adding Co to pure Ni, R_1 decreases rather than increases.

It appears that investigations of the Fe-Co alloys and the Fe rich Fe-Ni alloys would be interesting in examining the detailed variations of R_0 as a function of electron concentration.

I would like to thank Professor Emerson M. Pugh and Professor J. E. Goldman for their comments and interest in this work. I am also grateful to the Bell Telephone Laboratories and Westinghouse Research Laboratory for the materials used in this investigation and the Office of Naval Research for support of this work.

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Long-Wavelength Neutron Transmission as an Absolute Method for Determining the Concentration of Lattice Defects in Crystals*

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The scattering of long-wavelength neutrons by lattice defects has been used to measure in an absolute way the number of isolated interstitial atoms and vacancies introduced in graphite by reactor irradiation. For an exposure of 1.1×10^{20} neutrons/cm^2 the fraction of displaced atoms was found to be 0.0263. This value is more accurate than present theoretical estimates largely because of uncertainties in exposures. Within this limitation the experimental value is in excellent agreement with that derived from Seitz's theory.

I. INTRODUCTION

IT is well known by now that an appreciable number of lattice defects, presumably primarily interstitial atoms and vacant lattice sites, can be introduced into a solid by high energy particle bombardment.[1] The number of defects introduced by such bombardment has been estimated theoretically by Seitz.[2] Experimentally only indirect methods have been available for determining the concentration of lattice defects. The basic difficulty is that the dependence of changes in various physical properties due to the introduction of defects is not well enough understood theoretically to furnish reliable methods for an absolute (in contrast to relative) determination of defect concentration. The purpose of this paper is to describe a method, based on the scattering of long-wavelength neutrons by the lattice defects, which has been used successfully to determine the concentration of imperfections introduced by exposure in the Brookhaven reactor.

Optical methods (for color centers) and residual resistivity measurements (for defects not present as color centers) have been the most successful methods so far employed for determining the concentration of various defects in crystals. Both of these, of course, depend either on absorption or scattering. In F-center work, it is possible to obtain absolute numbers for the color centers by optical absorption methods. Residual restistivity measurements have not yielded absolute numbers because the scattering cross sections for conduction electrons are not known with sufficient theoretical accuracy.

It will be shown that long-wavelength neutrons can be used very similarly to conduction electrons and their scattering by vacancies and interstitials may be measured. Neutrons of sufficiently long wavelength are scattered isotropically by isolated point defects and the scattering can be measured when crystalline effects (Bragg scattering) are absent. Babinet's principle may be applied under such conditions and, therefore, vacancies and interstitials scatter in exactly the same manner. The cross section for this nuclear type of scattering is accurately known from other measurements in contrast to scattering of conduction electrons by the atomic electrons. Thus, if the scattering from these defects is measurable an absolute method is at hand for determining their concentration. In the theoretical section the above scattering process is described mathematically. The experimental results and their discussion are given in Secs. III and IV.

II. THEORY

Let long-wavelength neutrons be incident on a crystal in the wavelength region of several angstroms, i.e., the energy region of 0.001 ev. For such extremely low-energy neutrons the solution of Schrödinger's equation is the sum of an incident plane wave and a radially scattered wave. The scattered radiation at a

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[1] For recent reviews, see: J. C. Slater, J. Appl. Phys. **22**, 237 (1951); G. J. Dienes, Ann. Rev. Nuc. Sci. **2**, 187 (1953).

[2] F. Seitz, Discussions Faraday Soc. No. 5, 271 (1949).

large distance is

$$\psi=\sum_p ae^{i\mathbf{K}\cdot\mathbf{r}_p}, \tag{1}$$

where $\mathbf{K}=\mathbf{K}'-\mathbf{K}_0$=phase difference and $\mathbf{r}_p$=vector distance between origin and pth scatterer in the crystal. Let a monatomic crystal contain m point scatterers per unit volume in the form of interstitial atoms and vacant lattice sites and N atoms per unit volume. The scattering is then described by

$$\psi=\sum_{j=1}^{N} ae^{i\mathbf{K}\cdot\mathbf{r}_j}+\sum_{i=1}^{m} be^{i\mathbf{K}\cdot\mathbf{r}_i} \tag{2}$$

where b is negative for the vacancies. The differential cross section for scattering is given by

$$\sigma(\theta)=\psi\psi^*=a^2\sum_{j,j'}^{N} e^{i\mathbf{K}\cdot(\mathbf{r}_j-\mathbf{r}_{j'})}+b^2\sum_{i,i'}^{m} e^{i\mathbf{K}\cdot(\mathbf{r}_i-\mathbf{r}_{i'})} +\text{cross terms}. \tag{3}$$

