

## Intermediate Isotope Effect of Molybdenum and $\text{Mo}_3\text{Ir}^\dagger$

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The superconducting isotope effect has been investigated in elemental Mo and the compound  $\text{Mo}_3\text{Ir}$ . In both cases the transition temperature depends approximately upon the  $-\frac{1}{3}$  power of the mass. The significance of such an intermediate effect is discussed.

THE dependence of the transition temperature of superconductors upon isotopic mass, known as the isotope effect, is of importance for any hypothesis about the mechanism causing superconductivity. Until recently it had been assumed that isotopes of all superconductors show the same behavior, namely, the proportionality of the transition temperature to the inverse square root of the mass,  $T_c \propto M^{-0.5}$ . This result follows quite naturally from the ideas developed by Fröhlich and Bardeen in 1950 and has been considered as a strong indication that superconductivity universally is caused by an electron-phonon interaction. The subject has been reviewed by Bardeen and Schrieffer<sup>1</sup> and pertinent references are given there. However, only nontransition elements had been investigated at the time of their review. This limitation was due to two difficulties. There were only a few known superconducting transition elements, namely, Ti, Zr, Ru, and Os, which had stable isotopes of substantially different mass. Unfortunately, these elements have low critical temperatures. Of the first two, only Ti could be obtained in metallic form. Furthermore, small amounts of gaseous impurities substantially changed the transition temperature of Ti as could be seen in the results of Netzel and Dillinger,<sup>2</sup> and presumably can also do the same in Zr. The disadvantage of having the transition temperature sensitive to gaseous impurities disappears for Ru and Os as these elements do not form nitrides or oxides, nor dissolve any of these gases at high temperatures. However, here again, their transition temperatures are rather low. When finally they were obtained in a purified state and measured accurately<sup>3,4</sup> in a  $\text{He}^3$  cryostat, no isotope effect at all was observed, that is, the transition temperature was found to be independent of mass.

<sup>†</sup> Preliminary results have been reported at the Eighth International Conference on Low-Temperature Physics in London, 1962.

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<sup>1</sup> J. Bardeen and J. R. Schrieffer, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. III.

<sup>2</sup> R. G. Netzel and J. R. Dillinger, *Proceedings of the Seventh International Conference on Low-Temperature Physics, 1960* (University of Toronto Press, Toronto, 1960), Paper 16-5. H. W. Lewis and one of us (B.T.M.) had obtained the Ti isotopes in 1955 in order to check their superconductivity. As temperatures below 1°K were not available they were passed on to Professor Dillinger.

<sup>3</sup> T. H. Geballe, B. T. Matthias, E. Corenzwit, and G. W. Hull, Jr., *Phys. Rev. Letters* **6**, 275 (1961).

<sup>4</sup> T. H. Geballe and B. T. Matthias, *I.B.M. J. Res. Develop.* **6**, 256 (1962).

The only other isotope experiment for transition metal superconductors which had been done previously was that of Devlin and Corenzwit<sup>5</sup> who measured  $\text{Nb}_3\text{Sn}$  samples with different tin isotopes. The effect was—if at all present—less than  $\frac{1}{3}$  of what might have been expected on the basis of  $T_c \sim M^{-0.5}$  if  $M$  is taken as the total  $\text{Nb}_3\text{Sn}$  mass. This lack of an isotope effect was not what would have been anticipated for superconductivity caused by an attractive phonon-electron interaction, but interpretation involved assumptions as to the coupling between the Sn and the Nb atoms in the modes responsible for the attractive interaction. If one were to make the rather forced assumption that they are decoupled, then a nonisotope effect could have followed.

The fact that ruthenium and osmium now show no isotope effect at all suggests that a mechanism other than the conventional electron-phonon interaction causes superconductivity. It is nevertheless astonishing why the electron-phonon interaction apparently disappears altogether.

