ing warm-up.

Since all of the low He^3 concentration mixtures seem to follow the same positive-sloped freezing curve below 0.37°K, this portion of the common curve is interpreted to be the univariant hcp-L_1-L_2, where hcp represents the hexagonal close-packed phase of solid helium. Its intersection with the negative-sloped bcc-L_1-L_2 is then a quadruple point[1,8] with the four phases bcc, hcp, L_1, and L_2 coexisting. Since the quadruple-point pressure as shown in Fig. 2 is 26 atmospheres and since the hcp-L_1-L_2 univariant must merge with the pure He^4 melting curve at 0°K, the total pressure range spanned by the positive-slope region is small, placing restrictions on the sample pressure before cooling.

The portion of the freezing curve with negative slope below 0.37°K is the univariant bcc-hcp-L_2. Four univariant lines must terminate at a quadruple point.[8] The fourth line must be hcp-bcc-L_1 in this case. The high-temperature terminus of this line is at the melting curve of pure He^4 and has been shown to occur at 1.45°K and 26.2 atmospheres by Vignos and Fairbank.[9] An attempt to measure this univariant at lower temperatures is now under way in our laboratory.

Zinovieva observed visually the stratification of an 86.3% mixture into two liquid phases at temperatures of 0.3 and 0.35°K and a pressure of 26 atmospheres with no solid being present.[10] Her result is in qualitative agreement with the data in Fig. 2 and with the phase diagram presented in reference 1. Zimmerman[11] has noted peaks in the specific-heat curves of mixtures dilute in He^3 in the vicinity of the liquid-solid boundary which might provide indirect evidence for the positive-slope region in Fig. 2.

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CRYSTAL STRUCTURE OF SUPERCONDUCTING V_3Si

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We wish to report the discovery of a martensitic phase transformation at low temperatures for the superconducting compound V_3Si and observations suggesting that related transformations occur in other substances having the "β-tungsten (A-15)" structure.

The first evidence for anomalous structural behavior near the superconducting transition temperature, $T_c = 17.0$°K, of V_3Si was inferred from neutron diffraction studies by Shull.[1] He observed a broadening of diffraction lines on cooling below T_c. We have studied the transformation over a range of temperatures by means of x-ray diffraction (Berg-Barrett) topographs and by means of determination of the relative lattice spacings of various hkl reflections using single-crystal x-ray techniques.

Figure 1 is a topograph from a single crystal of V_3Si at 4.6°K using Cu $K\alpha$ radiation reflecting in the second order from a cube face of a single crystal. The vertical and horizontal bands are in the [001] and [010] directions. (The deviation

FIG. 1. X-ray topograph of single crystal of V_3Si at 4.6°K showing the twinned tetragonal structure. Magnification 12×.

from orthogonality is because film and diffracting plane are not exactly parallel; other topographs have established the orthogonality.) Tests show that the contrast in the image is primarily due to tilts of the order of several tenths of a degree between adjacent bands. From topographs using diffracting planes not parallel to the crystal surface, such as (420) and (421), the clear region of Fig. 1 can also be seen to contain bands, which lie along the traces of (011) and (01$\bar{1}$) planes.

These data are consistent with the bands being traces of {110} planes on the crystal surface. Above the transformation temperature T_m (for this crystal 27°K), the bands completely disappear and the entire topograph is uniformly grey as in the left side of Fig. 1.

By using an x-ray focusing technique we can examine the d spacings for the various reflections and eliminate any line shifting that might be caused by the tilting of the lattice in the various bands. With this technique we have found that at temperatures below T_m the (h00) reflections are split, revealing the presence of two different spacings; other split reflections are also found.

The structural conclusions to be drawn from the topographs and lattice spacings can be summarized as follows: The transformation is from a cubic β-tungsten (A-15) structure above T_m to a tetragonal structure below this temperature. The loss of cubicity is complete on cooling through a few tenths of a degree Kelvin and is reversible. In all tests made thus far the crystallography of the transformation is of the well-known martensitic type found in the cubic-to-tetragonal transformation in the indium-thallium system,[2-4] which would imply that the bands in the topograph are from twin-related tetragonal lamellae. Quantitative measurements on a particular single crystal give $c/a = 1.0025$ at 4.6°K and a T_m of 30.0°K.

To check on a possible orthorhombic form we can give the limits $a/b = 1.0 \pm 0.000\,06$; c and a vary continuously below T_m with a steep slope at T_m so that the c/a ratio increases very nearly to the 4.6°K value upon cooling a few degrees below T_m. The variation of c and a are such as to maintain very nearly constant volumes of the unit cells just above T_m and at 4.6°K, indicating that there is little or no volume change at T_m. All of these characteristics are consistent with a second-order martensitic phase transformation.

In the four single crystals investigated, T_m has ranged from 23°K to 30°K. In each specimen the transformation was sharp in temperature and reversible in cycling from a few degrees above T_m to 4.6°K. No temperature hysteresis was detected and the sample always returned to a single crystal of the original orientation. The maximum c/a ratio is different in different specimens.

Evidence for the transformation in V_3Si has also been obtained in x-ray powder diffraction patterns, but the general broadening of the lines did not allow a structure determination. The same general type of broadening in powders has been observed for Nb_3Sn with a T_m the order of 35°K, while for V_3Ir ($T_c < 0.3$°K) no indication of a transformation has been observed down to 4.6°K.

