these assumptions the final evaluation of eq. (3) is easily done and yields the following expressions for the additional contribution $\Delta\sigma_{\alpha\beta}(0) = \delta_{\alpha\beta}\Delta\sigma_{\alpha}$ to the static conductivity due to fluctuations:

1. Bulk material

$$\Delta\sigma_x = \Delta\sigma_y = \frac{3e^2 T}{\pi v l (2eH)^{\frac{1}{2}}} \left(\frac{T_c}{T-T_c}\right)^{\frac{1}{2}}$$

$$\Delta\sigma_z = \frac{e^2 (2eH)^{\frac{1}{2}}}{8\pi^2}\left(\frac{T_c}{T-T_c}\right)^{\frac{3}{2}}.$$

(6)

2. Thin films (H perpendicular to the film surfaces)

$$\Delta\sigma_x = \Delta\sigma_y = \frac{3e^2 T}{\pi v l e H d}\frac{T_c}{T-T_c}.$$

(7)

Here we have introduced a transition temperature T_c which is defined as a function of the external parameters H and T: $TH_{c2}(T_c) \equiv T_c H$. In these equations only the leading term (for $(T-T_c)/T_c \ll 1$) is written down. It is interesting to note that the conductivity is strongly anisotropic and that the conductivity parallel to the external magnetic field (c.f. eq. (6)) has the same singularity as one finds for thin wires.

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X-RAY TRANSITIONS NEAR DEFECTS IN METALS

A. M. STONEHAM

Coordinated Science Laboratory, University of Illinois, Urbana–Champaign and Theoretical Physics Division, AERE Harwell, UK

Intrinsic defects in metals affect the X-ray absorption and emission edges. Estimates are given for defects in Cu and Al, including the vacancy, interstitial and dislocation. The resulting structure should be observable and can distinguish between vacancy and interstitial.

Defects in insulators are usually studied optically. Optical techniques cannot be used for defects in metals since there is very complete absorption at frequencies below the plasma frequency; mechanical and electrical properties are usually studied, although these cannot easily identify the defects involved. However, X-ray spectroscopy is possible, since it involves frequencies well above the plasma frequency. A new technique is proposed here, the study of *changes* in the structure of the X-ray absorption or emission edges due to defects. The method resembles work on insulators, where the effects of defects on the exciton structure are observed, e.g. the measurement of vacancy concentrations in alkali halides from the intensity of the α-band [1].

In X-ray absorption an electron makes a tran-

sition from a core state of energy E_c to the conduction band. If the crystal is perfect the absorption is only appreciable above a fairly sharp minimum $E_L = E_f - E_c$, where E_f is the Fermi energy. Correspondingly, the emission rises sharply at energies below E_L. Even in the perfect crystal, the absorption edge shows considerable structure because of the variety and complexity of the possible excited states [2]; for example, the hole in the core state constitutes a strong local perturbation which may introduce local levels. However, the excited states are always less localised than the core states, and the details and origins of the fine structure near the edge in a perfect crystal prove to be of rather minor importance in the discussion which follows.

The X-ray spectrum is altered when a small concentration, F, of defects is introduced into an otherwise perfect crystal. Only intrinsic defects will be discussed here - interstitials, vacancies and dislocations. The point defects cause a very local perturbation, whose main effect is to change the energies of the core electrons near the defect. This alters E_L for atoms near the defect, and should give a step in the absorption or emission edge, with intensity proportional to the defect concentration and width of the order of the change in E_c.

The defects affect the excited states in several ways. First, they may shift the Fermi energy, so that transitions occur to a different set of excited states. Secondly, the excited states may change in energy. Thirdly, the excited state wave functions may be altered, changing the transition matrix elements and so affecting the structure near the edge. These effects appear to be only of secondary importance. There is no shift of the Fermi level linear in the concentration, and the energies of the excited states are not significantly affected, since the corresponding wavefunctions spread over many unit cells, and the perturbation is appreciable only over a few cells.

The core energies may change appreciably, since the core states can be localised where the perturbation is strongest. To a first approximation, the shift in core energy of a given crystal atom is

$$\Delta E_c = \sum_i \left[V(r_i) - V(r_{i0}) \right] . \tag{1}$$

This assumes that the core wavefunction is strongly localised, and neglects the variation of V over the core orbital. The same shift should occur for all core oribtals which are well localised. If Z is the valence of the metal, $V(r) \equiv Ze^2 \times \times \exp(-\lambda r)/r$ is the usual screened interaction;

the neighboring atoms are at r_i in the defect lattice and at r_{i0} in the perfect lattice. The pseudo atom approximation is used, i.e. the screening clouds move rigidly with each atom.

$V(r)$ is attractive for electrons, so the core electron energies are reduced in regions where the atoms are packed closer together, e.g. near interstitials. In X-ray emission the contribution from interstitials will be in a range where the perfect crystal contribution has low intensity. Similarly, it may be possible to detect vacancies in X-ray absorption. Note the changes in ΔE_c are of opposite sign for vacancies and interstitials, so it should be possible to distinguish between these defects without ambiguity.

