

given by $\tau = \nu_0^{-1} \exp(E/kT)$, where ν_0 is the average lattice frequency (*ca* 10^{13} sec $^{-1}$), and E is the potential barrier between the sites. In the region close to the vacancy there is elastic deformation of the lattice which results in progressively smaller potential barriers and shorter jump times as one approaches the vacancy. In this region the interstitial has a preference for jumps toward the vacancy. Thus, the time required for recombination will be approximately the time in which the interstitial will jump out of its initial site in the deformed region. This gives rise to the N_M (M for monomolecular) term of the annealing, $N_M = \sum_i N_i \exp(-t/\tau_i)$, where N_i is the number of interstitials located initially at the i th site, τ_i is the corresponding average jump time towards the vacancy, and the summation \sum_i is over all sites within the deformed region.

For those interstitials which are located outside this deformed region, which we will assume extends out to radius r_c , the probability of jumping in any direction is the same. Thus these atoms wander according to a random walk process, some wandering back within r_c where they are subsequently captured, and the rest wandering off through the crystal. The interstitials which are thus liberated can eventually be captured by other vacancies. If we neglect capture at surfaces and dislocations, the liberated atoms will recombine by a bimolecular process. These two processes give rise to the N_L (L for liberation) and N_B (B for bimolecular) terms of the annealing expression:

$$N_L = \sum_2 N_i \frac{r_c}{r_i} \operatorname{erf} \left[\frac{r_i - r_c}{(2\langle b^2 \rangle)^{1/2}} \left(\frac{t}{\tau} \right)^{1/2} \right],$$

$$N_B = \sum_2 N_i \left(1 - \frac{r_c}{r_i} \right) \left/ \left[1 + 4\pi r_c^2 \langle b \rangle \left(\frac{t}{\tau} \right) \sum_2 N_i \left(1 - \frac{r_c}{r_i} \right) \right] \right.,$$

where r_i is the distance of the i th interstitial site from the vacancy, b is the magnitude of the change in this distance for each jump, the brackets $\langle \rangle$ indicate the average over all possible jumps, and \sum_2 is the summation over-all sites outside r_c . In order of time, N_M will vanish before N_L because $\tau_i < \tau$ and because the atoms in the N_L mechanism require many jumps of time τ before capture. N_L will vanish before N_B if r_c is less than the separation between adjacent vacancies, as it will be except with extremely heavy bombardments. By defining r_c we have assumed that there is a sharp division between the N_M and the N_L stages. Since actually there is a smooth transition between these stages, the given expression for the annealing is only approximately correct for those centers initially near r_c . The expression for N will be the same if vacancies are considered to jump instead of interstitials, τ now being the jump time of a vacancy.

It should be noted that the annealing time t appears only in the ratio, t/τ . By comparing the times at which the same degree of annealing occurs for different temperatures, the barrier energy can be determined without an actual fit of the theoretical expression to experimental data. The barrier energy, so determined, will be constant in the stages of the annealing governed by N_L and N_B , but will decrease with decreasing time (or temperature) in the stage governed by N_M . The actual fit yields additional information about the capture radius r_c and the initial distribution of interstitials N_i .

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The Extra-Resistivity Owing to Vacancies in Copper

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THE scattering of the conduction electrons by vacancies in copper is calculated using the well-known method of Faxén and Holtmark.¹ This is a rather elaborate method, as the radial

differential equation must be integrated numerically to obtain the asymptotic phase shifts α_l for the electrons at the top of the Fermi-distribution; but it must be used, as the scattering field of a vacancy is too large for these slow electrons to permit the use of Born's approximation.

In order that the vacancy may be neutral after the removal of the Cu^+ ion, one free electron must be displaced from the vacancy; thus according to Friedel² the following relation between the phase shifts α_l must hold:

$$-(2/\pi) \sum_l (2l+1) \alpha_l = 1.$$

We do not know very much about the scattering field of a vacancy. Therefore we shall take a suitable starting field and adjust its parameters until Friedel's equation holds.

We have done this for two different fields, but the results appear to be about the same.

(a) We suppose that the removal of an ion with its field is equivalent to adding a field of opposite sign. Therefore we take for the scattering field the negative of the field of a free Cu^+ ion, which can be found from Hartree and Hartree's³ effective nuclear charge $Z_p(r)$. Of course, this cannot be absolutely correct, since in the metal the field will be somewhat deformed, but it is taken as a first approximation.