Following the x-ray determination of T_m in V_3Si and Nb_3Sn, J. J. Hauser has observed resistivity anomalies in these compounds at comparable temperatures as well as in other β-tungsten structures.

We conclude that tetragonal V_3Si is a superconductor with a transition temperature of 17.0°K. It is also highly likely, but not proven, that all V_3Si is tetragonal in the superconducting state. It seems probable that other superconducting materials that have the A-15 structure at room temperature also undergo a similar martensitic transformation on cooling to temperatures near T_c. The possibility must be considered that both the structure transformation and the occurrence of superconductivity in A-15 structures may be the result of the same interaction, even though the tetragonal phase exists several degrees above T_c.

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OSCILLATORY PHOTOCONDUCTIVITY OF CdS

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Periodic oscillations of the photoconductivity in the impurity region have been observed previously for Ge,[1] InSb,[2] and in the intrinsic region for InSb[3,4] and GaSb.[4] Similar observations made at 4°K on selected CdS single crystals will be discussed here.

The photoconductivity near the absorption edge as a function of the exciting wavelength usually differs somewhat from crystal to crystal, even when grown as platelets and not intentionally doped. Many crystals exhibit photoconductivity peaks at energies corresponding to the positions of the free excitons.[5,6] Some crystals show, in addition to this, an oscillatory photoconductivity spectrum toward higher energies as shown in Fig. 1. Figure 1(a) is recorded with the E vector of the crystal perpendicular to the c axis and Fig. 1(b) for light polarized parallel to the c axis. The period between the minima is 0.036 ± 0.001 eV. There are two series of the minima indicated by long arrows and short arrows. The A series of minima, indicated by long arrows, is spaced successively by 0.036 eV from the A ($n = 1$) exciton peak ($\Gamma_5 = 4854$ Å), and the B series, originating from B ($n = 1$) exciton peak (4826 Å) by exactly the same spacing, is indicated by short arrows. The position of the B minima is less conspicuous because of the composite nature of the two series; however, their positions become more clear when the composite spectral response curves are decomposed as shown by the dashed curve.

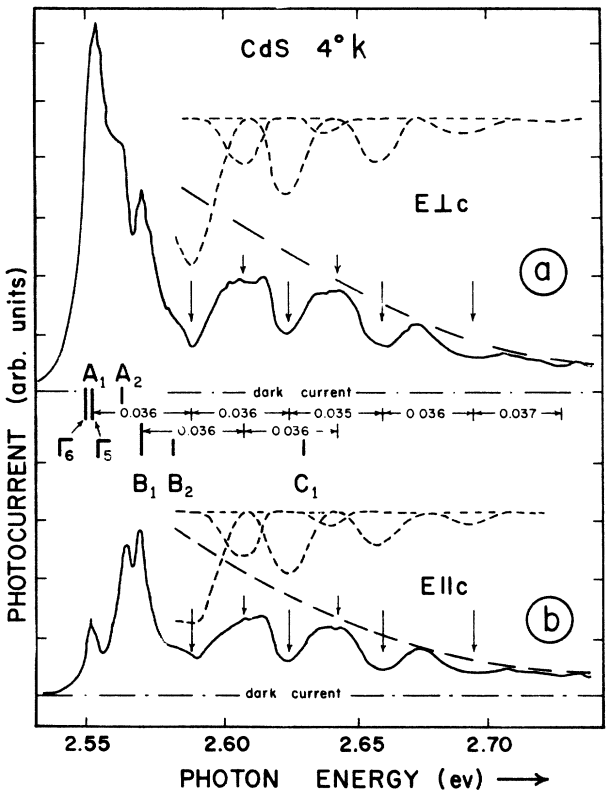

FIG. 1. Photoconductivity vs energy of exciting photons with (a) E vector perpendicular to the c axis and (b) E vector parallel to the c axis of a CdS platelet at 4.2°K. Indicated by bars are the positions of excitons A, B, and C. Long arrows indicate A minima, short arrows B minima, and the dashed curves show the separated contributions of the processes causing A and B minima.

No corresponding oscillatory structure is known to exist in the optical absorption or reflection spectra of CdS. These measurements, however, have not been made as accurately as those reported by Phillips[7] for Si.

The oscillatory behavior of the photoconductivity is due to an oscillatory value of the electron lifetime in the conduction band as function of its energy. The lifetime of the conduction electron at certain energy values is smaller than at adjacent energy values whenever that energy coincides with the sum of the energies of a shal-

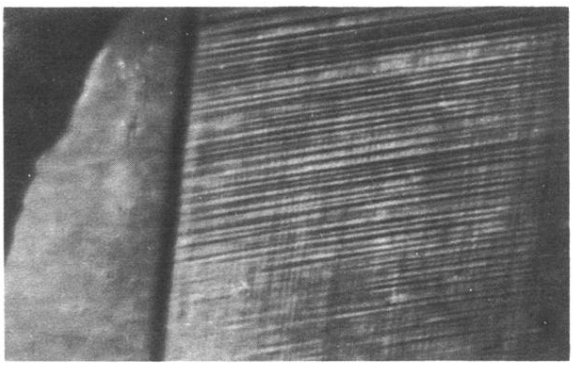

FIG. 1. X-ray topograph of single crystal of V_3Si at 4.6°K showing the twinned tetragonal structure. Magnification 12×.