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RESISTIVITY SATURATION

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1. Introduction

The term "resistivity saturation" was introduced by Fisk and Webb (1976) to describe a less-than-linear rise in dc electrical resistivity ρ when temperature T increases. It is now recognized that this effect is common in d-band compounds when ρ exceeds $\sim$80$\mu\Omega$cm, and that ρ seems bounded above by a value $\rho_{max} \sim$ 150$\mu\Omega$cm which varies somewhat with material. A brief review of theory was given by Allen (1980). Boltzmann theories require the ratio a/ℓ (lattice constant to mean free path) to be small. The fundamental assumption of this article is that a/ℓ is not small in the "saturation" region. Section 2 will attempt to define "saturation" in relation to the general context of highly resistive materials. Section 3 will attempt a more up-to-date description of the modes of breakdown of Bloch-Boltzmann theory.

2. Phenomenological

A15-structure metals exhibit saturation particularly clearly. Fig. 1 shows ρ for Nb_3Sn films. The cleaner samples have strong downward curvature of $\rho(T)$, as first noticed by Woodard and Cody (1964). All data exhibit convergence at high T toward $\rho_{max} \sim$ 140$\mu\Omega$cm. The six lower curves were fit by the "shunt resistor model" (SRM)

$$1/\rho = 1/\rho_{Boltz} + 1/\rho_{max} \qquad (1)$$

where ρ_{Boltz} is the resistivity "expected" from Bloch-Boltzmann theory. Excluding the more complicated interval $\Theta_D/10<T<\Theta_D/2$, ρ_{Boltz} was represented by $\rho_o+\rho_1 T$ where ρ_o comes from (elastic) defect scattering and ρ_1 is the slope of the high-T (inelastic) electron-phonon part. The best fits used ρ_1 fixed, ρ_{max} varying from 130 to 150$\mu\Omega$cm, and ρ_o varying from 12 to 1500$\mu\Omega$cm. The upper two curves with negative $d\rho/dT$ cannot be fit by eq (1). In wondering whether eq (1) is more than a fitting formula, several questions arise. Is $\rho_{max} \sim$ 150$\mu\Omega$cm unique and universal? Does only a single parameter, ρ_{Boltz}/ρ_{max}, determine the behavior of ρ/ρ_{max}? Do elastic and inelastic scattering act in equivalent ways in highly resistive metals?

First consider ρ_{max}. It is interesting that the combination of constants ha/e^2 equals 150$\mu\Omega$cm if the length parameter a is chosen to be 3.7Å, a typical lattice parameter. Furthermore, the electron gas formula $\rho = m/ne^2\tau$ with τ replaced by ℓ/v_F, yields

$$\rho = f\,(ha/e^2)\,(a/\ell) \qquad (2)$$

where the fudge factor f varies weakly with crystal structure and valence, and equals 1.23 for a monovalent fcc metal like Cu. Thus ρ_{max} is the value predicted by Boltzmann theory when $a/\ell=1$, agreeing with Mott's ideas about $\sigma_{min} = \rho_{max}^{-1}$ (Mott 1972, Mott and Davis 1979). These numerological arguments encourage belief in the uniqueness and universality of $\rho_{max} \sim$ 150$\mu\Omega$cm. Unfortunately, experiment is less cooperative. For example, Ba, not quite a d-band metal, has ρ=213$\mu\Omega$cm