One free electron must be displaced from the vacancy, so that there is a spherical hole with radius r_s in the electron gas. The corresponding reduced effective nuclear charge Z_p' can be found by subtracting from Z_p the quantity z_p given by:

$$z_p = \frac{1}{2} r (3r_s^2 - r^2) / r_s^3, \quad r < r_s;$$

$$z_p = 1, \quad r \geq r_s.$$

$Z_p' = Z_p - z_p$ can be represented very well by $Z_p' = 24e^{-2.5r}$ (note, that $24 \neq Z_{\text{Cu}}$), and the scattering field by $V = (24/r)e^{-2.5r}$ in atomic units.

The phase shifts α_l , calculated by using this field, are

$$\alpha_0 = -0.73, \quad \alpha_1 = -0.233, \quad \alpha_2 = -0.013.$$

Friedel's equation gives $-(2/\pi) \sum_l (2l+1) \alpha_l = 0.95$; this is sufficiently good. The solution could be somewhat improved by calculating the new free electron distribution from the wave functions; this would give a better z_p and thus a better field, etc. However, in view of our rather crude assumptions, the small improvement which might result is not thought to be of significance.

The above values of α_l give an effective scattering area of $2.2A^2$, and the extra-resistivity due to vacancies appears to be:

$$\rho_0 = 1.25 \times 10^{-6} \Omega \text{ cm per atomic percent vacancies.}$$

(b) Now we suppose the scattering field to be constant $= U_0$ for $0 \leq r < r_s$ and zero for $r \geq r_s$. U_0 must be chosen of such magnitude, that the phase shifts α_l obey Friedel's equation. For $U_0 = 6.35$ ev we find:

$$\alpha_0 = -0.796, \quad \alpha_1 = -0.229, \quad \alpha_2 = -0.028.$$

Friedel's equation gives $-(2/\pi) \sum_l (2l+1) \alpha_l = 0.99$. The effective scattering area is $2.42A^2$, and the extra-resistivity is given by:

$$\rho_0 = 1.35 \times 10^{-6} \Omega \text{ cm per atomic percent vacancies.}$$

We see that both fields give about the same result.

The relaxation of the lattice is estimated, using the ion-ion interaction $U = \text{Be}^{-r/\rho}$, and assuming that only nearest neighbors are displaced. Their shift is found to be about 1.5 percent of their distance. The influence of this displacement is roughly estimated by comparison with the temperature resistance, and is about 3 percent of the vacancy resistance; so it can be neglected.

Recently Dexter⁴ has published his calculations on the scattering of electrons from point singularities in metals; his result ($\sim 0.4 \times 10^{-6} \Omega \text{ cm per atomic percent vacancies}$) is, however, much smaller than ours.

To summarize, the extra-resistivity due to vacancies in copper is calculated to be $\rho_0 \approx 1.3 \times 10^{-6} \Omega \text{ cm per atomic percent vacancies}$, and is of the same order of magnitude as the extra-resistivity due to Ni in copper.

A detailed article will be published shortly in *Applied Science Research*.

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Paramagnetic Resonance in Manganese Formate

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THE paramagnetic resonance spectra of two salts of manganese have been studied in detail by Bleaney and Ingram,¹ and an analysis of the five groups of six hyperfine structure lines made in terms of the electronic splitting and crystalline field symmetries. Measurements are reported here on the spectra obtained from crystals of diluted manganese formate, and are of interest in that the electronic splitting is considerably greater than usual, being twice that observed in any inorganic salt so far.

All the measurements were made at room temperature and at a wavelength of 1.25 cm, the magnetic field being calibrated by means of normal proton resonance methods, and a modulating sweep being used for detection and display. The crystals of $Zn(HCOO)_2 \cdot 2H_2O$ and $Mn(HCOO)_2 \cdot 2H_2O$ are both monoclinic prismatic with very nearly equal axial angle and ratio; $\beta = 97^\circ 19'$ and $97^\circ 38'$, respectively.² The paramagnetic absorption spectra show that there are two ions per unit cell, as in the case of the Tutton salts.¹

Rotation in the plane of crystallographic symmetry (i.e., xz plane), in which the spectra of the two ions coincide, showed that the electronic splitting remains small in all directions, indicating that the crystalline field axes of the two ions must lie near the y axis. A maximum occurs at an angle of $+7^\circ$ to the z axis, and, in order to establish whether this direction was K_1 or K_2 , the crystal was rotated in the two planes (a) through the y axis and $+7^\circ$ to z , and (b) through the y axis and $+97^\circ$ to z .

