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High Pressure Studies of Point Defects*

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Studies of the rate of formation and motion of point defects as a function of external hydrostatic pressure permit, within the framework of reaction-rate theory, determination of the volume changes associated with the basic processes. Novel experimental arrangements have been developed for such studies. Measurements of the formation and motion of vacancies, interstitials, and color centers in a number of metals and ionic crystals indicate considerable relaxation about the point defects, generally more than predicted by many current theoretical models.

1. Introduction

Historically, there has been much scientific interest in elucidating the mechanisms which permit mass transport in solids. Systematic studies of diffusion-limited phenomena have shown conclusively that bulk diffusion can generally be attributed to the presence of mobile point defects, vacancies and interstitials, which are present in the lattice either through accidents of growth or by athermal processes, such as plastic deformation or irradiation. Through comparison of the results of diffusion measurements with studies of quenched resistivity and thermal expansion in metals, and ionic conductivity in pure and impure salts, it has been possible to make direct measurements of the concentrations of point defects, as well as the enthalpy changes associated with their formation and motion.

Much less is known about the actual sizes of the defects. To first approximation, a point defect such as a vacancy occupies one atomic volume, and a vacancy of such size would preserve the local lattice symmetry, considerably simplifying theoretical calculations of its properties. However, the removal of an atom to form a vacancy cannot be expected to be unaccompanied by considerable relaxation of the surrounding atoms, and the actual size of the vacancy may be quite different from a single atomic volume. With relaxation, the "point" defect involves many atoms, and theoretical treatments must be concerned with many-body defects of low symmetry. It therefore becomes important to determine the sizes of such defects by direct experimental means.

The theory of absolute reactions rates, despite possible objections, has proved extremely valuable for understanding and analysing diffusional phenomena. According to the rate theoretic treatment, the diffusion coefficient is given, for cubic solids, by

$$D=a^2\nu_0 f \exp\{-(\Delta G_f+\Delta G_m)/kT\}, \qquad (1)$$

where a is the lattice parameter, ν_0 a mean vibrational frequency interpretable in terms of the distribution of normal modes of the solid with and without defects, f the correlation factor (a constant of order unity for self-diffusion), and ΔG_f and ΔG_m are the increments in Gibbs free energy associated, respectively, with the formation and motion of the point defects.[1] From the definition of the Gibbs function, $dG=VdP-SdT$, we may determine the volume changes associated with formation and motion of defects from the pressure dependence of the diffusion rate, since

$$\left(\frac{\partial \ln D}{\partial P}\right)_T=-\frac{1}{kT}(\Delta V_f+\Delta V_m)+\left(\frac{\partial \ln(a^2\nu_0 f)}{\partial P}\right)_T . \qquad (2)$$

The second term on the right in Eq. (2) is expected to be small, and can be evaluated from the compressibility and the pressure dependence of the elastic constants. Thus measurements of the pressure dependence of diffusion rates are directly relatable to the volumes of formation and motion of defects.

2. Experimental

In high pressure studies of point defects, it is important to maintain hydrostaticity, since even mild plastic deformation may cause large changes in the equilibrium defect concentrations. Therefore gas or liquid pressure systems are essential. There are inherent

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difficulties in maintaining steady pressures for long times at high temperatures, due to limited lifetimes of materials at elevated temperatures and pressures of thousands of atmospheres, and while tracer diffusion measurements are possible, they are extremely difficult. Most data on high-melting materials have thus far been obtained by indirect methods, involving nuclear magnetic resonance, magnetic relaxation, anelastic relaxation, ionic conductivity, etc.

High pressure systems inevitably involve extremely small working volumes, and novel experimental arrangements are frequently required.[2)] With proper design, most of the techniques developed for studies of point defects at atmospheric pressure can be adapted to a high pressure environment. As an example of such design, Fig. 1 shows a pressure cell used to study the rate of formation of color centers in alkali halides over a pressure range of about 8000 atmospheres at temperatures from 10°K upwards.[3)] The pressure is applied with helium gas through small stainless steel capillary tubing at the top of the chamber. The crystalline specimen is mounted opposite a beryllium "window", allowing coloration by x-rays under pressure, and at right angles to a pair of sapphire windows which permit simultaneous measurement of the optical absorption. The whole assembly can be contained in a helium dewar for low temperature operation. The high pressure chamber itself is constructed of heat-treated beryllium-copper, about 2·1/2 inches in diameter, with a working volume of about 1 cm^3. For other experiments, such as diffusion measurements, much larger steel pressure chambers are employed, with working volumes of 100 cm^3 or larger.