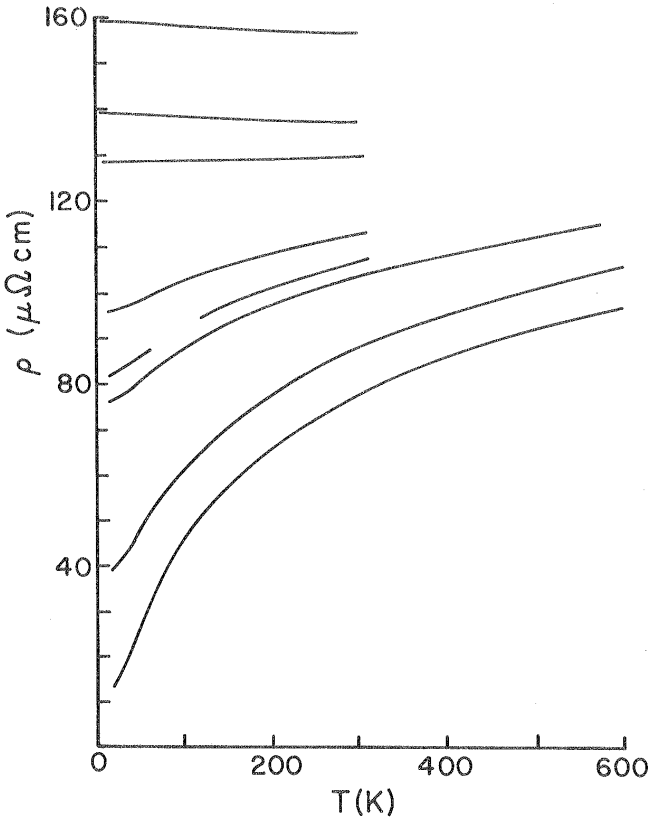

Fig 1. Resistivity of Nb_3Sn with various amounts of α-particle damage (Gurvitch 1978, 1980)

at 927K (just below melting) and no sign of saturation (Van Zytveld, 1977). To explain this, the free-electron parameter n/m must be replaced by a band effective mass

$$(n/m)_{eff} = 2N(o)\langle v^2\rangle/3 \equiv (2/3\Omega) \sum_k v_k^2 \delta(\varepsilon_k) \qquad (3)$$

where $\hbar v_k$ is $|\partial\varepsilon_k/\partial k|$. Then Boltzmann theory with $\ell = \langle v^2\rangle^{\frac{1}{2}}\tau$ gives eq (2), but the fudge factor f is

$$f = 3/2N(o)\langle v^2\rangle^{\frac{1}{2}} \hbar a^2 = 12\pi^3/a^2A \qquad (4a)$$

$$A \equiv \left(\int dS_k/v_k\right)^{\frac{1}{2}} \left(\int dS_k v_k\right)^{\frac{1}{2}} \qquad (4b)$$

Unless v_k is very anisotropic, A is the Fermi surface area. For a sphere, f is $3\pi^2/k_F^2a^2$. In Ba, A is small so f is large, enabling ρ to exceed 150μΩcm even with a/ℓ small. Another counter-example is Mott's analysis of metal-insulator transitions in low carrier-density systems, where $\rho_{max} \sim 3000\mu\Omega$cm. Even in d-band metals, ρ_{max} varies.

In layer metals like TaS_2, ρ_{max} is ∿ 300μΩcm (Fischer 1980), while in linear chain metals like $Tl_2Mo_6Se_8$ (Armici et al, 1980) or $Al_{11}Mn_4$ (Dunlop and Gruner, 1976), ρ can be large and unusual. Thus it is necessary to restrict to fully 3-dimensional d-band systems, excluding classes (such as perovskites) with low carrier density. Rare earth and actinide systems can tentatively be included, with the proviso that magnetic or mixed-valent systems are expected to be more complicated. Perhaps with these restrictions, $\rho_{max} \sim 150\mu\Omega$cm is "universal."

The SRM (eq 1) says that $\rho/\rho_{max} = x/(1+x)$ depends only on one parameter, $x = \rho_{Boltz}/\rho_{max}$, which according to eq (2) is also a/ℓ. Remembering that Boltzmann theory also gives only this parameter, and that $\sigma=1/\rho$ is the quantity which is actually calculated, the SRM has a nearly trivial interpretation. Assume that σ can be represented as a series of powers of a/ℓ. The leading term (for small a/ℓ) must be Boltzmann theory, which collects the terms which diverge as a/ℓ goes to zero. The series looks like

$$\sigma = \sigma_{min}\,[(a/\ell)^{-1} + c_o(a/\ell)^o + c_1(a/\ell)^1 + \ldots] \qquad (5)$$

The first term is eq (2), and the first two terms are eq (1). The SRM is then "derived" if the first coefficient c_o is positive and of order 1 and if higher order corrections can all be neglected. This argument suggests that eq (1) is more than a convenient parameterization.