The primes here distinguish between scatterers of the same kind. The cross terms are strongly peaked in the forward direction and, therefore, do not contribute to the scattering. The first term of Eq. (3) represents Bragg diffraction which under these conditions (long wavelength) is absent. Thus

$$\sigma(\theta)=a^2\sum_{i,i'}^{m} e^{i\mathbf{K}\cdot(\mathbf{r}_i-\mathbf{r}_{i'})}. \tag{4}$$

Equation (4) for $i\neq i'$ is zero because a random distribution of scatterers is assumed. Therefore,

$$\sigma(\theta)=ma^2. \tag{5}$$

The integrated scattering cross section for these scatterers is,

$$\sigma=4\pi ma^2. \tag{6}$$

The cross section per atom is, therefore,

$$\sigma_d=\sigma/N=4\pi a^2m/N=4\pi a^2f, \tag{7}$$

where f is the atomic fraction of scatterers in the material and σ_d is the cross section for scattering by defects alone. The scattering process is fully described, therefore, by $4\pi a^2$ which is the scattering cross section for vacancies and interstitials, and is the bound-atom cross section, σ_b, for the atoms of the crystal.

It is not practical to attempt to measure directly the isotropically scattered neutron intensity. Instead, the attenuation of a long-wavelength neutron beam during its passage through the material is measured in a transmission experiment. There are other sources of attenuation which have to be taken into account and whose cross sections should be very small compared to the cross section for defect scattering. The total attenuation of the neutron beam is determined by a cross section:

$$\sigma=\sigma_a+\sigma_i+\sigma_{\text{dis}}+\sigma_d, \tag{8}$$

where σ_a=cross section for absorption (capture), σ_i=cross section for inelastic scattering, σ_{dis}=cross section for disorder scattering other than crystal defects (isotopic, spin, etc.), and σ_d=cross section for defect scattering [Eq. (7)].

In the absence of defects and past the last Bragg cutoff ($\lambda>2d_{\max}$), the transmitted intensity, I_s, is given by

$$I_s=I_0\exp[-NX(\sigma_a+\sigma_i+\sigma_{\text{dis}})], \tag{9}$$

where I_0=incident intensity, N=number of nuclei per cm^3, and X=path length traversed through the sample. If m defects are present, the transmitted intensity, I_d, is

$$I_d=I_0\exp[-NX(\sigma_a+\sigma_i+\sigma_{\text{dis}})-mX\sigma_b], \tag{10}$$

or

$$I_d=I_0\exp[-NX(\sigma_a+\sigma_i+\sigma_{\text{dis}}+\sigma_b f)]. \tag{11}$$

A direct comparison of a crystal containing a fraction, f, of defects to a control crystal gives

$$I_d/I_s=\exp(-NX\sigma_b f). \tag{12}$$

The quantity f is then finally calculated from

$$f=\frac{-\ln(I_d/I_s)}{NX\sigma_b}. \tag{13}$$

III. EXPERIMENTS

Graphite was chosen for study because it fulfilled very well the theoretical and experimental requirements. Samples available to us were expected to contain of the order of a few percent defects on the basis of Seitz's[2] theory. This concentration should be easily measurable. It has already been mentioned that the cross section for defect scattering should be much larger than any other in the energy region where the scattering occurs. For graphite,[3]

$$\sigma_b=4.7 \text{ barns},$$
$$\sigma_a+\sigma_i\simeq 0.9 \text{ barn at 8 A},$$
$$\sigma_{\text{spin}}=0, \text{ zero spin},$$
$$\sigma_{\text{isotope}}=0.$$

σ_{isotop} is negligibly small because of the combination of a low abundance of C^{13} (1.1 percent) relative to C^{12} and a similarity in cross sections, 4.5 b and 5.5 b, respectively. The graphite specimen served also as a neutron filter, as described below, which resulted in a most economical use of the very low intensity available in a long-wavelength beam.

