fold. Such degeneracies, if they exist, will require a modification of the interpretation of certain experimental results to a significant extent.

It is easily shown that if there are g_c degenerate conduction bands and g_v degenerate valence bands, the usual formula relating the carrier densities becomes

$$n_e n_h = 4(2\pi mkT/\alpha h)^3 g_c g_v \exp(-E_g/kT), \qquad (1)$$

in which $\alpha \equiv m/m_{\text{eff}}$ is the geometric mean of α_e and α_h, the effective mass ratios for the electrons and holes, respectively, and the other symbols have familiar meanings. Equation (1) with $g_c = g_v = 1$ has been used to interpret experiments designed to determine the change of E_g with temperature.[3,4] Writing E_g as $E_0 - \beta T$, it is seen that the factor $\exp(\beta/k)$ occurs in Eq. (1) in just the same way as the factor $g_c g_v$. Accordingly, if $g_c g_v$ is different from unity the value of β deduced from the experiments must be corrected.

On the basis of Herman's results we would choose $g_v = 3$ and $g_c = 3$, 6. The uncertainty in g_c arises from the circumstance that there are two points of lowest energy in each conduction band with a low maximum in between. The expected behavior depends strongly on the height of the maximum, so we have considered two values of g_c to indicate the range of uncertainty. Thus the combined effect of the degeneracies is a factor 9, 18 in Eq. (1). Expressing this factor as a correction to β we get values $\Delta\beta = -1.9$, -2.5×10^{-4} ev/°K. The presently accepted value[5] is $\beta \equiv 1 \times 10^{-4}$ ev/°K corresponding to a "pre-exponential" factor of 3.5.

Since β has been determined in several ways with substantial agreement among the various experimental values, it seems reasonable to absorb the degeneracy factor by a changed interpretation of another quantity in Eq. (1). The most natural assumption is that the effective mass factor is actually much smaller than unity. In order to leave β unchanged one must postulate values $\alpha = 2.1$, 2.6.

It is not clear how the change in α should be divided between α_e and α_h. There exists some evidence[6] that most of the change is due to the difference of α_e from unity. If we adopt this assumption and take $\alpha_h = 1$ we find $\alpha_e = 4.4$, 6 which values are probably consistent with the data on impurity scattering.[6] It should be noted that although a value of $\alpha_e \sim 3$ has been suggested by Fan,[4] the present considerations should not be considered as improving agreement between the optical data and the electrical data. On the contrary, the value of α we deduce is one which leaves the disagreement exactly as it was before. A mass still smaller than we suggest would be required if Fan's results are to be in agreement with the interpretation of the electrical data.

According to the deformation potential theory the electron mobility is proportional to $\alpha_e^{5/2}/\beta_c^2$ if β_c denotes that part of β which arises from the conduction band. The smaller values of the effective mass which were deduced above would imply considerably larger theoretical mobilities. With the most optimistic adjustment of values the theoretical mobilities would be too large by a factor 5. Thus, our smaller effective mass values would force the conclusion that some other mechanism of energy loss, e.g., band-to-band scattering, is more important than the scattering due to the deformation potential.

The discussion above may be summarized as follows: the additional density of states resulting from the degeneracy of bands predicted by Herman would require a changed interpretation of existing data on carrier densities. Effective masses would have to be smaller than unity, the range of values being such that $\alpha_e \alpha_h \sim 4$–6. The deformation potential as the dominant source of lattice scattering would have to be abandoned.

Since silicon probably has the same band structure as germanium and diamond to the approximation of Herman's calculation, the above considerations and conclusions apply to silicon *mutatis mutandis*. Since the present situation as regards relation of theory to experiment is satisfactory, the existing harmony would disappear when account is taken of the degeneracy.

While the current theoretical situation in germanium and silicon undoubtedly needs to be improved upon, it seems to be rather more satisfactory without the additional degeneracy predicted by Herman. We think it worth while to point out, therefore, that even if the predicted band structure should eventuate, a relatively weak mechanism may be acting to at least partly remove this degeneracy. The spin-orbit coupling,[7] for example, might provide the requisite splitting of the degenerate P bands, since the overall splitting of the corresponding P levels in Ge is of the order[8] of 0.2 ev. A band structure split by spin-orbit coupling would permit a number of interesting possibilities for special properties in the infrared. However, putting aside the question of mechanism, we believe that the considerations discussed above provide weak but definite evidence that the predicted degeneracy in the band structure of Ge and Si does not in fact occur.[9]

† This work supported in part by the U. S. Air Force.

[1] Frank Herman, Phys. Rev. **88**, 1210 (1952).

[2] F. Herman and J. Callaway, Phys. Rev. **89**, 518 (1953).

[3] J. Bardeen, and W. Shockley, Phys. Rev. **80**, 72 (1950).

[4] H. Y. Fan, Phys. Rev. **82**, 900 (1951).

[5] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 336.

