

TABLE II. Activation volumes for gold. V_M : molar volume of gold, 10.2 cm³/mole.

ΔV_f (cm ³ /mole)	ΔV_m (cm ³ /mole)	ΔV (cm ³ /mole)	$\Delta V/V_M$	$\Delta V_f/V_M$
...	...	7.2 ^a	0.71	...
5.6 ^b	1.5 ^a	7.1	0.70	0.55
5.8 ^c	1.5	7.3	0.72	0.57
4.6 ^d	1.5	6.1	0.60	0.45

- ^a Present experiment.
^b Huebener and Hoffman (Ref. 18).
^c DeSorbo (Ref. 15).
^d Simmons and Balluffi (Ref. 3).
^e Emrick (Ref. 14).

cm²/sec. The error limits shown are the standard deviations.

Combining the slopes of these lines with the much smaller terms involving K_T and γ_G in the expression for ΔV above, one obtains the following values of ΔV :

$$860^\circ\text{C}: \Delta V = 6.1 \pm 0.8 \text{ cm}^3/\text{mole},$$

$$910^\circ\text{C}: \Delta V = 7.7 \pm 0.5 \text{ cm}^3/\text{mole},$$

$$960^\circ\text{C}: \Delta V = 6.2 \pm 1.4 \text{ cm}^3/\text{mole},$$

where the error limits here are derived from the standard deviations of the slopes.

It was assumed that the temperature dependence of the activation volume, if any, is very small compared to the uncertainties in the present results, and a weighted average of ΔV was computed from the 860 and 910°C values. The result is

$$\Delta V = 7.2 \pm 0.4 \text{ cm}^3/\text{mole},$$

where the error limit here is the standard deviation of the weighted average. The difficulties encountered in making successful runs at the highest temperature, 960°C, limited the data to such an extent that the uncertainty in ΔV for that temperature was great enough to produce a negligible effect on the value of the weighted average.

Table II shows values of ΔV_f for gold determined by other experimental investigations. These are combined with Emrick's value for ΔV_m to give a total value for the

TABLE III. Activation volumes for fcc metals.

Metal	ΔV (cm ³ /mole)	V_M (cm ³ /mole)	$\Delta V/V_M$
Au ^a	7.2	10.2	0.71
Ag ^b	9.2	10.3	0.89
Au in AuAg ^c	7.5	10.3	0.73
Ag in AuAg ^c	7.2	10.3	0.70
AgZn ^d	5.4	10.0	0.54
Pb ^e	13.0	18.2	0.71
Pb ^f	11.6	18.2	0.64

- ^a Present experiment.
^b Tomizuka (Ref. 11).
^c Albrecht and Tomizuka (Ref. 12).
^d Tichelaar and Lazarus (Ref. 24).
^e Nachtrieb, Resing, and Rice (Ref. 8).
^f Hudson and Hoffman (Ref. 9).

activation volume. Comparison of these values with the result of the present investigation shows good agreement.

Experimental results for activation volumes in several of the fcc metals are collected in Table III. The radioactive tracer and sectioning technique was used in all but one of these investigations: Tichelaar and Lazarus²⁴ determined the activation volume for AgZn by measuring the effect of pressure on the anelastic relaxation in that alloy.

The values given for the activation volumes in Tables II and III indicate that considerable relaxation occurs about a vacant lattice site in an fcc crystal. Many theoretical calculations are in disagreement with this finding. For example, Kanzaki²⁵ and Nardelli and Repanai²⁶ predict a volume contraction about a vacancy in an fcc lattice of less than 1% of an atomic volume. Negligible relaxations also are predicted by calculations of static lattice energies and configurations by Hall²⁷ and by Girifalco and Streetman.²⁸ Lawson, Rice, Corneliussen, and Nachtrieb²⁹ argue that the above calculations could not have correctly predicted the relaxation, since they did not include the anharmonic forces which are responsible for relaxation. They perform a calculation which includes such anharmonic terms, and predict a volume relaxation of 33% about a vacant lattice site in a cubic crystal.

Many detailed calculations of energies and lattice distortions of various defects in copper have been made during the past few years. Although Gibson, Goland, Milgram, and Vineyard³⁰ find the volume relaxation about a vacant site to be quite small—10% at most—others have calculated much larger relaxations. Calculations by Tewordt,³¹ Tewordt and Bennemann,³² Seeger and Mann,³³ Bennemann,³⁴ and Johnson and Brown¹³ yield values of $\Delta V_f/V_M$ which are in good agreement with the experimental indications of considerable volume relaxation about vacancies in fcc metals. Table IV contains most of the results of these calculations, in the form of $\Delta V_f/V_M$. It should be noted that these calculations of the lattice distortion take into account an important effect first pointed out by Eshelby.³⁵ He showed that the stress-free surface of a finite crystal gives rise to an image term in the displacement about a point imperfection; this term has a large effect upon the magnitude of the volume relaxa-

²⁴ G. W. Tichelaar and D. Lazarus, Phys. Rev. **113**, 438 (1959).

²⁵ H. Kanzaki, Phys. Chem. Solids **2**, 24 (1957).

²⁶ G. Nardelli and A. Repanai, Physica **24**, S182 (1958).

²⁷ G. L. Hall, Phys. Chem. Solids **3**, 210 (1957).

²⁸ L. A. Girifalco and J. R. Streetman, Phys. Chem. Solids **4**, 182 (1958).

²⁹ A. W. Lawson, S. A. Rice, R. D. Corneliussen, and N. H. Nachtrieb, J. Chem. Phys. **32**, 447 (1960).

³⁰ J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. **120**, 1229 (1960).

³¹ L. Tewordt, Phys. Rev. **109**, 61 (1958).

³² K. H. Bennemann and L. Tewordt, Z. Naturforsch. **15a**, 772 (1960).

³³ A. Seeger and E. Mann, Phys. Chem. Solids **12**, 326 (1960).

³⁴ K. H. Bennemann, Z. Physik **165**, 445 (1961).

³⁵ J. D. Eshelby, J. Appl. Phys. **25**, 255 (1954).