When we discovered that pure molybdenum becomes superconducting<sup>6</sup> between 0.9 and 1.0°K another transition element superconductor became available for testing the isotope effect. We had previously carried out this experiment for the compound  $\text{Mo}_3\text{Ir}$ , which is isomorphous to  $\text{Nb}_3\text{Sn}$ . The present investigation of the isotope effect on the superconductivity of Mo and  $\text{Mo}_3\text{Ir}$  has begun to shed some more light on the mechanism of superconductivity among the transition elements.

Mo isotopes of mean mass 92.37, 96.04, 97.94, and 99.24 were obtained from the Oak Ridge National Laboratory. Together with natural Mo of mass 95.95, they form a well-spaced group of masses with which to study the isotope effect. However, the requirement on chemical purity is severe, as is apparent from the fact that trace impurities succeeded in suppressing the superconductivity of Mo for so long. A study of the isotope effect requires measurements to be meaningful in the millidegree range. We first carried out experiments on the reproducibility of the transition temperature of small quantities (0.200 mg) of arc-melted Mo. In the same series of experiments we established that less than 100 ppm Fe could reduce the transition temperature by

<sup>5</sup> G. E. Devlin and E. Corenzwit, *Phys. Rev.* **120** 1964 (1960).

<sup>6</sup> T. H. Geballe, B. T. Matthias, E. Corenzwit, and G. W. Hull, Jr., *Phys. Rev. Letters* **8**, 313 (1962).

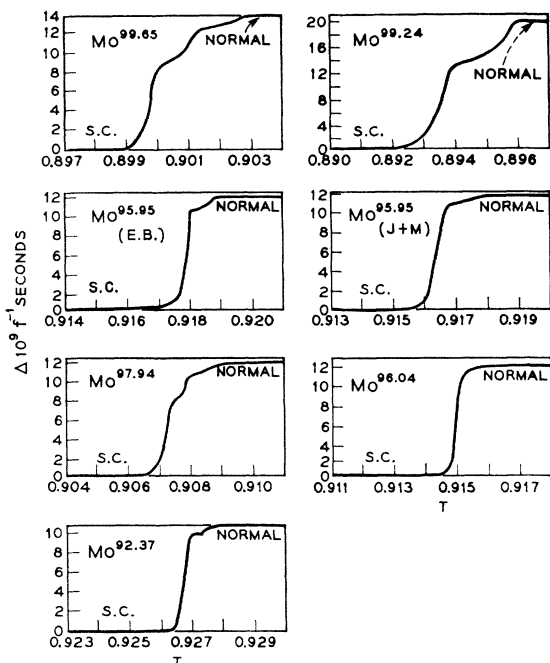


FIG. 1. Normal to superconducting state transition for the seven molybdenum samples of different isotopic composition.

0.6°K.<sup>7</sup> Thus, the transition temperature is depressed more than 60 deg per at. % of iron. Just 1 ppm Fe in solution is sufficient to interfere with a quantitative investigation of the isotope effect. We have not yet been able to establish the most reliable method for measuring trace impurity concentrations at this level. Quantitative emission spectrography<sup>7</sup> seems to give an order of magnitude larger concentration than other methods<sup>8</sup> at levels  $\lesssim 20$  ppm. One, of course, could assume linearity be-

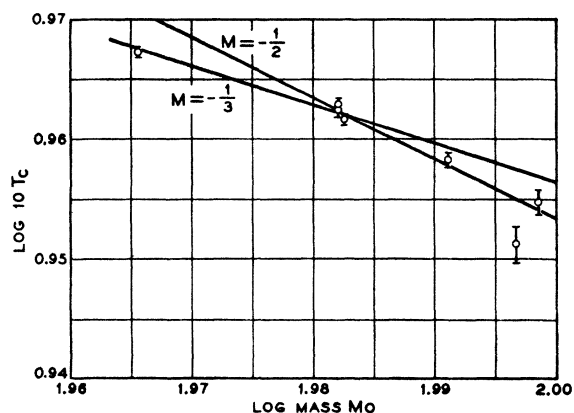


FIG. 2. Logarithm of the transition temperature (taken as the temperature at which the frequency change from normal to superconducting is  $\frac{1}{2}$ ) vs logarithm of the mean molybdenum mass.