Unfortunately, experiments show that this picture is not fully adequate. The upper two curves of fig. 1 cannot be fit by eq (1) and suggest that elastic and inelastic scattering are inequivalent if the elastic mean free path is very short. Elastic (T=0) scattering mechanisms seem capable of causing ρ at T=0 to exceed ρ_{max}, although never by very much. (Occasional reports of very high ρ in heavily damaged samples may be due to cracking as explained by Franz et al (1978)). When ρ exceeds ρ_{max}, temperature causes ρ to diminish. Many data demonstrating this effect have been assembled by Mooij (1978). Clearly a/ℓ is not the only parameter. I see three possible descriptions of this state of affairs. (1) Perhaps we must acknowledge that temperature provides more than an inelastic scattering mechanism, also causing thermal smearing of the Fermi distribution and other effects. This allows ρ_{Boltz} and ρ_{max} to have additional temperature dependence. Unfortunately, this picture suggests no simple law, whereas the data seem simple enough. (2) Perhaps ρ saturates at a higher value for elastic scattering alone than it does when inelastic scattering is also present. This suggestion is based on my belief that otherwise it is hard to explain why ρ at T=0 never exceeds 150μΩcm by much. (3) Perhaps with elastic scattering alone, ρ doesn't saturate. Then the difficulty in raising ρ above 150μΩcm must be caused by a limit on the degree of static damage that can be done to a material. Allen et al. (1978) showed that in A15 metals at 300K, thermal disorder makes a/ℓ ∿ 1. It is hard to believe that 300K of thermal disorder exceeds the amount of disorder possible by heavy alloying. Suppose an impurity, which scatters only in angular momentum channel L, is introduced in a free electron gas. Then the maximum scattering cross section Σ is $\Sigma_{max} = 4\pi(2L+1)/k_F^2$. Since $a/\ell = \Sigma\, n_i a$ (n_i is impurity density) one has $(a/\ell)_{max} = 2.1(2L+1)c$ for a monovalent fcc crystal with impurity concentration c. Thus a/ℓ=1 can in principle be achieved with L=2 scattering and c=0.1. This Boltzmann mechanism (Friedel 1958) gives an

upper limit to ρ significantly higher than ordinary experimental values. Further experiments on T=0 defect resistivity are needed to provide guidelines for theory. It is necessary to choose systems where ρ_{Boltz} rises very rapidly as a

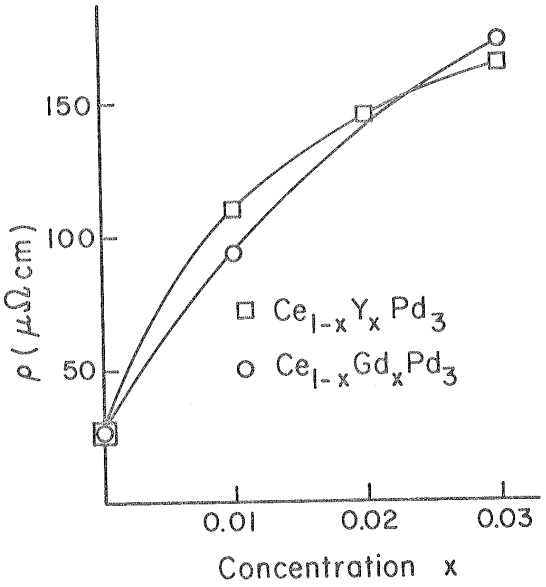

Fig 2. Low temperature ρ of $CePd_3$ with dilute Y or Gd (Schneider, 1980). Solid lines are SRM fits with ρ_{max} = 230 and 380μΩcm

function of defect concentration. An example from rare earth compounds is shown in fig 2, and provides evidence for "saturation" occuring with elastic scattering (description (2) above.)

3. Theoretical

There are several ways of getting anomalous ρ(T) from Bloch-Boltzmann theory, but they alter σ in uncontrolled ways and depend on unlikely parameters (see Allen, 1980), whereas "saturation" is an enhancement of σ and seems to depend on the parameter a/ℓ. Both quantum and classical Boltzmann theories assume collisions are independent. This is safe only when a/ℓ is small, as can be seen from the classical picture given in fig 3. It is less well known that the acceleration term of semiclassical Bloch-Boltzmann theory is also approximate (Chakraborty and Allen 1979, 1981.) The expansion parameter is closely related to a/ℓ. Since the Bloch-Boltzmann equation for dc σ has only an acceleration term and a collision term, I believe that there are no other assumptions of the theory, and that "saturation" must be caused by the failure of at least one of these assumptions. In a model with only a single electron band, semiclassical acceleration is exact and the independent collision approximation can be studied in isolation. For strong elastic scattering, Anderson (1958) localization occurs. Langer and Neal (1966)found a divergence of higher coefficients c_n of the