The slow-neutron beam was obtained from the Brookhaven reactor by filtering the thermal-neutron spectrum.[4] This spectrum has a Maxwellian energy distribution peaked near 1 A with a "tail" on the long-

[3] D. J. Hughes, *Pile Neutron Research* (Addison-Wesley Press, Cambridge, 1953), pp. 349–366, 250.
[4] Reference 3, pp. 239–242.

wavelength side. If a polycrystalline material of sufficient length is placed in such a beam, Bragg scattering removes all neutrons from the incident beam except those having

$$\lambda > 2d_{\max}, \tag{14}$$

where $d_{\max}$ is the largest interplanar spacing for which diffraction is possible. Equation (14) is merely the Bragg equation for diffraction for $\theta > 90°$. All neutrons of wavelengths given by Eq. (14) pass through the polycrystalline filter almost unattenuated and constitute a spectrum of long wavelength neutrons for experimental use. In these experiments the graphite specimens were made long enough (approx. 9 in.) to constitute efficient filters by themselves. A typical spectrum of the neutrons transmitted by a 9-in. graphite specimen is shown in Fig. 3 as the "unirradiated" curve. The "cut-off" wavelength is clearly marked by an abrupt increase in transmitted intensity at $\lambda = 2d_{(002)} = 6.70$ A.

Originally it was intended to measure directly the total intensities I_d and I_s transmitted by an irradiated and an unirradiated specimen by placing the graphite in the beam with a $B^{10}F_3$ counter immediately behind it. However, pile irradiation increases the c-axis lattice parameter which determines $d_{(002)}$ in graphite. The larger "cutoff" wavelength decreases the transmitted intensity independent of defect scattering and this effect is very hard to correct for. It was decided, therefore, to obtain a plot of transmitted intensity *vs* wavelength using a crystal spectrometer. The irrelevant change in intensity could then be disregarded and the transmitted intensity obtained by computing the areas under the curves for $\lambda > 7.30$ A (see Fig. 3). Onset of second-order reflections at about 13.4 A would place a limit on the usable wavelength region but is of no consequence in these experiments since the beam intensity is too weak to be detected past 12 A.

The presence of a large number of pores in graphite broadens the transmitted beam considerably by multiple small angle scattering. Care was taken in the placement of the counter relative to the specimen and

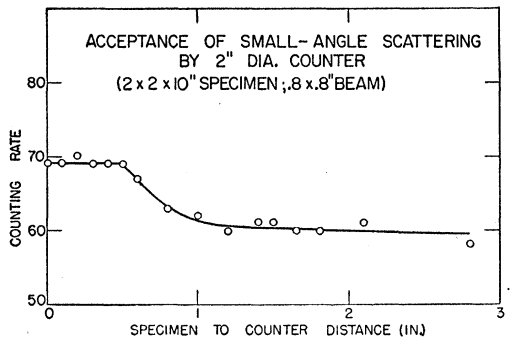

FIG. 1. Recorded transmitted intensity as counter is moved away from the specimen. For the geometry used, loss of small-angle-scattered neutrons does not occur until the separation is $\frac{1}{2}$ inch.

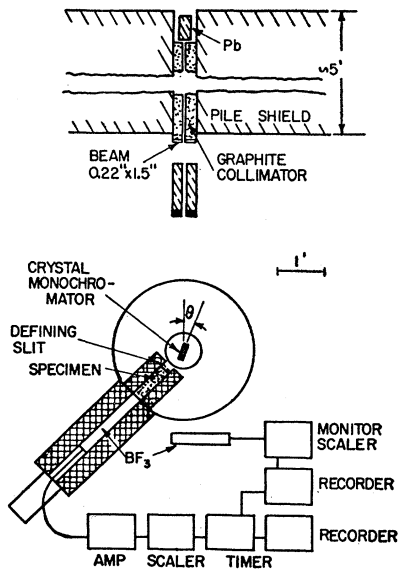

FIG. 2. Crystal spectrometer as employed in these studies. The crystal monochromator is a stack of mica sheets reflecting from the (001) cleavage planes, so that $\lambda = 19.908 \sin\theta$. The defining slit dimensions are 0.81 in.×0.81 in. Six inches of Pb at the collimator provide fast neutron and γ-ray attenuation. A portion of the slow-neutron beam transmitted by the Pb is intercepted by a BF_3 counter to provide monitoring of any spurious fluctuations in incident intensity.

in defining the incident beam in order that all small angle scattered neutrons be accepted. Figure 1 shows that this was accomplished with the counter kept adjacent to the specimen during all runs. The spectrometer setup itself is described in Fig. 2.