<sup>7</sup> We are indebted to E. K. Jaycox for the quantitative spectroscopic analyses.

<sup>8</sup> E. Buehler and J. E. Kunzler, *Trans. Met. Soc. AIME* **221**, No. 5, 957 (1961).

tween depression of superconduction and Fe concentration in solution out to the fairly reliable 100-ppm region and then use the transition temperature itself to estimate the concentration of Fe in solution.

The transition temperature curves of the samples investigated after being molten 18 min in the arc furnace are shown in Fig. 1. These curves are  $x$ - $y$  recordings of the shift of the inverse frequency in units of  $10^{-9}$  sec as a function of temperature. The frequency shift is proportional to the change of inductance of the coil as the sample goes from normal to superconducting. In the normal state the sample reduces the inductance of the coil because the rf field (16 kc/sec) can only penetrate the sample for a distance the order of  $10^{-2}$  mm, the skin depth. In the superconducting state the field can penetrate only the much smaller distance characteristic of the penetration depth  $< 10^{-4}$  mm. Since the samples were all approximately the same size and shape and penetration depth is always very small, the magnitude of the ordinate in the normal state is a function of the skin depth, or resistivity in the normal state. It can be seen from both the skin depth, and width and shape of the mass-99.24 transition curve that it is less pure than the other samples. We were unable to improve the transition appreciably by continued arc melting. We were, however, able to obtain a different lot of enriched  $\text{Mo}^{100}$  from Oak Ridge of mean mass 99.65. This was treated in the same way as the other material and gave the transition curve shown in Fig. 1. While it is a considerably sharper transition than the 99.24, and has a much smaller skin depth, it is unfortunately again not so good as the others. It should be noted, furthermore, that the improvement in transition characteristics is accompanied by a shift of the midpoint of the transition of  $+0.006^\circ$ , the equivalent of 1 ppm Fe. It is interesting that even the very pure natural and mass-92 samples show fine structure in the transition curve even though the transitions are only  $0.002^\circ$  or less in width. This fine structure is reproducible upon warming and cooling and thus does not seem to be a hysteresis effect; perhaps, it is associated with small spatial fluctuations of impurity concentration.

The samples were measured after being molten in the arc for 6, 18, and 30 min. The characteristics of the transition curves (shown for the 18-min melt in the figures) are summarized in Table I. The column labeled "Relative resid.  $R$ " is the measure of residual resistance given by the ratio of the frequency shift of the coil when the sample goes from superconducting to normal to the frequency shift caused by the introduction of the superconducting sample into the coil. For the reasons given in the previous paragraph this ratio would be a simple function of the skin depth in the normal state if the sample geometry were properly controlled; for our purposes it is a qualitative measure of sample purity.

In Fig. 2 the logarithm of the transition temperature is plotted against the logarithm of the mass for the samples studied. The widths of the transitions are repre-

TABLE I. Molybdenum isotopes.