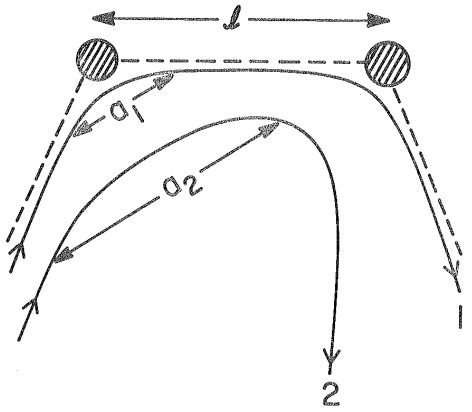

Fig. 3. Two scattering centers separated by a mean free path ℓ. For trajectory 1, the interaction range a<<ℓ and the path approximates the Boltzmann path (dashed line). For case 2, a ∼ ℓ and Boltzmann theory is wrong.

series (5). Anderson's 1958 work shows that there is a fundamental singularity in the function σ(a/ℓ), at a critical scattering strength $(a/\ell)_{max} \sim 1$ such that for larger a/ℓ, σ at T=0 is strictly zero. It should be noted that a/ℓ is used here as a measure of the scattering strength, corresponding to the parameter Anderson called $(W/V)^2$, where W measures disorder and V measures bandwidth. If a/ℓ is not small, the concept of a mean free path makes no sense, but the mathematical parameter x = a/ℓ is still well-defined. It is now widely believed that as x approaches $x_c = (a/\ell)_{max}$, σ vanishes with a critical exponent $(x_c-x)^s$. Expansions around dimension d=2 (Wegner 1979) give $s = 1 + O(d-2)^2$. This theory (if correct) is valid only in the "critical region" $|x-x_c|<<1$. Götze (1979,1980) has an approximate self-consistent theory which (if correct) is valid not too close to $x=x_c$ but gives results qualitatively consistent with Wegner. Götze finds that an excellent approximation in 3 dimensions is given by the first correction to Boltzmann theory

$$\sigma = \sigma_{min}\,[(a/\ell)^{-1} - (a/\ell)_{max}^{-1}] \qquad (6)$$

which corresponds to s=1. Note that this is just the series (5) with c_o taking the negative value $-(a/\ell)_{max}^{-1}$ and higher coefficients all surprisingly unimportant. Note also that this is a shunt resistor model except that ρ_{max} is negative. This is a zero temperature theory and thus not directly comparable with saturation data. The effect of T>0 inelastic scattering on this theory is still not well known. Jonson and Girvin (1979) have solved numerically for σ at T=0 in a one-band model on a Cayley tree (an infinite dimensional lattice of coordination number = 3) and find an Anderson transition for large enough disorder a/ℓ (in what follows, ℓ denotes only the elastic mean free path.) Then they add the effect of finite T electron-phonon interactions in perturbation theory, finding a crossover value $(a/\ell)_o < (a/\ell)_{max}$ below which dσ/dT has a normal negative value and above which it is positive. The mechanism for thermally-enhanced

conductivity is phonon-assisted hopping between partially localized states. Imry (1980) has given roughly the same picture based on a speculative extension of scaling arguments, except that his value of $(a/\ell)_o$ depends on temperature. These theories imply that metals with $d\rho/dT < 0$ (such as the upper two curves of fig 1) are close to the threshold of Anderson localization. Thus ρ(at T=0) should be described eq (6), i.e. increasing more rapidly with disorder than Boltzmann theory predicts, rather than less rapidly as in fig 2. This makes it hard to understand the difficulty of raising ρ (at T=0) much above 150$\mu\Omega$cm. There are also CPA theories along the same lines (Chen et al 1972; Richter and Schiller 1979) but they are probably less reliable since CPA cannot describe localization.

The ideas described so far have been worked out for single-band models, whereas materials exhibiting saturation have many overlapping bands, bringing a new possibility, the failure of semiclassical acceleration. According to Bloch (1928), if an electron is initially described by a wave packet in a single band

$$\psi = \sum_{\underset{\sim}{k}} a_{n\underset{\sim}{k}}\, \psi_{n\underset{\sim}{k}} \tag{7}$$

then the envelope $a_{n\underset{\sim}{k}}$ of the Bloch states $\psi_{n\underset{\sim}{k}}$ evolves according to

$$\partial a_{n\underset{\sim}{k}}/\partial t = -\,(e\underset{\sim}{E}/\hbar)\cdot \partial a_{n\underset{\sim}{k}}/\partial \underset{\sim}{k} \tag{8a}$$

$$a_{n\underset{\sim}{k}}(t) = a_{n\underset{\sim}{k}-e\underset{\sim}{E}t/\hbar}(0) \tag{8b}$$