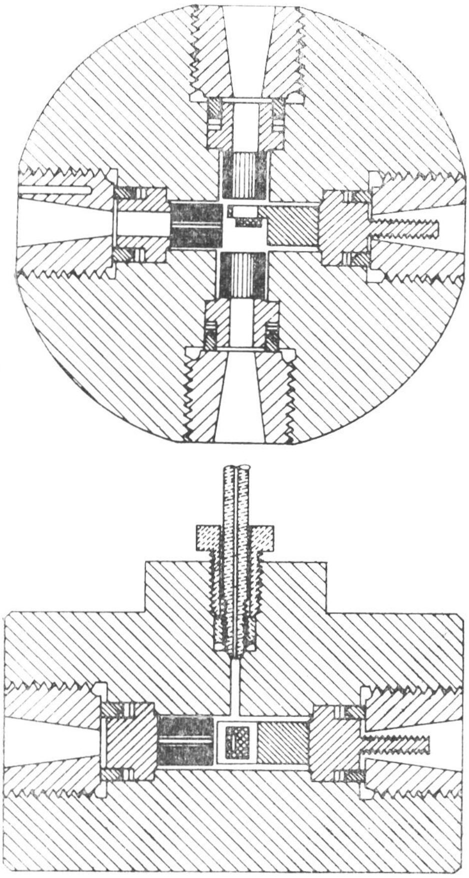

Fig. 1. Pressure cell for color center measurements.

Experimentally determined activation volumes for point defects in metals are shown in Table I, and for ionic solids in Table II.

Typical results for the pressure dependence of the rate of formation of F-centers in alkali halides are shown in Fig. 2.

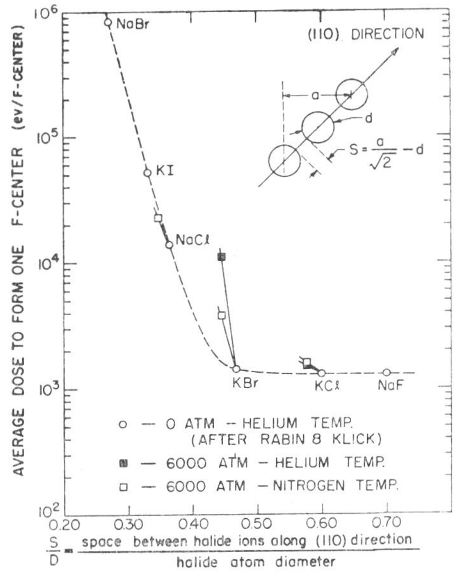

Fig. 2. Effects of pressure on *F*-center formation rates in NaCl, KCl, and KBr.

3. Discussion

From Table I, it is apparent that activation volumes for vacancy diffusion in metals, $\Delta V_f + \Delta V_m$ are quite small, in the range 0.25 to 0.9 atomic volumes, while, in a single

Table I. Activation volumes for metals

System	Technique	Quant. Meas.	Meas. ΔV cm^3/mole	Molar Vol. cm^3/mole	Ref.
Ag	tracer diff.	$\Delta V_f+\Delta V_m$	9.2	10.3	a
Au	quenched R.	ΔV_m	1.5	10.2	b
AgZn	anelast. rel.	$\Delta V_f+\Delta V_m$	5.4	10.0	c
Li	NMR	$\Delta V_f+\Delta V_m$	3.4	13.1	d
Na	tracer diff.	$\Delta V_f+\Delta V_m$	12.4	24.0	e
Pb	tracer diff.	$\Delta V_f+\Delta V_m$	13.0	18.2	f
Sn	creep	$\Delta V_f+\Delta V_m$	5	27.0	g
Fe-C	mag. rel.	ΔV_m	0.0	2	h
	anelast. rel.	ΔV_m	0.0	2	i
Fe-N	mag. rel.	ΔV_m	0.0	2	h
V-N	anelast. rel.	ΔV_m	1.1	2	j
V-O	anelast. rel.	ΔV_m	1.7	2	j

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Table II. Activation volumes for ionic solids

System	Technique	Quant. Meas.	Meas. ΔV cm^3/mole	Molar Vol. cm^3/mole	Ref.
AgBr	ion. cond.	ΔV_f-Frenkel	13	9(vol. Ag)	a
		ΔV_f-Schottky	44	29(vol. AgBr)	a
		ΔV_m-Ag interstit.	2.7	9(vol. Ag)	a
		ΔV_m-Ag vac.	7.4	9(vol. Ag)	a
AgBr	tracer diff.	$\Delta V_f+\Delta V_m$-Br. vac.	44	20(vol. Br)	b
NaCl	ion. cond.	ΔV_m-Na vac.	7.7	5(vol. Na)	c
			9.5	5(vol. Na)	d
		ΔV_f-Schottky	43	31(vol. NaCl)	d
KCl	ion. cond.	ΔV_m-K vac.	7.0	11(vol. K)	c
			10	11(vol. K)	d
		ΔV_f-Schottky	67	43(vol. KCl)	d

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measurement, ΔV_m for gold is extremely small, only 0.15 atomic volumes. Even taking proper account of the elastic boundary conditions,[4] the volumes for formation and motion of vacancies in metallic systems are considerably smaller than a single atomic volume.

