to the average value of $\rho\|c$ agrees well with the measurements on one crystal (crystal 22) for which $\rho\perp c/\rho\|c$ is 4, as also obtained in dc measurements. Temperature coefficients (i.e., φ in $\rho=\rho_0e^{q\varphi/k_t}$, where q = electronic charge) are given in the last column of the table. The best values are considered to be those for crystal 22 which were constant from a temperature of 147°K to 435°K. Some crystals were heated to the melting point with no changes in the coefficients. The data of Schaller[5] from measurements of crystals condensed from the vapor are given in the lower portion of the table. The kink that occurs at room temperature has been noted and studied in a distinct type of microcrystalline specimen.[6] None of the crystals we studied exhibited this behavior, so it is attributed to defects in the crystals deposited from the vapor.

The anisotropy ratio of some crystals deposited from the vapor have been reported to be of the order of ten. (Lower values of the order noted above have been personally communicated to the author.) From photomicrographic examinations we expect that crystals deposited from the vapor are less perfect. Moreover, the kink observed by Schaller indicated additional defects[6] not found in our crystals. It seems natural to expect larger differences in properties perpendicular to the c axis since the lattice constant in this direction is the one sensitive to structural changes.

TABLE I. Room temperature resistivities and temperature coefficients (i.e., φ in $\rho=\rho_0e^{q\varphi/kT}$, where q = electronic charge) for conduction perpendicular and parallel to the c axis.

Crystal No.	$\rho\|c$ axis (ohm-cm)	$\rho\perp c$ axis (ohm-cm)	φ (ev)
4	···	$1.2-2.1\times10^4$	0.018
6	5.4×10^3	···	0.007
8	$4.1-5.7\times10^3$	···	0.009
20	5.0×10^3	···	···
22	$3.6-3.9\times10^3$	1.5×10^4	0.0045 ($\|c$) 0.0066 ($\perp c$)
27	···	1.9×10^4	···
Average	4.8×10^3	1.7×10^4	
Schaller[5]	$1\sim1\times10^4$	···	0.005 under 300°K 0.21 over 300°K
	$2\sim1\times10^4$	···	0.038 under 300°K 0.18 over 300°K

The value of 3.5 or 4 for the anisotropy ratio justifies the use of the relations for thermoelectric power in isotropic materials in determining the order of the carrier densities. This use, in conjunction with the development of a general model to explain the dc properties of crystals and the behaviors of microcrystalline specimens, is made in reference 6. This value is smaller than might be expected for the chain-like structure of hexagonal selenium and indicates considerable cross coupling between chains.

Using then the average values of acceptor densities found in selenium crystals and the exhausted condition of these acceptors indicated by the data in the table, an upper limit on the extrinsic activation energy for holes is 0.15 ev. Measurements will shortly be extended to lower temperatures.

The theoretically small dependence of mobility on temperature cannot be distinguished within the precision of the measurement of thermoelectric power and in view of possible residual effects of internal barriers even at 200 Mc/sec. At 50°C the mobility parallel to the c axis is 5–17 cm²/volt sec ($n=1\text{–}3\times10^{14}/\text{cm}^3$); at 180°C this mobility is 33 cm²/volt sec, the temperature dependence reflecting the behavior of the thermoelectric power. Since the material does not become intrinsic below the melting point, an upper limit of effective mass can be determined.

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Some Predicted Effects of Temperature Gradients on Diffusion in Crystals

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SINCE the discovery of the Kirkendall effect,[1] it has been appreciated that the mass transport associated with diffusion caused by interstitial atoms or by vacancies may be used to distinguish experimentally between these mechanisms on one hand and interchange mechanisms on the other. The analysis of the Kirkendall effect does not, however, permit distinguishing experimentally between vacancies and interstitials.[2]

Various experiments have been proposed which in principle can distinguish between vacancies and interstitials. In general, these involve quenching a specimen so that a high density of defects may be trapped at a lower temperature. The effects of this high density have, in general, been below the range of detection.

In this communication, it is proposed that observable effects can be produced by dealing with specimens with temperature gradients. If the density ρ_d of defects has the value $\rho_d(T)$ characteristic of the local temperature $T(x, y, z)$, then the temperature gradient will give rise to a corresponding defect gradient. A diffusion current of defects will exist under steady-state conditions. This current will produce mass transport through the lattice towards high temperature for vacancies and towards low temperature for interstitials.