However, when interband matrix elements $\langle n\underset{\sim}{k}|\underset{\sim}{p}|n'\underset{\sim}{k}\rangle \equiv m\underset{\sim}{v}_{\underset{\sim}{k}nn'}$ of the momentum operator $\underset{\sim}{p}$ are kept, eq (8a) must be supplemented by terms on the right describing interband transitions

$$-\sum_{n'\neq n} a_{n'\underset{\sim}{k}}\,[e\underset{\sim}{E}\cdot \underset{\sim}{v}_{\underset{\sim}{k}nn'}/(\varepsilon_{n\underset{\sim}{k}}-\varepsilon_{n'\underset{\sim}{k}})]\; e^{i(\varepsilon_{n\underset{\sim}{k}}-\varepsilon_{n'\underset{\sim}{k}})t/\hbar} \tag{8c}$$

These terms oscillate at the interband frequency $\Delta E/\hbar$ and thus carry no dissipative current, i.e. $\underset{\sim}{j}$ is out of phase with $\underset{\sim}{E}$ unless the external frequency ω is on resonance with an interband transition. Fig 4 shows the situation schematically - instead of a shunt resistor (8a), there is a shunt resonator.

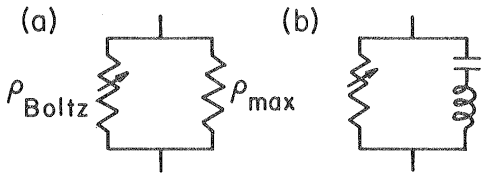

Fig 4.
(a) Shunt resistor model
(b) Usual semi-classical picture

Suppose a collision occurs at a time τ before 8c has completed an oscillation. Then (8c) will not average to zero, and the dc current will be affected --- the capacitor will leak. The criterion for ignoring (8c) is

$$\Delta E\tau/\hbar >> \pi \tag{9}$$

which is easily violated. A15 metals have 6 d-atoms per cell, or 30 d-bands in a total bandwidth $\sim$ 10eV, giving $\Delta E \sim 1/3$eV. The electron-phonon scattering rate for $T \gtrsim \Theta_D$ is $1/\tau = 2\pi\lambda k_B T/\hbar$, and λ can be large, 1.5-2.0 for high-T_c Nb_3X compounds. Thus at room temperature, $\Delta E\tau/\hbar$ is $\sim$1 for Nb_3X, and the quantum corrections (8c) are large. Another measure of the importance of (8c) comes from the f-sum rule, which says that the instantaneous current j(t=0+) responding to an impulsive $\underset{\sim}{E}$ field $\delta(t)$ is given by the classical Newton's law. Since j(t=0+) is $\int d\omega\sigma(\omega)$, this gives

$$\int_0^\infty d\omega\sigma(\omega) = \omega_p^{\,2}/8 = \Omega_p^{\,2}/8 + \text{interband} \tag{10a}$$

where $\Omega_p^{\,2}$ is $4\pi e^2(n/m)_{eff}$. The ratio $\Omega_p^{\,2}/\omega_p^{\,2}$ measures the fraction of the instantaneous current carried by the Boltzmann resistor, i.e. the part driven by semiclassical acceleration, (8a). For s-p metals, this ratio often exceeds 0.8, whereas for d-elements it is usually < 0.3 and for A15's, < 0.05. Semiclassical theory grossly underestimates the full t=0 response. A dc measurement yields $\int dt\, j(t)$ rather than j(t=0+), but it is clear that interband effects (8c) have the potential to enhance greatly the conductivity. These arguments have persuaded me that the mechanism for "saturation" is breakdown of semiclassical approximation rather than of independent collision approximation, since the latter seems more naturally to diminish rather than enhance the current.

A quantitative calculation of the quantum corrections has not yet been done, but a formal answer has been achieved by Chakraborty and Allen (CA) (1979,1981). The independent collision approximation is made in their work. Kragler (1980a,b) has verified their results by a different method, and Garik and Ashcroft (1980) and Kragler and Thomas (1980) have obtained similar results from phenomenological equations. The formal result of CA can be expanded in the form (5), with expansion parameter $\pi\hbar/\tau\Delta E$ replacing a/ℓ. These two expansion parameters are very similar. If the bands were simple in shape (i.e. monotonically varying between $\underset{\sim}{k}$=0 and Brillouin zone boundaries $k\sim\pi/a$, then ΔE could be replaced by $(\pi/a)\partial E/\partial k = \pi\hbar\bar{v}_k/a$, and $\pi\hbar/\tau\Delta E$ would be identical to a/ℓ. However, d-bands are oscillatory more than monotonic, so ΔE is generally less than $\pi\hbar\bar{v}_k/a$. Therefore $\pi\hbar/\tau\Delta E$ may exceed a/ℓ, suggesting again that in d-band compounds, the semi-classical approximation may break down earlier than independent collisions. The result of CA for the expansion (5) is