[6] P. P. Debye, and E. Conwell, Phys. Rev. **87**, 1131 (1952).

[7] I am indebted to Dr. R. J. Elliot of Harwell for pointing out to me this possibility. I believe that he plans to give a detailed discussion of the spin-orbit coupling in Ge in a forthcoming paper.

[8] C. Moore, *Ultraviolet Multiplet Tables*, National Bureau of Standards Circular No. 488 (1952), Sec. II, p. 89.

[9] It has been called to my attention that in some as yet unpublished work Debye and Conwell consider using $|E_{1v}| - |E_{1c}| = |E_{1G}|$ rather than $|E_{1v}| + |E_{1c}| = |E_{1G}|$ as Bardeen and Shockley did. Nothing in the present study should be understood to assert that the deformation potential theory in its present form would not permit such an analysis. However, if one believes that existing agreement between theory and experiment is fortuitous (or unconvincing), there is not any difficulty in finding a theoretical model to account for the small mobilities in any case, since scattering between degenerate bands would normally be expected to occur and can always be invoked to reduce the mobilities. The point of this note is just to remark that if satisfactory agreement between theory and experiment *already exists* on the assumption of nondegenerate bands and the deformation potential theory, and if the assumption of degeneracy destroys the existing agreement, then there is some reason to suspect that the degeneracy is not actually present.

Radiation Damage in Insulators

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The behavior of the properties of a number of insulators exposed within a nuclear reactor is currently under investigation.[1] Among other effects which take place, changes in properties have been observed which are attributed to phenomena such as those discussed by Seitz,[2] resulting from processes initiated by the passage of energetic neutrons through the material. Some of the changes thus far determined have been—in diamond: increases in energy content, increases in lattice constant, decreases in density; in silicon carbide: a decrease in density, an increase in lattice constant, an increase in energy content; in quartz: a decrease in density, an increase in lattice constant and a marked diffuseness in the back-reflection region of the x-ray diffraction patterns (not present in diamond and silicon carbide), a marked change in rotatory power and a decrease in refractive index, a change in heat capacity;[3] in vitreous silica: increases in density, and increases in the refractive index. The energy content increases produced in diamond and silicon carbide were of the order of magnitude 100 cal/g; the density changes in all these substances were of the order of magnitude of one percent. These changes were found to be progressive. They cannot be described in terms of the product of slow-neutron flux and time. A complete description requires specifying the neutron flux as a function of energy which is not available; but as well as it is known, it gives in conjunction with Seitz's theory the correct order of magnitude for the number of displaced atoms one estimates from some of the property changes.

The changes in properties which take place on heating the irradiated substances are termed annealing phenomena. It has been found that the different properties of a substance may not all anneal simultaneously and different substances may behave quite differently. As examples of this complexity, the increases in energy content of diamond and silicon carbide were found to begin to anneal at 150°C and were progressive (though not uniform) over some hundreds of degrees while the changes in lattice constant (and density) seemed to anneal less readily, requiring somewhat higher temperatures. On annealing irradiated quartz, two of the properties, the density and refractive index, were found to exhibit further decreases below temperatures of about 600°C, and it was not until higher temperatures were reached that a change in the direction of the properties of unirradiated quartz began to take place. Annealing of the major properties in quartz was sluggish below the quartz-Tridymite transition, and it is therefore presumed that restoration of the original state of the substance by annealing may not be possible after extensive irradiation. All of the observed effects are similar to those described for the metamict minerals.[4] Magnesium oxide, spinel, and sapphire have been irradiated and show effects which are an order of magnitude smaller than for the above substances, as might be expected from conclusions reached in studies of metamict minerals.[5] The damaging which is here described may therefore be termed, in the older nomenclature, an artificial metamictization.

Radiation damage in quartz has been reported by Berman[6] who measured its thermal conductivity. Wittels' recent announcement of the marked alteration in its x-ray diffraction pattern[7] has made it desirable to make our results on this subject more widely known even though the work is still in progress. Wittels' work and ours seem to be in substantial agreement although we have found that small changes in the x-ray diffraction patterns are easily observed between 500 and 600°C, somewhat lower than reported by him, and small changes in the density occur by 450°C, the region in which Berman observed substantial annealing of the thermal conductivity changes.

The results announced here were obtained by a number of people. The irradiations were prepared by L. H. Fuchs and W. Primak, who with P. Day measured some of the properties. W. H. Zachariasen and later S. Siegel and J. Taylor made the x-ray diffraction studies. The energy contents were determined by E. J. Prosen, W. H. Johnson, W. A. Fraser, and L. B. Eddy at the National Bureau of Standards. The results will be reported in detail in several papers.

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[1] An oral paper on this subject was delivered by W. Primak at a Ceramic Conference, Battelle Memorial Institute, October 28, 1952 (unpublished).

[2] F. Seitz, Discussions Faraday Soc. 5, 280 (1949).

