further studies. Also, the concept will be useful for rare-earth metals where it is important to consider the screening of the ionic interaction by conduction electrons.¹²

I would like to thank Mr. M. Tominaga for his help with numerical calculations.

¹For a review and references, see B. Lüthi, T. J. Moran, and R. J. Pollina, J. Phys. Chem. Solids 31, 1741 (1970).

²For references, see H. S. Bennett and E. Pytte, Phys. Rev. 164, 712 (1967); K. Tani and H. Mori, Prog. Theor. Phys. 39, 876 (1968); G. E. Laramore and L. P. Kadanoff, Phys. Rev. 187, 619 (1969); K. Kawasaki, Int. J. Magn. 1, 171 (1970); M. Tachiki and S. Mawkawa, Prog. Theor. Phys. 51, 1 (1974).

³D. Pines, *Elementary Exictations in Solids* (Benjamin, New York, 1964).

⁴D. J. Kim, J. Phys. Soc. Jpn. 40, 1244, 1250 (1976). ⁵B. Golding and M. Barmatz, Phys. Rev. Lett. <u>23</u>, 223 (1969).

⁶D. J. Kim, B. B. Schwartz, and H. C. Praddaude, Phys. Rev. B 1, 205 (1973).

J. Hubbard, Proc. Roy. Soc. London, Ser. A 43, 336 (1957).

⁸For references, see L. R. Testardi, Rev. Mod. Phys. 47, 639 (1975). ⁹T. Izuyama, D. J. Kim, and R. Kubo, J. Phys. Soc.

Jpn. 18, 1025 (1963).

¹⁰T. Komatsubara, A. Ishizaki, S. Kusaka, and E. Hirahara, Solid State Commun. 14, 741 (1974); B. Ferry and B. Golding, in Magnetism and Magnetic Materials-1974, AIP Conference Proceedings No. 24, edited by C. D. Graham, Jr., J. J. Rhyne, and G. H. Lander (American Institute of Physics, New York, 1975), p. 290. ¹¹R. H. Paulson and J. R. Schrieffer, Phys. Lett. <u>27A</u>, 289 (1968).

¹²D. T. Vigren, Phys. Rev. Lett. <u>38</u>, 1159 (1977).

Resistivity in Amorphous and Disordered Crystalline Alloys

P. J. Cote and L. V. Meisel

Benet Weapons Laboratory, Watervliet Arsenal, Watervliet, New York 12189 (Received 21 March 1977)

The Evans modification of Ziman liquid-metal theory is extended to apply to amorphous and disordered crystalline alloys. In particular, the theory is shown to explain such common behavior of these systems as the change in sign of the temperature coefficient of resistivity with alloy composition, the quadratic temperature dependence of resistivity at low temperature, and the linear temperature dependence of resistivity at high temperatures.

The anomalous temperature and composition dependence of electrical resistivity of amorphous and of many crystalline alloys has been the subject of considerable recent work.¹⁻¹⁴ The behavior of these systems is characterized by (i) temperature coefficients of resistivity which change sign as alloy composition changes, (ii) changes in resistivity which vary as T^2 at low temperature and as T at higher temperatures, and (iii) a generally S-shaped curve of resistivity versus temperature. These common characteristics strongly suggest a common origin. Among the suggested explanations for these effects are localized spin-fluctuation scattering,^{1,2} d-band effects,^{3,4} the Ziman liquid-metal theory,^{5,6} and the Evans, Greenwood, and Lloyd modification of the Ziman theory.⁷⁻¹² We will demonstrate that the modified Ziman theory correctly predicts the observed T^2 and T temperature dependences and explains the effects of composition changes. Furthermore, we present a unified description of the behavior common to amorphous and disordered crystalline metals.

The resistivity of pure metals is given in the modified Ziman theory as

$$\rho = \frac{12\pi\Omega_0}{e^2\hbar V_F^2} \int_0^1 \frac{dq}{2k_F} \left(\frac{q}{2k_F}\right)^3 \tilde{S}(q) |t(k,k')|^2, \tag{1}$$

where Ω_0 is the atomic volume, V_F is the Fermi velocity, k_F is the corresponding wave vector, and $\tilde{S}(q)$ may be written in terms of the dynamic structure factor as

$$\tilde{S}(q) = \int_{-\infty}^{\infty} S(q, \omega) \frac{\hbar \omega}{k_{\rm B} T} \left[\exp\left(\frac{\hbar \omega}{k_{\rm B} T}\right) - 1 \right]^{-1} d\omega.$$

(2)