Mean mass (Oak Ridge analysis)	6-min molten			18-min molten			30-min molten		
	$T_c$ (°K)	Width in deg (90% of signal)	Relative resid. R	$T_c$ (°K)	Width in deg (90% of signal)	Relative resid. R	$T_c$ (°K)	Width in deg (90% of signal)	Relative resid. R
92.37	0.9265	$1.3 \times 10^{-3}$	0.040	0.9272	$0.9 \times 10^{-3}$	0.041	0.9275	$1.1 \times 10^{-3}$	0.042
95.95 (Nat.)									
Wah Chang	0.9150	$2.8 \times 10^{-3}$	0.036	0.9159	$2.8 \times 10^{-3}$	0.039			
Zone-refined (Buehler)							0.9182	$1.2 \times 10^{-3}$	0.034
Johnson Matthey							0.9169	$1.6 \times 10^{-3}$	0.041
96.04	0.9160	$3 \times 10^{-3}$	0.039	0.9153	$1.0 \times 10^{-3}$	0.036	0.9167	$1 \times 10^{-3}$	0.039
97.94	0.9090	$2.3 \times 10^{-3}$	0.038	0.9082	$1.7 \times 10^{-3}$	0.040	0.9079	$2.0 \times 10^{-3}$	0.051
99.24	0.8930	$4.5 \times 10^{-3}$	0.067	0.894	$4.0 \times 10^{-3}$	0.066	0.8950	$5.5 \times 10^{-3}$	0.066
99.65	0.9004	$3.2 \times 10^{-3}$	0.048	0.9010	$2.8 \times 10^{-3}$	0.050	0.9008	$2.6 \times 10^{-3}$	0.058

sented by the vertical bars. Since the transitions for the lighter masses are more reliable than for the heavier two by the criteria discussed in the last two paragraphs, they are given more weight. It is only necessary to shift the points for the Mo<sup>97.94</sup> and the Mo<sup>99.65</sup> +0.002° and +0.004°, respectively, to have them fall on the line of slope  $-\frac{1}{3}$ . Such shifts are not unreasonable in view of the +0.006° shift from the less pure mass-99.24 transition to the somewhat more pure mass-99.65 transition. Therefore, we consider the line with slope  $-\frac{1}{3}$  to be a reasonable fit to our data and find that an intermediate isotope effect occurs in elemental Mo.

The study of compounds such as Mo<sub>3</sub>Ir puts a much less stringent requirement on the purity of the Mo. The transition temperature is an order of magnitude higher and it is much less sensitive to trace impurities. This is most probably due to the fact that magnetic impurities such as iron will not show a localized moment in Mo<sub>3</sub>Ir. The samples were made in the arc furnace. Examination of them by x-ray powder diffraction methods done by Mrs. V. B. Compton showed the presence of a  $\sigma$  phase and occasionally a hexagonal phase in addition to the desired  $\beta$ -wolfram phase. Various annealing procedures seemed to eliminate the  $\sigma$  phase but increased the

hexagonal phase. The presence of a small quantity of  $\sigma$  phase with a lower transition temperature  $\sim 6.8^\circ\text{K}$  was seen in the transition curves of a few samples used in exploratory measurements but was not apparent in any of the series reported here. A typical curve is shown in Fig. 3. If, however, the sample is annealed the quantity of hexagonal phase which results has a transition temperature close to the  $\beta$  wolfram and does distort the transition curve as shown in Fig. 4. For this reason our most meaningful data were taken on the as-cast samples.

The samples were measured in the same cryostat and with the same circuitry as was used for the Mo samples. Instead of being immersed in liquid He<sup>3</sup>, the samples were in a gaseous ambient at about 0.1 mm of He<sup>4</sup>. The temperature was controlled by a heater of manganese wire wound on a split brass cylinder which surrounded the sample. A lead sample was incorporated in the holder and measured during each run as a monitor. Its reproducibility of better than 0.01° served as an over-all check of the measurements. A series of 10 samples of 0.200 g were prepared from stoichiometric quantities of the elements; two each from the different isotopes and two from natural material. The shapes of the transition curves were symmetrical as shown in Fig. 3 and made

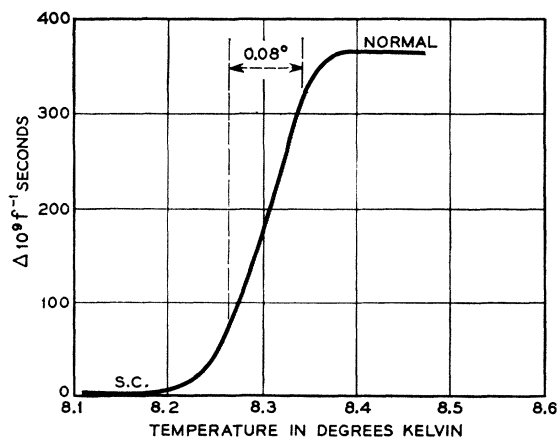


FIG. 3. Typical transition from normal to superconducting state for Mo<sub>3</sub>Ir sample 243 as cast in arc furnace.