$$\sigma = \sigma_{Boltz} + \sigma_{min}\,\frac{\alpha n_i + \beta T}{\gamma n_i + \delta T} + \ldots \tag{11}$$

where $\alpha,\beta,\gamma,\delta$ are complicated coefficients depending on energy bands and scattering matrix elements. The first correction to Boltzmann conductivity is formally independent of collisions (i.e. $(a/\ell)^o$) but depends linearly on collision strengths in both the numerator and the denominator. Eq (11) allows a higher ρ_{max} from static disorder than from thermal disorder (if α/γ is smaller than β/δ.) There is no proof (or even hint) of why the higher order terms of the series (5,11) should be negligible, nor is there any justification except practical necessity for assuming the collisions independent.

Infrared measurements would be particularly helpful in choosing between

theoretical alternatives. Götze (1980) has studied $\sigma(\omega)$ near the Anderson transition and finds that as σ_{dc} diminishes (approaching the transition) a peak develops in $\sigma(\omega)$ in the infrared. The interband effects of Chakraborty and Allen predict completely different infrared behavior, namely

$$\sigma(\omega) = \frac{\sigma_{Boltz} + \sigma_a}{1-i\omega\tau} + \sigma_b \qquad (12)$$

where σ_a and σ_b are different contributions of interband effects and add up to σ_{min}. If σ_b were zero, (12) would be experimentally equivalent to Drude theory. Preliminary evidence for $\sigma_b > 0$ can be seen in Yao (1978).

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References

Allen P B 1980 Superconductivity in d- and f-Band Metals ed H Suhl and M B Maple (New York: Academic) pp 291-304

Allen P B, Pickett W E, Ho K M, and Cohen M L 1978 Phys. Rev. Lett. 40 1532

Anderson P W 1958 Phys. Rev. 109 1492

Armici J C, Decroux M, Fischer Ø, Potel M, Chevrel R, and Sergent M 1980 Sol. State Commun. 33 607-611

Bloch F 1928 Z. Phys. 52 555-600

Chakraborty B and Allen P 1979 Phys. Rev. Lett. 42 736-8

Chakraborty B and Allen P 1981 to be published

Chen A-B, Weisz G, and Sher A 1972 Phys. Rev. B5 2897

Dunlop J B and Grüner G 1976 Sol. State Commun. 18 827-9

Fischer Ø 1980 Private communication

Fisk Z and G W Webb 1976 Phys. Rev. Lett. 36 1084

Franz W, Griessel A, Steglich F, and Wohlleben D 1978 Z. Phys. B31 7-17

Friedel J 1958 Nuovo Cim., Supp. 7 287-311

Garik P and Ashcroft N W 1980 Phys. Rev. B21 391-405

Götze W 1979 J. Phys. C 12 1279-96

Götze W 1980 Phil. Mag. (in press)

Gurvitch M 1978 Ph.D. Thesis State University of New York Stony Brook

Gurvitch M 1980 Superconductivity in d- and f-Band Metals ed H Suhl and M B Maple (New York: Academic)

Imry Y 1980 Phys. Rev. Lett. 44 469-71

Jonson M and Girvin S M 1979 Phys. Rev. Lett. 43 1447-51

Kragler R 1980a Physica 143A (in press)

Kragler R 1980b Physica 144A (in press)

Kragler R and Thomas H 1980 Z. Phys. B (to be published)

Langer J S and Neal T 1966 Phys. Rev. Lett. 16 984

Mooij J H 1973 Phys. Stat. Sol. (a)17 331

Mott N F 1972 Phil. Mag. 26 1015

Mott N F and E A Davis 1979 Electronic Processes in Non-crystalline Materials (Oxford University Press) 2nd Ed.

Richter J and Schiller W 1979 Phys. Stat. Sol. (b) 92 511-7

Schneider H 1980 Diplomarbeit, Universität zu Köln (unpublished)

Van Zytveld J B 1977 Liquid Metals, 1976 ed R Evans and D A Greenwood (Bristol: Inst. of Phys.) pp 212-218

Wegner F 1979 Z. Phys. B 35 207-210

Woodard D W and G D Cody 1964 Phys. Rev. 136 A166

Yao W W 1978 Ph.D. Thesis, Princeton Univ.