The x-ray interference function or structure factor is written in terms of the dynamic structure factor $S(q, \omega)$ as

$$S(q) = \int_{-\infty}^{+\infty} S(q, \omega) d\omega.$$

The transition matrix t(k, k') is given as

$$t(k, k') = -\frac{2\pi\hbar^3}{m(2mE_{\rm F})^{1/2}} \frac{1}{\Omega_0} \sum_{l} (2l+1) \sin\eta_l(E_{\rm F}) \exp(i\eta_l(E_{\rm F})) P_l(\cos\theta).$$

The phase shift $\eta_l(E_F)$ for angular momentum quantum number l is evaluated at the Fermi energy E_F . For binary alloys,¹² the quantity $\tilde{S}(q) |t(k, k')|^2$ is replaced by

$$\langle T_{\text{alloy}} \rangle^2 = c_1 |t_1|^2 [c_2 + c_1 \tilde{S}_{11}(q)] + c_2 |t_2|^2 [c_1 + c_2 \tilde{S}_{22}(q)] + c_1 c_2 (t_1 * t_2 + t_1 t_2 *) [\tilde{S}_{12}(q) - 1],$$

where t_i is the *t* matrix of element *i* with concentration c_i , and \tilde{S}_{ij} is the partial structure factor. For brevity, the pure-metal form will be used throughout, recognizing that the results apply to each of the partial structure factors in $\langle T_{allov} \rangle^2$.

We consider only the effects of temperature on $\tilde{S}(q)$. The thermal expansion of Ω_0 , for example, is approximately canceled by a corresponding reduction in $V_{\rm F}$.

In order to include the effect of thermal vibrations on the elastic structure factor $S_0(q)$, a Debye-Waller damping factor e^{-2M} and a background term $A(q)(1 - e^{-2M})$ are included so that the x-ray structure factor becomes

$$S(q) = S_0(q)e^{-2M} + A(q)(1 - e^{-2M}).$$

A(q) = 1 represents the assumption of independent atomic vibrations¹⁵ which is sometimes made for amorphous metals.¹⁶

The dynamic structure factor for an amorphous Debye solid can be written as

 $S(q, \omega) = S_1(q, \omega) + S_2(q, \omega),$

where

$$S_1(q, \omega) = S_0(q)e^{-2M(q)}\delta(\omega),$$

with

$$2M(q) = \frac{3(\hbar q)^2}{mk_B\theta} \left(\frac{T}{\theta}\right)^2 \int_0^{\theta/T} \frac{xdx}{2} \coth(\frac{1}{2}x) \equiv \frac{3(\hbar q)^2}{mk_B\theta} \left(\frac{T}{\theta}\right)^2 I_1\left(\frac{\theta}{T}\right) \,.$$

as given, for example, in Chap. 11 of Ref. 15, and

$$\frac{S_2(q,\omega)}{e^{-2M(q)}} = \begin{cases} \frac{3}{2} \frac{\hbar}{k_{\rm B}T} \frac{(\hbar q)^2}{mk_{\rm B}\theta} \left(\frac{T}{\theta}\right)^2 \frac{x}{1-e^{-x}} A(q) \text{ for } |x| \le \frac{\theta}{T} \\ 0 \text{ for } |x| > \frac{\theta}{T} \end{cases},$$

with $x = \hbar \omega / k_B T$. It will be shown in another publication that A(q) varies smoothly with temperature, being approximately 1 at high temperatures and equal to $S_0(q)$ at absolute zero in the resistivity expression.

Substituting this form into Eq. (1), the Ziman expression¹⁷ for the resistivity, one finds that

 $\rho = \rho_1 + \rho_2,$

with

$$\rho_1 = C \int_0^1 d(q/2k_{\rm F}) (q/2k_{\rm F})^3 S_0(q) |t(k, k')|^2 e^{-2M(q)}$$

and

$$\rho_{2} = CD(T/\theta)^{2} \int_{0}^{1} d(q/2k_{\rm F}) (q/2k_{\rm F})^{5} A(q) |t(k, k')|^{2} I_{2}(\theta/T) e^{-2M(q)},$$

where

$$C = 12\pi\Omega_0/e^2\hbar V_{\rm F}^2$$
, $D = 12\hbar^2 k_{\rm F}^2/mk_{\rm B}\theta$,

and

$$I_2(X) = \int_0^X \frac{x^2 dx}{[\exp(x) - 1][1 - \exp(-x)]}$$

The sum $\rho_1 + \rho_2$ is the analog for amorphous metals of the crystalline Bloch-Grüneisen function. At high temperatures $I_2(X) \rightarrow X$ so the resistivity goes as $\pm T/\theta^2$. At low temperatures $I_2(X) \rightarrow 3.29$, so the resistivity varies as T^2/θ^3 . The sign will be determined by the integrals over $q/2k_{\rm F}$.