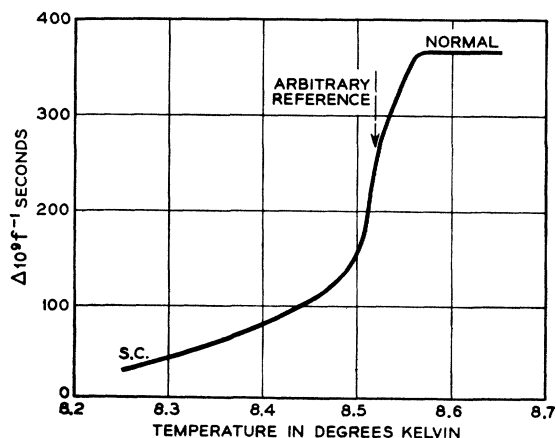


FIG. 4. Typical transition from normal to superconducting state for Mo<sub>3</sub>Ir sample 243 after annealing sample.

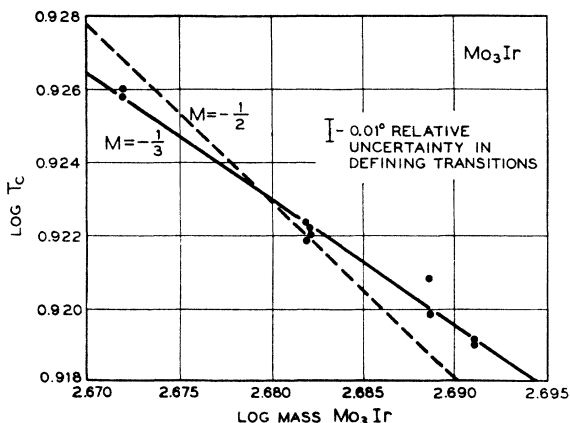


FIG. 5. Logarithm of the transition temperature vs logarithm of the mean mass of  $\text{Mo}_3\text{Ir}$  for the ten samples studied.

comparisons to  $0.01^\circ$  possible even though the width is an order of magnitude greater. The data for the ten samples are summarized in Table II. If one assumes the mass =  $(3 \text{ Mo} + 1 \text{ Ir})$  then a log-log plot of  $T_c$  vs mass, Fig. 5, shows that  $T_c \sim M^{-1/3}$ .

We do not know at present whether the similarity between the exponents of  $-\frac{1}{3}$  for both pure Mo and  $\text{Mo}_3\text{Ir}$  is significant. But it is somewhat reassuring to see that the electron-phonon interaction—here at least—has not *entirely* disappeared. An exponent of about  $-0.33$  for Mo had been predicted theoretically by Morel and Anderson.<sup>9</sup> Unfortunately their theory also predicts an exponent of about the same size for Ru, Os, and Zn. As the first two gave a zero effect and Zn has more or less the normal isotope effect<sup>10</sup> [ $T_c(\text{Zn}) \propto M^{-0.45 \pm 0.05}$ ], the theoretical predictions are not reliable.