Figure 1 illustrates one example of an effect to be expected for vacancy diffusion currents. A specimen containing a tilt type grain boundary is made in the form of a wire and heated by passing current through it lengthwise. Vacancies generated at edge dislocations then diffuse from the hotter center to the cooler outside with the resultant motion of dislocations shown in (a). This results in the non-uniform distribution of dislocations shown in (b) which is equivalent to (a) plus (c). The stress distribution due to (c) places the center of the specimen under a compressive stress τ_2 and the outside under tensile stress τ_1. These stresses tend to reduce the vacancy density near the center and increase it near the outside. To a first approximation, the steady state will be reached when the vacancy density is uniform along the grain boundary, and this leads to

$$\tau_2-\tau_1\doteq(E/v)\Delta T/T,$$

where E is the activation energy of forming a vacancy, v the atomic volume, and ΔT and T the difference and average value of the temperature, respectively. From this, one concludes that strains of the order of 10^{-3} might readily be produced. In addition to observing the strains, it may be possible to observe dislocation displacements in the grain boundary for small angle grain boundaries.[3]

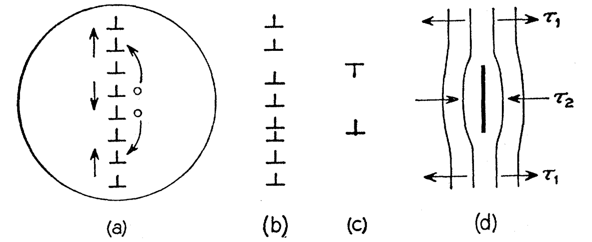

FIG. 1. Predicted effect of temperature-gradient-provoked diffusion of vacancies upon a grain boundary.

Figure 2 illustrates a modification of the Kirkendall effect in which the temperature gradient of Fig. 1 replaces the concentration gradient as a driving force for defects. Motion (b) of the markers should be produced by interstitial atoms and (c) by vacancies. Combined with data on self diffusion, the effect of

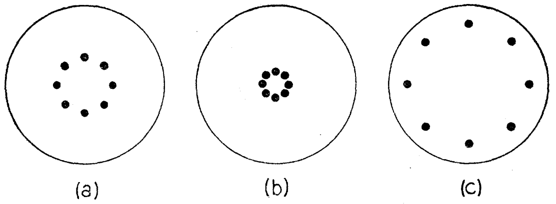

FIG. 2. Predicted effect of a radial temperature gradient upon markers. (a) Initial condition; (b) effect produced by interstitial diffusion; (c) effect produced by vacancy diffusion.

Fig. 2 should make possible a determination of both vacancy density and jump frequency in a pure metal.

Figure 3 represents a predicted effect for a plate, (b) corresponding to interstitials and (c) to vacancies.

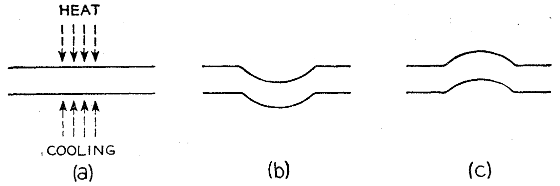

FIG. 3. Predicted effect of a linear temperature gradient (a), for interstitial diffusion (b), and vacancy diffusion (c).

It should be noted that stress gradients due to differential thermal expansion accompany temperature gradients. Effect (b) of Fig. 3 could arise after cooling from this cause. However, the defect flows continue in time and should thus be separable from the thermal expansion effects. This conclusion is particularly clear for Fig. 2.

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Radiation Damage and Rate Processes

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IN several recent investigations,[1-3] electrical resistance changes have been employed as a measure of the damage incurred in the low-temperature cyclotron irradiation of pure metals, and a resistivity index has been used to follow the kinetics of the resulting thermal recovery processes. In the interpretation[4] of this data the lattice defects were considered to be overwhelmingly of the Frenkel type, i.e., interstitial-vacancy, or $i-v$, pairs.[5]

