

# Strain Scattering by Vacancies and Impurities in Metals

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A simple model is proposed by means of which nearest neighbor displacements round a vacancy and an impurity in a metal may be taken into account in calculating excess resistivities. Using Tewordt's calculated nearest neighbor displacement for a vacancy in copper we obtain from our model an excess resistivity of  $0.94 \mu\text{ohm cm}$  per atomic percent. The same model without strain yields  $0.97 \mu\text{ohm cm}$ . The case of silver impurities in copper is also considered and it is shown that a radial increase of  $\sim 3\%$  in the nearest neighbor distance is sufficient to account entirely for the observed excess resistivity.

## 1. INTRODUCTION

MOST treatments of the vacancy problem so far proposed have neglected relaxation of the lattice which, it seems, must occur when an atom is removed. Recently Tewordt<sup>1</sup> has reported detailed results for the nearest-neighbor displacements expected theoretically in copper metal, and the present work represents an attempt to incorporate such relaxation into the free-electron model of a vacancy. Some comments will also be made on the problem of substitutional impurities in metals.

We recall first that earlier workers have made calculations in which some account has been taken of lattice strains, and we have in mind particularly the work of Blatt<sup>2</sup> on substitutional impurities in the noble metals, in which a modification of the Friedel sum rule, due to Harrison, was invoked, and that of Potter and Dexter<sup>3</sup> on interstitials in copper. Our work is quite different in concept from these earlier treatments, and represents an attempt to formulate a more fundamental approach to the problem of relaxation. Even so, we are well aware that the proposed model can provide only quite a rough description of the situation occurring in real metals.

## 2. MODEL USED

We start from the free electron approximation, and to be definite we consider the vacancy case. We attempt to describe the effect of a single vacancy in an infinite monovalent metal in the following way. As a model for the unstrained case, we take a single negative charge embedded in the free electron gas. The conduction electron cloud adjusts itself to screen out the perturbing field and the screening may be described approximately by the Thomas-Fermi method. The appropriate numerical solution has been worked out by Alfred and March<sup>4</sup> in their study of impurity-vacancy interaction in a metal, and it is found that the earlier analytical approximation given by these writers<sup>5</sup> is fairly satis-

factory for describing the perturbing potential. In order to facilitate the carrying-through of the calculations in the case when lattice strain is included, we shall adopt this analytical approximation.

We now introduce lattice strain by first removing the twelve nearest neighbor ions (for a monovalent face-centered cubic metal) by placing single negative charges at their undisplaced positions. The ions are then replaced, at their new, radially displaced, sites, by adding single positive charges. The resulting self-consistent field problem seems too formidable to solve even within the present framework, and we shall adopt the method of expansion of the perturbing potential in spherical harmonics, which, as we pointed out earlier,<sup>6</sup> seems useful in this type of problem. In the present case the symmetry is high, and after the  $s$  term, no spherical harmonic of lower than  $g$  symmetry will appear. Therefore we assume that to a sufficient approximation the problem may be reduced to one of spherical symmetry, and the result is then equivalent to smearing the ionic charges over two spheres centered on the vacancy.

## 3. APPROXIMATE SELF-CONSISTENT FIELD FOR VACANCY

We now proceed to set up the equations which describe the model of Sec. 2. The method is a generalization of that employed by Alfred and March.<sup>5</sup> Let the original nearest-neighbor sites be at a distance  $R$  from the vacancy, and let  $R'$  be the new nearest-neighbor distance. Then we adopt the following form for the perturbing potential  $V$ :

$$V^{(1)} = -\frac{1}{r} + \beta - \frac{2^{\frac{1}{2}} E_m^{\frac{3}{2}}}{9\pi} r^2; \quad r \leq r_c, \quad (1)$$

$$V^{(2)} = A_2 \frac{\exp(-qr)}{r} + B_2 \frac{\exp(qr)}{r}; \quad r_c < r \leq R', \quad (2)$$

$$V^{(3)} = A_3 \frac{\exp(-qr)}{r} + B_3 \frac{\exp(qr)}{r}; \quad R' < r \leq R, \quad (3)$$

$$V^{(4)} = A_4 \frac{\exp(-qr)}{r}; \quad r > R, \quad (4)$$

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<sup>1</sup> L. Tewordt, Phys. Rev. **109**, 61 (1958).

<sup>2</sup> F. J. Blatt, Phys. Rev. **108**, 285 (1957).