Experimental data on amorphous alloys support the above conclusions. The reversible effects of temperature on $S_0(q)$ for amorphous $\operatorname{Ni}_{75}\operatorname{P}_{25}{}^9$ were found to be described by Eq. (2). The results support modification of the $1 - e^{-2M}$ term by a factor A(q) which peaks in the vicinity of the structurefactor maxima in analogy with thermal diffuse scattering in crystalline materials. According to our model the temperature coefficient of resistivity α is determined by the temperature de-

$$\langle T_{\text{alloy}} \rangle^2 = c_1 c_2 |t_1(K) - t_2(K)|^2 [1 + 2\sum_{l=1}^{\infty} \alpha(R_l) \cos(\vec{K} \cdot \vec{R}_l)],$$

where $\vec{\mathbf{K}} = \vec{\mathbf{k}} - \vec{\mathbf{k}}'$, the order parameter $\alpha(R_i) \equiv 1 - N_{12}(R_i)/c_2 = 1 - N_{21}(R_i)/c_1$, and N_{ij} is the probability of finding a type-*j* atom at R_i , given a type-*i* atom at the origin. This expression is completely analogous to the result for x-ray scattering in a disordered binary alloy given by Guiner.¹⁹ For a perfectly disordered alloy $[\alpha(\mathbf{R}) = \delta_{R_i0}]$, treated in the pseudopotential approximation, the equation reduces to a form given by Harrison.²⁰

The Nordheim rule²¹ and generalized Norbury-Linde²¹ rule are seen to result directly from this model. $\langle T_{alloy} \rangle^2$ may be rewritten in terms of an effective *t* matrix *t'* and structure factor $\tilde{S}(q)$ so that

$$\langle T_{\text{alloy}} \rangle^2 = c_1 c_2 |t'(k, k')|^2 \tilde{S}'(q).$$
 (3')

The effects of thermal vibrations on the x-ray $S_0'(q)$ are discussed by Warren.¹⁵ $S_0'(q)$ will be thermally broadened as are the amorphous peaks so that we may wirte

$$S'(q) = S_0'(q)e^{-2M} + A'(q)(1 - e^{-2M}).$$

The treatment of the temperature dependence of the resistivity from disorder scattering is thus identical to that for amorphous alloys and will result in T and T^2 high- and low-temperature dependence of the structure factor $\tilde{S}(q)$. X-ray results in Ni₇₅P₂₅ yield $\Delta \ln S(q)/\Delta T \approx -10^{-4}$ K⁻¹ in the vicinity of the main peak and $\approx 3 \times 10^{-4}$ K⁻¹ around the peak tails. These values are consistent with the range of observed α values in NiP⁸ and other metallic glasses.^{4,6,13} The predictions of positive and negative values for α and the limiting T^2 and T dependences are in accord with the general observations described earlier. Detailed numerical calculations on NiP using the modified Ziman theory are also in agreement with the observed magnitudes of ρ .¹⁰

We now indicate how the model can be extended to apply to disordered, crystalline, metallic alloys. (The treatment given is in the spirit of Baym's theorem.¹⁸) X-ray scattering from disordered alloys exhibits diffuse short-range-order peaks between the Bragg peaks.¹⁵ The diffuse peaks resemble those seen in the structure factors of glassy metals. Since the structure responsible for the Bragg peaks will not scatter Bloch electrons, the structure responsible for the diffuse peaks represents the dominant conduction-electron scattering effect in disordered alloys. Straightforward analysis yields

(3)

pendences, respectively. The sign of the temperature coefficient of resistivity will again be determined by the magnitude of $2k_{\rm F}$ relative to the peak position in $\tilde{S}'(q)$.

Mooij¹⁴ has analyzed electrical conduction in concentrated, disordered, transition-metal alloys. His conclusions were that (i) concentrated, disordered, binary alloys with a transition element as one component generally have high ρ and low α values (i.e., $\rho \ge 100 \ \mu\Omega$ cm and $|\alpha| < 2 \times 10^{-4} \ \mathrm{K}^{-1}$), (ii) negative α 's are found at compositions with the largest ρ values, and (iii) no alloys with a low α are found that contain only elements from the same column of the periodic table.

Equation (3') provides an explanation for all these points. The disorder resistivity will be large for concentrated alloys because of the c_1c_2 factor. In transition elements, t(k, k') is large and weights high-angle scattering^{7,12} so that the largest resistivity is predicted for transitionmetal-nontransition-metal alloys. This disorder resistivity should be small for elements from the same column in the periodic table because $t_1 \approx t_2$, resulting in a small t'. Finally, the correlation between a negative α and large ρ is predicted because large ρ values occur when $2k_{\rm F}$ overlaps the peak in $\tilde{S}'(q)$. This same condition produces a decrease in ρ on heating because of the peak reduction. As in the case of amorphous alloys, the room-temperature value of α is determined by the Debye-Waller factor only so that $|\alpha| \sim 10^{-4}$ K⁻¹ is predicted in agreement with observed values.