It is possible, however, that another mechanism, the same one which presumably causes superconductivity in

ruthenium and osmium, is also present in Mo together with the phonon-induced interaction. This second mechanism presumably does *not* involve phonons. Another electron-electron interaction one might visualize is a magnetic one along the following lines.<sup>11</sup> Upon collision of a conduction electron with an atom, the latter is polarized through an  $s$ - $d$  scattering exchange. This polarization of the ion core, in turn, induces magnetic polarization in its surrounding neighbors. These polarized neighbors now interact in their turn with other conduction electrons. Only a closer examination shows whether this leads to a parallel or antiparallel pairing of the conduction electrons—whether it leads to ferromagnetism or superconductivity. However, the energy of the magnetic interaction is of the right magnitude to give the observed transition temperatures. On the other hand, a *localized* magnetic moment, as the case for Fe in Mo, lowers the free energy of normal state electrons<sup>12</sup> and rapidly destroys superconductivity. The superconductivity seems, thus, to be connected with the non-existence of a localized moment and its disappearance with the existence of a permanent moment.<sup>13</sup>

The minimum concentration at which a localized magnetic moment could destroy superconductivity is when such a magnetic atom could be found within a correlation length. This corresponds to an atom fraction of about 1 part in  $10^{11}$ , an impurity concentration that is clearly outside of any experimental possibilities for a long time to come. The decrease in  $T_c$  with impurity concentration is, however, strongly dependent upon the relative position in the periodic system; the extreme of 1 part in  $10^{11}$  constitutes only a limit and may not be relevant for the pure elements. For example, the minimum in transition temperature of the Nb-Mo system for an alloy of 30% niobium and 70% molybdenum may be due to a maximum in the rate of decrease of  $T_c$  with impurity concentration. Unfortunately, the corresponding minimum in the 5d row is much closer to pure tungsten than it was to pure molybdenum as has already been demonstrated by Nb-W and W-Re solid solutions.

A look at the periodic system is of help in arriving at some empirical conclusions as to the existence and occurrence of the two mechanisms. The transition elements of interest are:

TABLE II.  $\text{Mo}_3\text{Ir}$  samples.

Sample No.	Nominal mass of Mo isotope	Mean molar mass <sup>a</sup>	$T_c$ ( $^\circ\text{K}$ )	Transition width (deg) ( $\frac{1}{3}$ of total signal)
243	100	490.8	8.300	0.09 <sup>b</sup>
244	100	490.8	8.300	0.08
245	98	487.0	8.313	0.08
246	98	487.0	8.335	0.07
237	96	481.1	8.356	0.07
239	96	481.1	8.357	0.06
238	Natural	481.0	8.351	0.065
242	Natural	481.0	8.359	0.07
240	92	470.2	8.430	0.06
241	92	470.2	8.431	0.065

<sup>a</sup> Using mass Ir = 193.1.

<sup>b</sup> Curve for this sample shown in Fig. 3.

<sup>9</sup> P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

<sup>10</sup> Further work along the lines reported in reference 4 gives the above-quoted results.

3	4	5	6	7	8	9	10
(Sc)	Ti	V	(Cr)	(Mn)	(Fe)	(Co)	(Ni)
(Y)	Zr	Nb	Mo	Tc	Ru	(Rh)	(Pd)
La	Hf	Ta	(W)	Re	Os	Ir	(Pt)
	Th		U				

(The elements not yet found to become superconducting are in parentheses.)

<sup>11</sup> We are obliged to Professor Mottelson for suggesting this model.

<sup>12</sup> H. Suhl and B. T. Matthias, Phys. Rev. **114**, 977 (1958).

<sup>13</sup> A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. **125**, 2 (1962).

The behavior on the two borders, left and right, of the transition superconductors, namely, in the column headed 3 and again in columns 8 and 9, is the opposite to the behavior of the elements in the center. In the center the elements in the middle row having 4*d* electrons, such as Zr, Nb, Mo, and Tc, have the highest transition temperatures in their respective column, while at the fringes the 5*d* electron superconductors of the last row have the highest transitions, such as La, Os, and Ir. For the last three, clearly any dependence on mass goes—if anywhere—in the opposite direction to what might be expected from a regular isotope effect. Thus, not only Ru and Os, but also La and Ir, might be expected to have at least a vanishing isotope effect. This should also be true for Sc, Y, and Rh once their superconductivity has been detected, as may happen in the future.