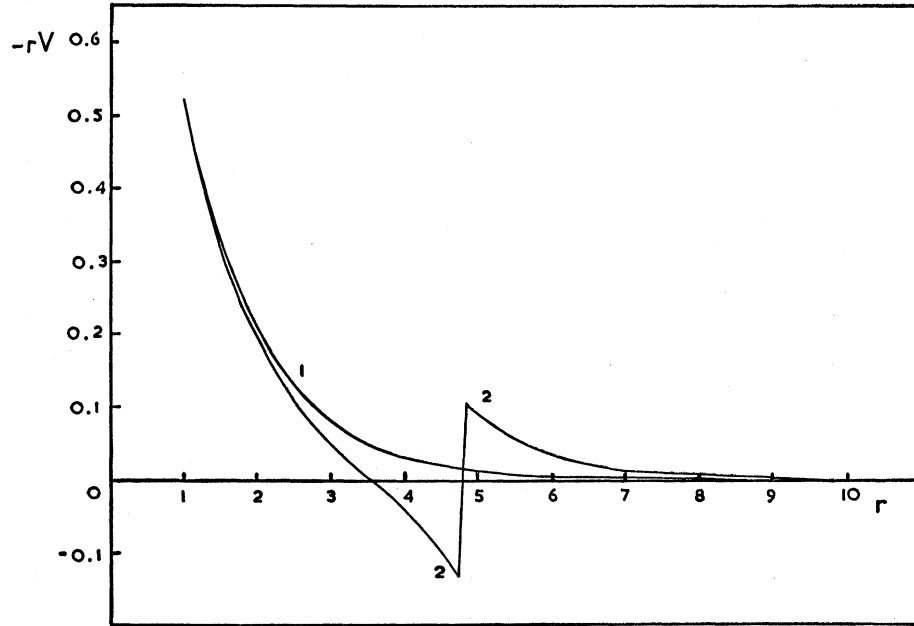
<sup>3</sup> R. J. Potter and D. L. Dexter, Phys. Rev. **108**, 677 (1957).

<sup>4</sup> L. C. R. Alfred and N. H. March, Phil. Mag. **2**, 985 (1957).

<sup>5</sup> L. C. R. Alfred and N. H. March, Phys. Rev. **103**, 877 (1956).

<sup>6</sup> P. M. Lee and N. H. March, Phil. Mag. **2**, 1226 (1957).

FIG. 1. Form of perturbing potential for vacancy in copper. 1.  $-rV$  neglecting strain. 2.  $-rV$  including strain.



Eqs. (2), (3), and (4) being solutions of the linearized Thomas-Fermi equation

$$\nabla^2 V = q^2 V. \quad (5)$$

Here  $E_m$  is the Fermi energy, which is related to the screening radius  $q^{-1}$  by

$$q^2 = 2\frac{1}{2} E_m^{3/2} / \pi, \quad (6)$$

and  $r_e$  is the classical radius defined by

$$-V(r_e) = E_m. \quad (7)$$

We should note at this point that in general the possibility of a further classically forbidden region around the negative surface charge distribution arises. In the vacancy case, however, our numerical calculations for copper show that outside  $r_e$ ,

$$E_m > |V| \quad (8)$$

and hence no such region exists for the present problem.

The remaining constants of integration are now to be determined by imposing appropriate electrostatic boundary conditions on the potential  $V$ . In particular we must account for the discontinuity in the field as we cross a surface charge distribution, and then we have

$$(dV^{(2)}/dr)_{R'} - (dV^{(3)}/dr)_{R'} = 4\pi\sigma_1, \quad (9)$$

and

$$(dV^{(3)}/dr)_R - (dV^{(4)}/dr)_R = 4\pi\sigma_2, \quad (10)$$

where  $\sigma_1$  and  $\sigma_2$  are the surface charge densities on the spheres of radii  $R'$  and  $R$ , respectively. In the present case we have explicitly

$$\sigma_1 = 12/4\pi R'^2, \quad (11)$$

$$\sigma_2 = -12/4\pi R^2. \quad (12)$$

The remaining conditions are simply the continuity of  $V$  at  $R'$  and  $R$  and of  $V$  and its first derivatives at the other boundary surfaces.

The choice of  $R-R'$  was made on the basis of Tewordt's calculations.<sup>1</sup> For two different Born-Mayer potentials, values of  $R-R'$  of 0.111 and 0.092 atomic unit were obtained. In our computations of the perturbing potential  $V$  we therefore adopted for convenience

$$R-R' = 0.10 \text{ atomic unit,}$$

together with  $R=4.84$ . The numerical results thus obtained are shown in Fig. 1, and for comparison the earlier results of Alfred and March<sup>5</sup> without strain are also plotted.

#### 4. RESULTS OF PHASE-SHIFT ANALYSIS FOR VACANCY

The perturbing potential obtained in Sec. 3 has been used to calculate the excess resistivity for one atomic percent of vacancies in copper, by the method of phase-shift analysis (see, for example, Schiff<sup>7</sup>).