Rotation in the first plane gives an electronic splitting which has a maximum along the y axis, with a subsidiary one at right angles, and this shows that it is the K_2K_3 plane. Hence K_1 makes an angle of $+97^\circ$ to z in the xz plane.

Rotation in the second plane (K_1K_3) gives two maxima, corresponding to the largest electronic splittings obtained in the crystal, at angles $\alpha = \pm 62^\circ$ to K_1 . This explains why the separation along K_1 is small, as the electronic splitting goes through a minimum at about 60° to the crystalline field axis.

The separations between the centers of the five groups along the three crystal axes, and the axis of the crystalline field of the Mn^{++} ion, are listed in Table I.

The hyperfine structure separation remains constant with a splitting of 98 gauss between successive lines. In analyzing the spectra the usual Hamiltonian,

$$\mathcal{H} = g\beta H \cdot S + D\{S_z^2 - \frac{1}{3}S(S+1)\} + E(S_x^2 - S_y^2) + F(a) + AS_xI_x + B(S_xI_x + S_yI_y),$$

is used, and from the expressions^{3,4} for the separation between successive groups along the field axis, one obtains for the coefficients, in units of 10^{-4} cm^{-1} :

$$A = B = 91, \quad D = 485, \quad E = 110, \quad a = 9.5.$$

The accuracies are to within 1 percent for A , B , and D , but since evaluation of E depends on second-order effects its accuracy

TABLE I. Electronic splittings along different axes.

Direction	Separation of groups (gauss)			
x axis	280	290	285	280
y axis	860	630	650	475
z axis	355	420	480	480
Field axis	1105	1020	1010	1065

is much smaller. E can also be estimated from the splitting obtained along different directions at right angles to the field axis. These vary from 1060 gauss to 2950 gauss, measured between the extreme groups, and give 85 ± 40 as a probable value of E .

The g value was determined by means of a free-radical marker and, allowing for the second-order corrections, was evaluated as $g = 1.999 \pm 0.0015$.

It is of interest to compare these results with those obtained from other manganese results,^{1,3-5} as is shown in Table II.

TABLE II. Comparison of splittings in different salts. The coefficients are given in units of 10^{-4} cm^{-1} .

Salt	D	A	a	E	Reference
$Mn(COOH)_2 \cdot 2H_2O$	485	91	9.5	110	—
$Mn(CH_3COOH)_2 \cdot 4H_2O$	412	87	8	56	4
$Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$	243	91	5	100	1
	180	90	10	—	5
$Mn(NO_3)_2 \cdot 2Bi(NO_3)_3 \cdot 24H_2O$	164	88	10	—	—
$Mn(CH_3COOH)_2 \cdot 3H_2O$	252	—	—	27	3
$MnSiF_6 \cdot 6H_2O$	197	96	7	—	1

The first four salts all have two ions per unit cell, and it is seen that D decreases as the number of waters of crystallization increases; as is also the case for the last two, which have only one ion per unit cell.

This confirms the fact that the symmetry of the crystalline field round the paramagnetic ion is probably mainly due to the water molecules in all the salts investigated.

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An Excitation Curve for Photomesons from Beryllium*

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THE yields of 54-Mev π^- and π^+ mesons at 90° were obtained as a function of the maximum energy of the Cornell synchrotron. A double-focusing magnet deflects the mesons through 90° into a proportional counter telescope. The solid angle and energy resolution of the magnet were determined by means of a current-carrying wire. The full width at half-maximum was 25 Mev. The angular aperture was $\pm 7^\circ$ horizontally and $\pm 3.5^\circ$ vertically. Agreement was found with the strong energy dependence of the π^-/π^+ ratio observed by Littauer and Walker at 135° .¹ The following ratios were obtained.

Maximum gamma-ray energy (Mev)	310	275	250	225
Ratio π^-/π^+	1.65 ± 0.05	2.0 ± 0.1	2.4 ± 0.3	3.3 ± 0.5

The maximum energy of the bremsstrahlen was varied by turning off the accelerating rf at the appropriate part of the magnetic cycle. The beam was monitored by an ionization chamber behind 1 inch of copper. The response of the chamber is nearly proportional to the total energy in the gamma-ray beam in the region from 200- to 300-Mev maximum energy.² By the subtraction of the yields normalized to the same number of "equivalent quanta"