lennard-Jones and Devonshire[4] theory of liquids. This theory is based on the assumption that in a liquid each atom is hemmed in by its immediate neighbors with whom it suffers multiple collisions, and that the migration of the atom from its cage is an infrequent event when compared with the average time it spends inside its cage. The potential of an atom within its cage is computed, in the first approximation, as a function $U(r)$ of the distance r from the center of the cage by assuming the neighbors to be situated in a crystalline lattice, and then averaging the potential over the sphere of radius r. If a denote the distance to the nearest neighbors, c the number of nearest neighbors (coordination number), then on using expression (1) for the potential between a pair of atoms, one finds that

$$U(x)=4\epsilon c[(\sigma/a)^{12}A(x)-(\sigma/a)^6B(x)],\quad x=r/a, \tag{2}$$

$$A(x)=-1.011+(1.011+12x^2+25.2x^4+12x^6)/(1-x^2)^{10}, \tag{3}$$

$$B(x)=-1.200+(1.200+0.625x^2+0.185x^4+0.08x^6)(1-x^2)^4. \tag{4}$$

Here we have included a correction to the original expression of Lennard-Jones, introduced by De Boer and Lunbeck,[5] which takes account of the contribution from atoms which are not nearest neighbors. Lennard-Jones's theory yields values for the critical temperatures, boiling temperatures, and heats of evaporization of the heavy elements which are in good agreement with observations.

Using the experimentally determined values of $\epsilon=1.403\times 10^{-15}$ ergs, $\sigma=2.56\times 10^{-8}$ cm in (2), as quoted by De Boer[2] for helium, we have solved the Schrödinger equation for the atom in its cage and determined the proper value λ of the energy in the ground state. If N denotes Avogadro's number, then the energy E per mole at 0°K is given by

$$E=\{2N\epsilon c[1.011(\sigma/a)^{12}-1.200(\sigma/a)^6]\}+N\lambda, \tag{5}$$

where the expression in braces represents the energy of a classical crystal.

With the spherically symmetrical potential $\varphi(r)$ of (1), the atoms would crystallize into a face-centered cubic, for which $c=12$ and $a^3=\sqrt{2}\cdot V$. Figure 1 shows E, computed from (5), as a function

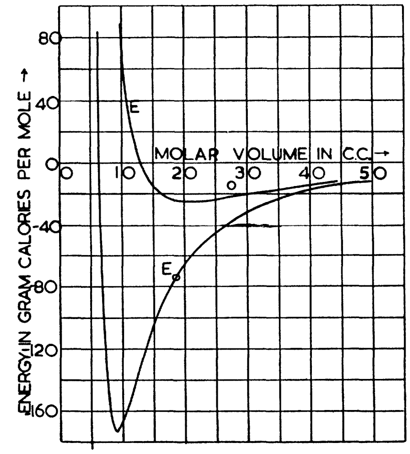

FIG. 1. Computed energy E of liquid helium as a function of the molar volume V. E_0 is the classical energy of a face centered cubic crystal (coordination number 12). ⊙ is the observed value for liquid helium.