The phase shifts  $\eta_l$  were calculated for the potentials shown in curves (1) and (2) of Fig. 1, and the results are presented in Table I. The excess resistivities  $\Delta\rho$  obtained from these results are:

$$(1) \text{ Without strain: } \Delta\rho = 0.97 \mu\text{ohm cm/atomic } \%,$$

$$(2) \text{ With strain: } \Delta\rho = 0.94 \mu\text{ohm cm/atomic } \%.$$

It is also of interest to note that for the Friedel sum<sup>8</sup>

<sup>7</sup> L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, New York, 1949).

<sup>8</sup> J. Friedel, *Phil. Mag.* 43, 153 (1952).

TABLE I. Phase shifts for scattering by vacancy.

$l$	Without strain	$\eta_l$ With strain
0	-0.668	-0.608
1	-0.182	-0.096
2	-0.047	-0.033
3	-0.012	-0.032
4	-0.003	-0.017

in the case when strain is neglected we find

$$\frac{2}{\pi} \sum_l (2l+1) \eta_l = -0.99.$$

With inclusion of strain, however, the Friedel sum is not converging satisfactorily at  $l=4$ , but the convergence of the corresponding resistivity series is still adequate.

### 5. SILVER IMPURITIES IN COPPER

With the model used here, and neglecting strain, the substitution of a silver atom for an atom in the copper lattice does not lead to any scattering of conduction electrons. However, relaxation of the nearest-neighbor atoms must contribute to the excess resistivity and its effect has been calculated.

The equations of Sec. 3 are easily modified to apply to this case. The significant difference is that the nearest-neighbor atoms now move away from the impurity, since the silver ion-core has a larger radius than the copper ion. Thus the inner shell has a uniform surface distribution of negative charge.

In order to display the effect of nearest-neighbor displacement on the excess resistivity, six different displacements in the range 0 to 3% were considered, and in each case the computed potential was used in a

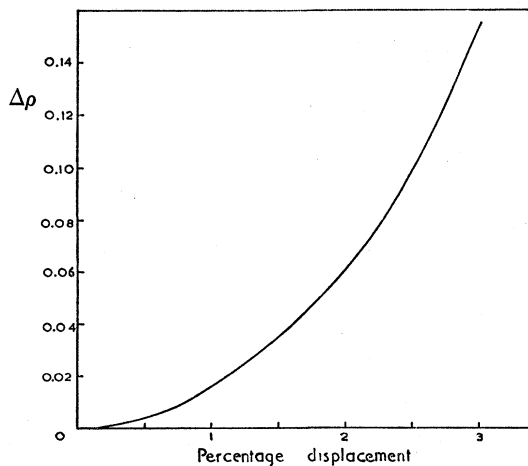


FIG. 2. Excess resistivity  $\Delta\rho$  in  $\mu\text{ohm cm}$  per atomic percent as a function of percentage displacement of nearest-neighbors for silver impurity atoms in copper.

partial wave analysis. The final results are shown in Fig. 2, where the excess resistivity  $\Delta\rho$  is plotted against the percentage displacement of the nearest-neighbors. The potential corresponding to 2.9% displacement is shown in Fig. 3.

### 6. DISCUSSION OF RESULTS

We consider first the vacancy problem. Here, our main conclusion is that the effect of strain scattering on the excess resistivity appears to be quite small. It also seems interesting that the inclusion of relaxation has led in this case to a decrease in the resistivity. This is similar to the findings of Potter and Dexter<sup>3</sup> for the interstitial problem.

Various points, however, remain to be considered. It will eventually be desirable to estimate the effect of going beyond nearest-neighbor displacements. Furthermore, the question arises as to whether the present

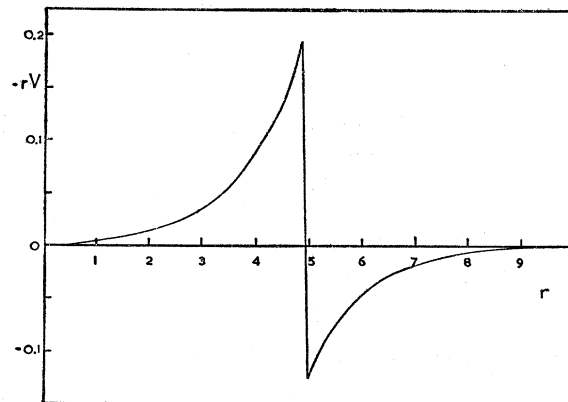


FIG. 3. Form of perturbing potential due to relaxation of nearest-neighbors around silver impurity in copper.  $-rV$  is plotted for a percentage displacement of 2.9.

model is adequate to describe the perturbing potential near to the shells of ions. Inclusion of the first harmonic allowed by symmetry might eventually throw some light on this point.