[3] It has been brought to our attention that M. H. Wittels has recently also observed such a change in heat capacity.

[4] A. Pabst, Am. Mineralogist 37, 137 (1952).

[5] P. Pellas, Compt. rend. 233, 369 (1951).

[6] R. Berman, Proc. Roy. Soc. (London) A208, 90 (1951).

[7] M. H. Wittels, Phys. Rev. 89, 656 (1953).

The Magnetic Susceptibility of Germanium*

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IN preparation for a study of the effect of fast neutron bombardment on the magnetic properties of Ge, the specific magnetic susceptibility χ of both p- and n-type Ge with various impurity concentrations has been measured as a function of temperature in the range from 65°K to 300°K. The Faraday method was used throughout and the specimens were single crystals cut in the form of cubes 0.5 cm on edge.[1] The susceptibility balance was a refinement of the type used by Hutchison and Reekie[2] as modified by McGuire and Lane,[3] special features of which will be described elsewhere. The balance is sufficiently sensitive to detect differential weight changes of 0.2 μg. An Arthur D. Little Bitter-type electromagnet furnished the inhomogeneous magnetic field, (HdH/dz $\sim 10^8$ gauss^2 cm^{-1}). The field was controlled to better than 0.05 percent by means of the Hall voltage developed across a germanium crystal.[4] The value of HdH/dz was determined for each specimen by the magnetic buoyancy effect of oxygen, whose volume susceptibility κ at 760 mm Hg and 20°C is $1.434\pm0.004\times10^{-7}$ cgs unit.[5] The absolute precision of the calibration is ±0.6 percent. The relative precision of χ *vs* T data on any one sample, however is better than ±0.1 percent. Measurements of χ as a function of field strength, indicated the absence of ferromagnetic impurity.

Curves of the diamagnetic susceptibility *vs* temperature for representative specimens are shown in Fig. 1. Curves 1, 2, and 5 are those of n-type samples whose room temperature electron concentrations were 7×10^{17}, 1×10^{18} and 1.3×10^{14} cm^{-3}-respectively, while curves 3 and 4 were obtained for p-type Ge in which the hole concentrations were 5.4×10^{17} and 2.1×10^{17} cm^{-3}-respectively. The carrier concentrations were inferred from Hall coefficient measurements made on plates cut adjacent to one of the cube faces.[6]

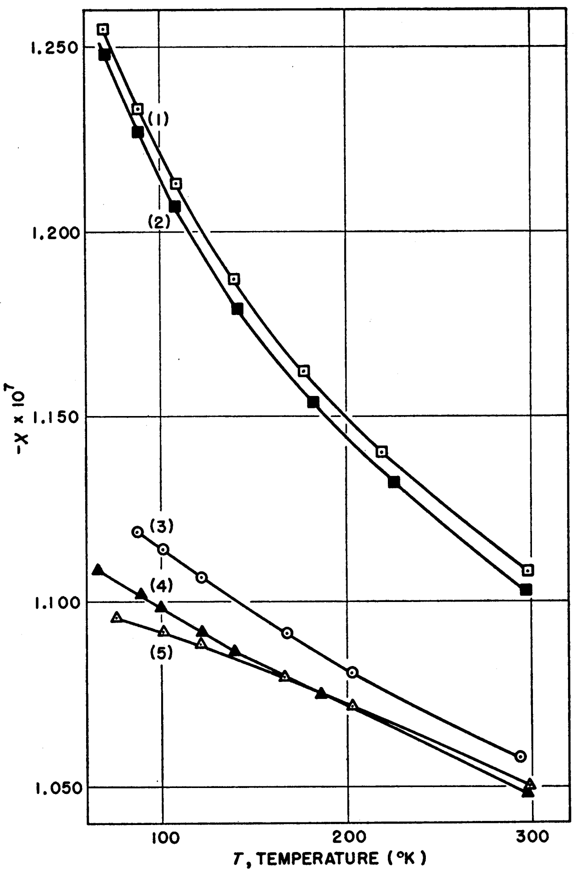

FIG. 1. Diamagnetic susceptibility *vs* temperature curves for single crystal cubes of germanium. Curves 1 and 2 are for low-resistivity n-type material, while 3 and 4 are for low-resistivity p-type material. Curve 5 is for high-resistivity n-type germanium.

In their treatment of the magnetic behavior of gray tin, Busch and Mooser[7] divide the magnetic susceptibility into three parts: (1) the diamagnetic contribution χ_a due to the tin atoms alone which they assume to be temperature-independent, (2) the paramagnetic contribution χ_I due to those impurity atoms or ions which possess an unpaired electron, and (3) the free carrier contribution χ_c which has both a paramagnetic spin component and a diamagnetic Landau orbital component, the latter being greater the smaller the effective mass of the carrier. In the case of Ge it appears from Fig. 1 that in contrast to the assumptions concerning $\alpha-$Sn the term χ_a is temperature-dependent, the slope of all of