In the f.c.c. structure the screening parameter, λ, is given by $\lambda d = 2.89\, Z^{1/6} d^{1/2}$ where d is the nearest neighbour distance in Å. Direct calculation gives the energy shift for the nearest neighbour of a vacancy is -0.055 eV for Cu and -0.043 eV for Al. These results ignore any distortion of the lattice. For a dumbbell interstitial* the shifts are 0.85 eV for Cu and 0.90 eV for Al. All atoms except the two components of the dumbbell were kept at their perfect lattice sites. The shifts were not sensitive to the separation, b, of the two components, and varied by less than 5% over the range $0.7 \leqslant b/d \leqslant 0.92$. Finally, calculations were made for dislocations in Al using anisotropic elasticity theory. All shifts associated with atoms near the core were less than 0.2 eV.

Structure should be observable if the shifts exceed 0.1 eV and if the defect concentration is sufficient. Interstitials and (possibly) dislocations should be observable, but it is unlikely that vacancies can be detected. If the structure due to defects can be resolved, then defect concentrations may be monitored, giving the temperature dependence of defect mobilities; reactions between defects may also be followed. Such experiments use structure only as labels to identify the defects. The size and sign of the shift gives a measure of the local strain near a defect and its vacancy or interstitial character. Further, polarised X-rays, from particle accelerators, may be used to give the symmetry of defects.

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* If an f.c.c. lattice is defined by $(d/\sqrt{2})\,(l,m,n)$, in which $(l+m+n)$ is even, then the dumbbell interstitial can be produced by replacing the atom at $(0,0,0)$ by two atoms at $(\pm \frac{1}{2}b, 0, 0)$.

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ISOTOPE EFFECT IN SUPERCONDUCTORS

A. ROTHWARF

RCA Laboratories, Princeton, New Jersey 08540, USA

It is shown that the conventional picture of superconductivity can't explain a positive isotope effect of greater than 0.5 at zero pressure.

The discovery of a large positive isotope effect $(T_c \sim M^{\alpha}, \alpha \approx 2)$ in α-uranium has raised the question of whether a new mechanism [1,2] is necessary to explain this result. In this letter we point out that the usual picture of superconductivity which explains the negative isotope effect, doesnot hold if α exceeds 0.5, at zero pressure. Since the results on α-uranium were obtained with the material under a pressure of ~ 11 k bar, the possibility remains that the observed value of α is due to a pressure effect. We discuss such a possibility.

In the conventional picture of superconductivity [3] one has, at $T = 0$, states outside the Fermi sphere occupied while holes appear within the sphere. One argues that while the kinetic energy of the electrons is greater in the superconducting state, this is more than offset by a lowering of the interaction energy to give the lowest energy state. The connection between this picture and the isotope effect is through a result obtained by Chester [4]. On very general grounds Chester obtained the following expression for the difference in the kinetic energy of the electrons in the normal and superconducting states at $T = 0$, (1)

$$(\text{K.E})^e_s - (\text{K.E})^e_n = (1 - 2\alpha) \frac{V H_c^2}{8\pi} - 4P \left[\frac{\partial [V H_c^2/8\pi]}{\partial P} \right]_{T,M}$$

where V is the volume of the system, H_c the critical magnetic field, P the pressure, T the temperature and M the isotope mass. In obtaining eq. (1) the usual assumptions $H_c \sim M^{\beta}$ and $T_c \sim M^{\alpha}$, with $\alpha = \beta$, have been made. It is clear than at $P = 0$ the conventional picture and eq. (1)

can only be consistent if $\alpha > 0.5$. This means that if $\alpha > 0.5$ at zero pressure, the kinetic energy of the electrons is less in the superconducting state than in the normal state. If we picture a normal metal at $T = 0$ as containing a full Fermi surface there is no obvious way of finding lower kinetic energy states. Before one starts to picture rearrangements of electrons in overlapping bands etc., it is well to consider first some further points.

If one were dealing with the electrons alone there would be no way of producing a lower energy state without *increasing* the kinetic energy of the electrons. This follows directly from the Coulomb nature of the interactions in solids and the virial theorem [5], which predicts that the *increase* in the kinetic energy of the particles equals the magnitude of the condensation energy (for $P = 0$, case). It is thus clear than by consideration of the electrons alone no satisfactory theory for a large positive isotope effect is possible. Chester has shown, however, that when *any* isotope effect exists there is a change in the kinetic energy of the nuclei. This change is given by

$$(\text{K.E})^{nuc}_s - (\text{K.E})^{nuc}_n = 2\alpha V H_c^2/8\pi . \qquad (2)$$

From this result it is clear that *any* mechanism which leads to an isotope effect is intimately related to the lattice vibrations. Thus any theory which involves a decrease in the electronic kinetic energy in going to the superconducting state must also involve an increase in the lattice energy.

Since the only experimental results which give a large positive α, are in the uranium under pres-