We shall finally comment on the results for silver impurities in copper. Here we have used the present model to predict the excess resistivity due to strain, there being no charge shift contribution within the valence model adopted. The most accurate work available on this latter point seems to be that of Roth, whom Blatt<sup>2</sup> quotes as having calculated a contribution, neglecting lattice strain, of only  $0.001 \mu\text{ohm cm}$  per atomic %. If we accept the inference that the excess resistivity is indeed predominantly due to strain scattering, then the present model indicates that a nearest-neighbor displacement of about 3% is all that is required to account for the experimental value of  $\Delta\rho$ . On the other hand, if, as seems unlikely, the charge

shift and strain scattering contributions turn out to be of comparable importance, then a larger relaxation may perhaps be permitted, due to the possibility of interference effects.

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## Effects of Double Exchange in Magnetic Crystals\*

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This paper discusses some effects of mobile electrons in some antiferromagnetic lattices. It is shown that these electrons (or holes) always give rise to a distortion of the ground state spin arrangement, since electron transfer lowers the energy by a term of first order in the distortion angles. In the most typical cases this results in: (a) a nonzero spontaneous moment in low fields; (b) a lack of saturation in high fields; (c) simultaneous occurrence of "ferromagnetic" and "antiferromagnetic" lines in neutron diffraction patterns; (d) both ferromagnetic and antiferromagnetic branches in the spin wave spectra. Some of these properties have indeed been observed in compounds of mixed valency such as the manganites with low  $Mn^{4+}$  content. Similar considerations apply at finite temperatures, at least for the (most widespread) case where only the bottom of the carrier band is occupied at all temperatures of interest. The free energy is computed by a variational procedure, using simple carrier wave functions and an extension of the molecular field approximation. It is found that the canted arrangements are stable up to a well-defined temperature  $T_1$ . Above  $T_1$  the system is either antiferromagnetic or ferromagnetic, depending upon the relative amount of mobile electrons. This behavior is not qualitatively modified when the carriers which are responsible for double exchange fall into bound states around impurity ions of opposite charge. Such bound states, however, will give rise to local inhomogeneities in the spin distortion, and to diffuse magnetic peaks in the neutron diffraction pattern. The possibility of observing these peaks and of eliminating the spurious spin-wave scattering is discussed in an Appendix.

## I. INTRODUCTION

WE are concerned here with magnetic compounds of mixed valency, of which the best known example is the series  $(La_{1-x}Ca_x)(Mn_{1-x}^{3+}Mn_x^{4+})O_3$ . At both ends of the composition diagram, these manganites behave like antiferromagnetic insulators.<sup>1,2</sup> However, to take a definite example, if we substitute 10% of calcium in pure  $LaMnO_3$  the room temperature conductivity is increased by two orders of magnitude.<sup>1</sup> This shows that the 10% extra holes which have been added are comparatively free to move from one manganese ion to another, and are able to carry a current. These carriers also have a strong effect on the magnetic properties of the material: at low temperatures there is a nonzero spontaneous magnetization (approximately 0.4 of what is expected for complete lining up of the spins on the above example), indicating that some sort of ferromagnetic coupling is present. This was first explained by Zener<sup>3</sup> in the following way: (1) intra-atomic exchange is strong so that the only important

configurations are those where the spin of each carrier is parallel to the local ionic spin; (2) the carriers do not change their spin orientation when moving; accordingly they can hop from one ion to the next only if the two ionic spins are not antiparallel; (3) when hopping is allowed the ground state energy is lowered (because the carriers are then able to participate in the binding). This results in a lower energy for ferromagnetic configurations. This "double exchange" is completely different from the usual (direct or indirect) exchange couplings, as pointed out by Anderson and Hasegawa.<sup>4</sup> The coupling energy is shared between the carriers, and cannot be written as a sum of terms relating the ionic spins by pairs. Also, the dependence of the carrier energy on the angle between different ionic spins is quite remarkable. This brings in special effects which do not seem to have been considered up to now. For instance, if the pure material is antiferromagnetic, it will turn out that the carrier energy in the mixed material is lowered if the sublattices become canted. This gain in energy is of first order with respect to the angle of canting, while the loss of antiferromagnetic exchange energy is only of second order; as a result, the canted arrangement is indeed more stable. It is the

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<sup>2</sup> E. O. Wollan and W. C. Koehler, *Phys. Rev.* **100**, 545 (1955).

<sup>3</sup> C. Zener, *Phys. Rev.* **82**, 403 (1951).

<sup>4</sup> P. W. Anderson and H. Hasegawa, *Phys. Rev.* **100**, 675 (1955).