Because the irradiated graphite specimen was not run previous to exposure, an unirradiated specimen of the same type of graphite (high-purity AGHT—*CS*) was selected as a standard. Several samples of this graphite each 2 in.×2 in.×10 in., were taken from various large extruded blocks. The neutron spectrum transmitted by each for various orientations was examined and it was quite evident that neither nonuniformity of the graphite nor preferred orientation were of any consequence in this experiment and no special care in selection and positioning of these large specimens was required. In order that the unirradiated specimen have an absorption in the neutron beam identical to that of the irradiated specimen, the number of atoms per unit volume, N, was made closely the same in both. Since

$$N = (A/M)\rho l,$$

where A is Avogadro's number and M is the molecular weight of graphite, the product of density ρ and length l should be the same in both specimens. The density of the irradiated specimen was obtained from its weight and gross dimensions to give $\rho l = 40.277$ g/cm². It was possible to adjust the length of the standard to $\rho l = 40.188$ g/cm², a $\frac{1}{4}$ percent difference which does not

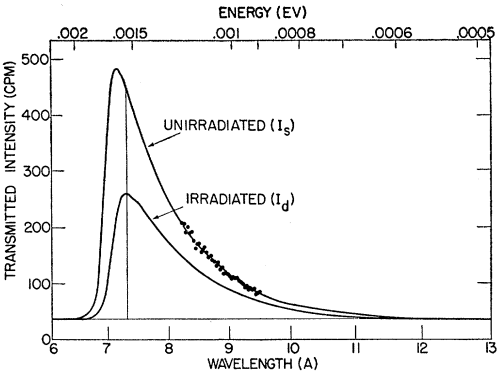

FIG. 3. Slow-neutron intensity transmitted by an irradiated and unirradiated graphite specimen. For clarity, only a typical group of experimental points have been reproduced along one curve to indicate their number and spread. Intensities only to the right of the vertical line at 7.30 A were considered in computing I_s and I_d.

affect the transmitted intensity well within the overall experimental error.

Several spectra were obtained from the spectrometer for the irradiated and standard (unirradiated) specimen run alternately and averaged. Figure 3 shows the resultant transmitted spectra. The areas under each curve give

$$I_d/I_s=0.608.$$

The estimated accuracy of this figure is about ±9 percent. By Eq. (13),

$$f=0.0526,$$

where f is the total fraction of single scatterers, i.e., interstitials and vacancies. The fraction of displaced atoms is, of course, just one-half of this number, namely $f/2=0.0263$.

Annealing experiments were also carried out on another sample of irradiated graphite whose initial defect concentration was smaller. Values of f were determined after various anneals as shown in Table I.

An unirradiated sample was also heated at 900°C for 1 hr. No difference in the transmitted spectra was found before and after annealing. Further, after the 2000°C anneal the sample and the control agreed very closely. The above results show clearly, therefore, that a true irradiation effect was measured in these experiments. The annealing data showed that at or past a 900°C heat treatment the defects could no longer be measured by long-wavelength neutron transmission within the accuracy of the present experiments. Since it is known that many physical properties do not recover completely unless the graphite is heated to about 2000°C, these results can only mean that the major fraction of the remaining defects are present in such a form that they no longer are effective as single scatterers for long-wavelength neutrons. One might expect that pairs of defects or larger clusters should be observable after a partial anneal. The present experiments were not sufficiently accurate over a wide enough wavelength region past 9 A to warrant an analysis for such clusters.

IV. DISCUSSION

An estimate of the number of displaced atoms expected on the basis of Seitz's[2] theory may be obtained from the equations:

$$\tfrac{1}{2}f=(nvt)\times\sigma_s(\Delta\bar{E}/E_0)^{\frac{1}{2}},\quad \Delta\bar{E}=2mME/(M+m)^2, \quad (15)$$

where m = mass of neutron, M = mass of carbon atom, $\Delta\bar{E}$ = energy loss per collision, E_0 = energy required to displace a carbon which will be taken as 25 ev, E = average energy of fast neutron causing displacement, which will be taken as 1 Mev, σ_s = collision cross section for carbon atom = 2.5×10^{-24} cm², and (nvt) = effective total integrated flux of fast neutrons causing displacement (nv is the flux of neutrons per cm² per second).

The number to be used for (nvt) is the most uncertain quantity in these equations since the fast flux and its energy distribution are not known with any accuracy. Our best estimate of the effective (nvt) for the graphite sample used in these experiments is 1.1×10^{20} neutrons/cm².