This result implies that there must be considerable relaxation of neighboring atoms inward about vacancies in metals, even in f.c.c. lattices, despite the theoretical predictions to the contrary.[5] These results are, however, quite consistent with the recent calculations of Tewordt and co-workers.[6] If large relaxations are indeed present, this fact should be taken into account in calculations of the formation energy of vacancies. There are no detailed calculations of ΔV_m to permit comparison with experiment, but the small value observed is quite inconsistent with a hard-sphere model of a solid, which would predict a value of ΔV_m some five times larger than that observed for gold.

All of the results on vacancy diffusion can be correlated by a simple semi-empirical expression due to Keyes,[7]

$$\Delta V = 4\beta\Delta H\,, \tag{3}$$

where β is the isothermal compressibility of the matrix and ΔH the enthalpy of activation of the process.

Values of ΔV_m for interstitial solid solutions, however, are inconsistent with Eq. (3), at least for Fe alloys, where no pressure dependence on the mobility is found. There appears to be a fundamental difference in the nature of the interstitial in vanadium and in iron, since the former shows a considerable pressure dependence. This may be attributable to a difference in the electronic configuration of the interstitial for the two cases, the interstitial being more highly charged in iron. Such a conclusion would be consistent with the observed large rate of migration of carbon atoms to the negative electrode when Fe-C alloys are heated in an electrical gradient.[8]

In ionic solids, the measured activation volumes for formation and motion of vacancies are quite large, generally larger than the atomic volume, implying outward relaxation of neighboring atoms about the vacancy. This result is consistent with theoretical calculations,[9] which attribute the expansion to coulombic repulsive forces between the unscreened nearest neighbors of a vacancy. Such effects might enter strongly in the capture cross section of vacancies to form color centers, although these have not been considered explicitly.

Results of study of pressure effects on the rate of coloration of alkali halides suggest strongly that the same mechanism cannot be operative for KBr and the two chlorides NaCl and KCl. The latter show only a small pressure dependence, consistent with an athermal vacancy creation mechanism, while the bromide shows a definite suppression by pressure of a thermal process for formation of vacancies.

In conclusion, it appears that high pressure studies may provide important new insight into the nature of point defects and should stimulate a critical reexamination of the electronic configurations of these defects in various classes of solids.

References

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DISCUSSION

Smoluchowski, R.: The occurrence of a Varley type mechanism in bromides would be expected to be less probable than in chlorides because of the dependence of the Auger process on the atomic number. Perhaps bromides require still another type of mechanism.

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Effect of Hydrostatic Pressure on the Rate of Atomic Movement in Noble Metals*

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In recent years it has become possible to estimate some physical constants and properties of vacancies in noble metals. Of these determinations the volume of a vacancy is one of the most uncertain quantities due to the fact that the volume is estimated indirectly by the combination of two or more independent experiments. In order to offer more direct approach to this problem, Nachtrieb, Lawson and their co-workers measured the self-diffusion rates in sodium and lead in a pressurized liquid system. For noble metals it is necessary to employ pressurized gas systems due to the requirement of high temperatures.

The vacancy volume obtained by this method (activation volume) is the volume of a vacancy at a saddle point configuration, *i. e.*, the volume of a vacancy in motion. The measurement of self-diffusion rates in single crystals of silver at high pressures up to 8KB was carried out in a pressurized argon system. The activation volume thus obtained was 90 percent of the atomic volume. This value represents the sum of the two volumes: the volume of a vacancy at rest (ΔV_f) and the volume expansion introduced by the migration of a vacancy into a saddle point configuration (ΔV_m). This latter quantity was estimated by Emrick in gold by measuring the pressure effect on the annealing rate of the quenched-in vacancies in gold. The value of 15 percent of the atomic volume was obtained by this method. If it can be assumed that a similar value holds for silver, then the static volume of a vacancy in silver is 75 percent of the atomic volume. This is considerably larger than the values estimated by indirect methods or by theoretical calculations.

It is necessary, however, to perform the quenching experiment under pressure in order to obtain the static vacancy volume directly. This can be accomplished if a sufficiently large quenching rate can be achieved at high pressure. Preliminary experiments indicate that the quenching rate of 10^4 deg./sec is possible at the pressure range of 2.5KB to 9KB. In order to increase the quenching rate and remove some difficulties associated with a dc heating, a pulse heating method is currently being tested.

It is hoped that the quenching experiment at high pressure, combined with the self-diffusion and vacancy annealing at high pressure, all of which are in progress in this laboratory, will yield significant information which can be added to the present knowledge of the vacancies in noble metals.

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