Pulse-annealing studies showed that the low-temperature (below $-150°C$) thermal recovery processes were characterized by activation energies as small as 0.2 ev in Cu, Ag, and Au[2].[2] A later investigation also resulted in a minimum estimate of 0.2 ev for the low-temperature recovery in Cu.[3] The very excellent isothermal annealing data obtained during this latter study showed that the low-temperature recovery processes were not uniquely resolved, indicating that the recombination of $i-v$ pairs in various states of predissociation[6] might provide a reasonable recovery mechanism in this region, an alternative suggested by previous investigators.[2] At about $-40°C$ a reasonably unique 0.68-ev process was observed to emerge from the unresolved background. This process was ascribed[3] to the migration of vacancies, although there seems to be no convincing discrimination against interstitial motion in the data themselves.[7]

It is important to note that the low-temperature reactions should be first-order reactions if the reacting entity is presumed to be the predissociated pair. When the excess concentration of predissociated pairs was exhausted, the annihilations would be governed by the random migration of the individual i or v defects, and the process should then revert to a second-order reaction.

Using the recoverable resistivity increment r as a reaction index, for an idealized second-order reaction one would expect to find that $dr/dt=Mr^2$, where M is an isothermal constant. When this criterion was applied to the 0.68-ev process, it was observed that $dr/dt=Mr^{2.5}$. Stipulating that the apparent higher order could not be the result of residual low-temperature processes, that author[3] rationalized the discrepancy in terms of elastic strain considerations.

The present writer would like to point out that the data may not actually require such interpretation. The preceding work,[3] and some other studies of solid state reactions, involves the tacit assumption that the N_j reactants are homogeneously distributed through the specimen volume V_0. While the resistivity increment may be a fair measure of the *gross* defect concentration $C_j=N_j/V_0$, it provides little information concerning the *microscopic* concentration $c_j=dN_j/dV$. Yet it is precisely this microscopic concentration that determines the velocity of any unique process of the second, or higher, order in inhomogeneous mixtures.

The distinction between homogeneous and inhomogeneous mixtures is best illustrated by considering two idealized second-order cases. Assume that the thermodynamic potential barrier ΔG is not a function of the c_j, so that the factor $\exp(-\Delta G/RT)$ may be included in an isothermal proportionality constant K. In the first case, N interstitials and N vacancies are uniformly distributed through a specimen of macroscopic volume V_0 at a given instant t_0, so that $c_i=c_v=C_0$. The resistivity increment r then decays at a rate

$$(dr/dt)_t=K\int^{V_0} c_i c_v dV=KC_0^2V_0=Mr^2. \qquad (1)$$

In the second case, the same N defects are thoroughly mixed and then concentrated within n microscopic, nonoverlapping subvolumes V_m contained within the original macroscopic volume V_0. For simplicity, the microscopic concentration has the constant value $c_i=c_v=c_m$ inside each subvolume. Since the gross defect concentration has not been changed, the resistivity increment will be the same for both cases, i.e., $r'=r$ at $t=t_0$. The decay rate for this case is

$$(dr'/dt)_{t_0}=Kn\int^{V_m} c_i c_v dV=Knc_m^2V_m=(c_m/C_0)_{t_0}Mr^2. \qquad (2)$$

The reaction rate is thus not uniquely determined for a given resistivity, but may be arbitrarily accelerated by localized concentration of the reactants.

If case (2) is superimposed on case (1), so that two different, nonzero concentrations exist within the same sample, an elementary extension of the preceding analysis shows that the order of the reaction will appear fictitiously high for the latter inhomogeneous case, an artefact resulting logically from the inhomogeneity itself. In general, whenever two or more reactants are mixed and the mixture distributed in *varying* concentrations throughout the specimen volume, the apparent order of even a rigorously unique reaction will appear higher the greater the inhomogeneity.

Idealized though it is, the simple model chosen for the inhomogeneous example affords a rough picture of a nucleon-damaged metal for small flux densities. For larger fluxes, the subvolumes V_m, which correspond to microscopic damage spots localized about each primary interstitial atom ejection[4,5] could be expected to overlap. After the excess of predissociated pairs has been annihilated, either by microcataclysms triggered by the passage of a nucleon through an existing damage spot, or by low-temperature thermal recovery, some individual defects remain. There is no reason to believe that these would be distributed in microscopic uniformity for the fluxes under discussion, although a uniform distribution might be approached at very large flux densities. Similarly, the reactants involved in plastic deformation damage recovery could also be expected to exist in localized concentrations.