In conclusion, extended Ziman-Evans theory provides a unified framework for the description of transport in glassy metals and disordered crystalline alloys as well as in liquid metals. Moreover, the procedure described does not depend on any particular model for $S(q, \omega)$ but is valid for any system whose structure factor $S_0(q)$ is a continuous function of q. Thus, the predicted temperature dependences will be universal features of such systems.

¹A. B. Kaiser and S. Doniach, Int. J. Magn. <u>1</u>, 11 (1970).

²R. Hasegawa, Phys. Lett. 38A, 5 (1972).

³F. Brouers and M. Brauers, J. Phys. (Paris) <u>36</u>, L17 (1976).

⁴G. L. Tangonan, Phys. Lett. <u>54A</u>, 307 (1975).

⁵J. M. Ziman, Philos. Mag. 6, 1013 (1961).

⁶A. K. Sinha, Phys. Rev. B <u>1</u>, 4541 (1970).

⁷R. Evans, D. A. Greenwood, and P. Lloyd, Phys. Lett. 35A, 57 (1971).

⁸P. J. Cote, Solid State Commun. <u>18</u>, 1311 (1976). ⁹P. J. Cote, G. P. Capsimalis, and G. L. Salinger, in Proceedings of the Second International Conference on Amorphous Magnetism, Troy, New York, 1976 (Plenum, New York, to be published).

 $^{10}L.$ V. Meisel and P. J. Cote, Phys. Rev. B (to be published).

¹¹H.-J. Guntherodt, H.-V. Kunzi, M. Liard, M. Muller, R. Muller, and C. C. Tsuei, in Proceedings of the Second International Conference on Amorphous Magnetism, Troy, New York, 1976 (Plenum, New York, to be published).

¹²O. Drierach, R. Evans, H.-J. Guntherodt, and H.-V. Kunzi, J. Phys. F 2, 709 (1972).

¹³B. Boucher, J. Non-Cryst. Solids 7, 277 (1972).

¹⁴J. H. Mooij, Phys. Status Solidi (a) <u>17</u>, 521 (1972).
¹⁵B. E. Warren, X-Ray Diffraction (Addison-Wesley,

Reading, Mass., 1969). ¹⁶G. S. Cargill, J. Appl. Phys. <u>41</u>, 12 (1970).

¹⁷J. M. Ziman, *Principles of the Theory of Solids* (Cambridge Univ. Press, Cambridge, England, 1972), 2nd ed.

¹⁸G. Baym, Phys. Rev. 135, A1691 (1964).

¹⁹A. Guinier, X-Ray Diffraction (Freeman, San Francisco, Calif., 1963), p. 266, Eq. (8.22).

²⁰W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966), p. 145, Eq. (4:24). ²¹J. M. Ziman, *Electrons and Phonons* (Oxford Univ. Press, London, 1970).

Spin Coherence and the Stark Modulation Effect in the Excited State of F_A -Mo Centers in CaO

D. J. Gravesteijn, J. H. Scheijde, and M. Glasbeek

Laboratory for Physical Chemistry, University of Amsterdam, Amsterdam, the Netherlands

(Received 26 May 1977)

Optically detected electron-spin coherence effects in the photoexcited triplet state of a new defect, the F_A -Mo pair in CaO, are presented. They include a Stark-field-stimulated modulation of the Hahn-echo decay.

Spin alignment in emissive triplet states of defect centers in ionic solids is known to occur¹ and, therefore, the zero-field double-resonance techniques that have been so valuable in spin coherence studies of excitations in molecular solids² are expected to be applicable in colar centers too. Our experiments concern the lowest emissive S = 1 state of a new color center in CaO, the F_A -Mo pair. It will be shown that spin coherence in the phosphorescent state can be achieved and that by analogy to spin-echo experiments on paramagnetic systems in the ground state,³ a modulation of the optically detected echo-decay envelope can be induced by an electric field. As a result, the experiments illustrate that the method offers a powerful means of studying small electric field effects in excited non-Kramers states with the sensitivity of optical detection. Furthermore, the dynamical cause for the loss of phase coherence in the triplet spin ensemble is briefly considered. A pseudo-Jahn-Teller coupling between excited ${}^{3}A_{1}$ and ${}^{3}E$ states of the pair center has been invoked⁴ on the basis of optically detected magnetic-resonance data. It turns out that the decay factor for the envelope of of the spin-echo signals reported here can be satisfactorily related to the vibronic nature of the excited states.