$\Delta\bar{E}$ is 0.142 Mev and with 1.1×10^{20} neutrons/cm² for nvt, Eqs. (15) give, for the number of displaced atoms,

$$\tfrac{1}{2}f=0.021.$$

The uncertainty in this number resulting from inaccuracy in (nvt) is of the order of 50 percent. There may be a further error because of possible annealing of the specimen although its temperature during irradiation probably has not been above 50°C.

The experimentally determined value of f is known, therefore, with far greater accuracy than any theoretically derived value largely because of uncertainties in the value of (nvt). Consequently, the theory itself cannot be judged critically. The fraction displaced atoms determined experimentally by this method is in excellent agreement with the theory within the limitations mentioned above.

The value of f determined in these experiments may be in error. One reason is that if the defects are aggregated into pairs or larger clusters their scattering will not be equivalent to those of isolated interstitials and vacancies. Another reason is that the inelastic cross section may be altered by the irradiation. It has been assumed that this effect is unimportant. It has also been assumed that there is negligible inhomogeneous distortion in the neighborhood of the defect. An outward

TABLE I. Effect of annealing on defect concentration.

Annealing treatment	f = fraction of single scatterers
None	0.033
250°C for 3 hr.	0.021
500°C for 1 hr	0.011
900°C for 1 hr	0.00
2000°C for 1 hr	0.00

inhomogeneous distortion around the interstitial can be shown to reduce the effective cross section of the interstitial (a similar distortion would increase the cross section of the vacancy). Theoretical estimates of this correction are at present unreliable but are probably not greater than 20 percent.

In principle, the occurrence of pairs is detectable by examining the wavelength dependence of the attenuation. These preliminary experiments are not sufficiently accurate past 9 A to establish the existence of a wavelength dependence. The fact that no wavelength dependence which would be outside experimental error is observable indicates that only a small fraction of the displaced atoms may be present in the form of pairs. More refined experiments will be necessary to establish this point definitely.

The technique described here is applicable, of course, to other materials. The most important limitation is that the absorption cross section has to be small. It appears that with some refinements the number of displaced atoms may be determined in, say, aluminum ($\sigma_a=0.215$ barn). Experimentation with such a metal calls for low-temperature irradiation and measurement because the defects are known to anneal out well below room temperature. Consequently, the necessary techniques are considerably more involved. Sensitivity may be gained, however, by measuring the total transmitted beam rather than using the spectrometer technique since very little change in lattice parameter is expected. The last cutoff for aluminum appears at $\lambda=2d_{(111)}=4.66$ A which, because of the nature of the pile neutron spectrum, also offers a substantial increase in intensity. However, this may be compensated for almost completely by the necessity of using a beam of smaller cross section and an external filter because present low-temperature irradiation facilities limit specimen sizes.

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Calculation of the Entropies of Lattice Defects*

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The entropy of lattice defects are here considered in somewhat greater detail than previously. Calculations are out to estimate the intrinsic entropies associated with such lattice defects as interstitialcies and vacancies, and with the activated complexes of vacancy and ring diffusion. The present application is to fcc metals and a very simplified force model representing only the closed-shell, ion-core repulsions of copper has been used. The problem consists in evaluating the change of lattice vibrations with the introduction of each defect. The method is in a first approximation to consider vibrations localized around the defect as separate from elastic vibrations at appreciable distance from the defect. Only in the region far from the defect is the entropy contribution always positive. The surface condition of zero pressure introduces a term which reduces the effect of the "localized" vibrations. In general the intrinsic entropy is less positive for those configurations where there is crowding of the atoms than for those configurations where the atoms have greater free volume.

IN any calculation of the number of defects which may be expected in a crystal at thermal equilibrium at fixed temperature and pressure one proceeds by minimizing the Gibbs free energy of the system. By the general arguments of statistical mechanics one shows that the fraction of the lattice sites which may be associated with a particular lattice defect is given by $\exp(-\Delta G/RT)$, where ΔG is the change in the Gibbs potential of the crystal with the addition of one mole of defects. The wide use of this expression is a natural consequence of the very great importance of the role of defects in the most of the active fields of present solid state physics, such as optical properties, radiation damage, plastic properties and electrical properties. For those phenomena which depend not simply on the existence of the defects but upon their stepwise motion (diffusion, ionic conductivity, and some aspects of internal friction), the expression[1] for the rate change includes a similar factor, $\exp(-\Delta G^*/RT)$, where ΔG^* is the change in the Gibbs potential with the addition of one mole of defects leaving out of consideration the degree of freedom associated with the direction of motion. Hereafter the asterisk will be omitted here

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[1] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).