The columns 3, 8, and 9 are also distinguished by another feature. While in the center of the periodic system the electronic specific heat,  $\gamma$ , and the superconducting transition temperature seem to be somewhat related in the way that a high  $T_c$  goes with a high  $\gamma$ , this behavior is precisely the *opposite* for the three groups of elements just mentioned. For almost all of these elements at both boundaries, superconductivity seems to *vanish* upon an increase of the electronic specific heat. Since there is no theory at present for the second mechanism the significance of this observation is not clear.

We would like to thank A. M. Clogston, P. A. Wolff, and P. W. Anderson for informative discussions concerning the isotope effect, and Mrs. V. B. Compton for her helpful x-ray investigations, and L. D. Longinotti for his careful help in preparing the samples.

## Theory of Cyclotron Resonance in Strained Silicon Crystals\*

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The valence band structure in silicon single crystals subjected to an external uniaxial stress is investigated. The cyclotron resonance line for holes in such crystals is predicted to display a significant shift with increasing stress, if the split band populated with holes is associated with the quantum number  $M_J = \pm \frac{1}{2}$ . This strain-induced shift is characterized by the following properties: (a) Its magnitude is of the order of 10% of the frequency for strains of the order of  $2 \times 10^{-3}$ ; (b) it is anisotropic with respect to the relative orientation of the external magnetic field to that of the stress; (c) it must be absent if the band populated with holes is associated with the quantum number  $M_J = \pm 3/2$ . These properties in conjunction with the experimentally determined shifts, presented in the paper by Hensel and Feher, lead to a unique assignment of the band parameters which had been left ambiguous by previous experiments. A discussion of the line shape of hole resonance in a deformed crystal is also presented.

### 1. INTRODUCTION

SINCE the first cyclotron resonance experiments were successfully carried out in germanium and silicon crystals by Dresselhaus, Kip, and Kittel,<sup>1</sup> and by Lax, Zeiger, and Dexter,<sup>2</sup> considerable information has accumulated from experiments about the energy band structures of these crystals. This information has stimulated extensive band-theoretical studies.<sup>3</sup> One of the major endeavors in the experimental investigations has been to elucidate the two degenerate valence bands

and also the third band that is split off from the first two by spin-orbit interactions.

Recently, Hensel and Feher have performed microwave cyclotron resonance experiments on silicon crystals strained by uniaxial stresses and, thus, have been able to determine the valence band inverse mass parameters as well as the band-splitting deformation potentials to an accuracy greater than previously. Full accounts of the experimental results are given in their paper.<sup>4</sup> Their preliminary results have already been reported elsewhere.<sup>5</sup> In the present paper we investigate theoretically the structure of the valence band in silicon influenced by external stresses in order to obtain cyclotron resonance frequencies of holes under such conditions.

The present investigation was undertaken in an attempt to settle a question raised in reference 5 con-

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<sup>1</sup> G. Dresselhaus, A. F. Kip, and C. Kittel, *Phys. Rev.* **98**, 368 (1955).

<sup>2</sup> B. Lax, H. J. Zeiger, and R. N. Dexter, *Physica* **20**, 818 (1954); *Phys. Rev.* **104**, 637 (1956). For recent results see B. Lax and J. G. Mavroides, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 11, p. 261.

<sup>3</sup> W. Kohn, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague 1961), p. 15.

<sup>4</sup> J. C. Hensel and G. Feher, following paper [*Phys. Rev.* **129**, 1041 (1963)]. It is frequently referred to with the abbreviation H-F in the present paper.

<sup>5</sup> J. C. Hensel and G. Feher, *Phys. Rev. Letters* **5**, 307 (1960).