PHYSICAL REVIEW B VOLUME 25, NUMBER 4 15 FEBRUARY 1982

Effect of pressure on electrical resistance of transition-metal-based alloys

P. J. Cote and L. V. Meisel

U. S. Army Armament Research and Development Command, Large Caliber Weapon Systems Laboratory,
Benet Weapons Laboratory, Watervliet, New York 12189

(Received 2 September 1981)

Measurements have been made of the effect of hydrostatic pressure to 8 kbar, at room temperature, on the electrical resistance of five transition-metal-based amorphous alloys and their crystalline counterparts. The resistivity dependence of the pressure coefficient of resistance of these alloys, and results from other alloys taken from the recent literature, exhibit a trend analogous to the Mooij correlation. The pressure coefficient of resistance for crystalline and disordered systems and these data are discussed in terms of the diffraction model of electrical transport. It is suggested that the observed correlation of the pressure coefficient of resistance with resistivity is a manifestation of the breakdown of standard theory for high-resistivity metals, i.e., another example of Mooij phenomena.

INTRODUCTION

One of the more interesting characteristics of high-resistivity amorphous and crystalline alloys is that they exhibit the Mooij correlation[1]: As the resistivities ρ increase to $\sim 150\ \mu\Omega\,\mathrm{cm}$, the temperature coefficients of resistivity (TCR) generally become very small or even negative. A related feature is that when ρ is $\sim 150\ \mu\Omega\,\mathrm{cm}$ it is difficult to increase its magnitude further; for example, in high-resistivity systems ρ is relatively insensitive to the structural changes which accompany phase changes[1]; in high-resistivity systems, unusually small changes in ρ occur upon melting[2] and during order-disorder transformations.[3] These characteristics are commonly termed "saturation" effects: When $\rho \gtrsim 150\ \mu\Omega\,\mathrm{cm}$, then $l \sim a$ (where l is the electron mean-free path and a the interatomic spacing) and cannot be decreased further. This constraint on l is known as the Ioffe-Regel limit.[4] Standard theory for electron transport no longer applies in this limit; for example, the Bloch-Gruneisen function[5] for crystalline alloys and the extended Ziman theory[6] for amorphous alloys are no longer valid.

Earlier, we gave strong evidence for failure of the Ziman theory for high-resistivity amorphous alloys[6,7]: It was shown that, according to this theory, the TCR of amorphous systems at low temperatures should be positive in sign and the resistivity ρ should increase in proportion to T^2, even when the high-temperature TCR is negative. This behavior is *not* observed when $\rho \gtrsim 150\ \mu\Omega\,\mathrm{cm}$; however, it is observed in lower-resistivity systems ($\rho < 100\ \mu\Omega\,\mathrm{cm}$), e.g., CuSn (Ref. 8) and AuSn (Ref. 9). We thus concluded that saturation effects dominate the temperature dependence of ρ in amorphous alloys for $\rho \gtrsim 150\ \mu\Omega\,\mathrm{cm}$.

In the present paper, we report on the effects of pressure on the resistivity of the amorphous and crystalline phases of five alloys. Besides attempting to learn more about the influence of pressure on transport in alloys, we were particularly interested in finding evidence for saturation effects in the pressure coefficients of resistance (PCR), which is equal to $d(\ln R)/dP\mid_T$, of high-resistivity alloys, analogous to the effects seen in the TCR. Amorphous alloys are convenient for this purpose since they generally have high resistivities and the transformations to lower-resistivity phases are easily obtained by annealing.

EXPERIMENTAL

The amorphous NiP and FeP samples were prepared by electrodeposition using baths described by Brenner[10] (NiP) and Logan[11] (FeP). Samples 2826*A* and *B*Ni2 were prepared by Allied Chemical Corp; the labels are their designations for alloys available under the trademark Metglas. Sample *B* was prepared by Dr. R. Maringer of Battelle Memorial Institute. Sample compositions are listed in Table I.

The crystallized samples used in this study were prepared by annealing the initially amorphous samples for approximately one hour near the crystallization temperatures. The FeP and *B*Ni2 samples crystallized in one stage. The NiP and Metglas 2826*A* crystallized in two stages: a metastable crystalline phase and then the stable crystalline phase. Sample *B* crystallized in three stages but only the first stage PCR was determined.

Sample resistances were measured using the standard four-probe technique. Sample leads were attached by spot welding or soldering. A Leeds and Northrop six-dial potentiometer was used for the voltage measurements. Pressures up to 8 kbar were obtained in a Bridgeman—Birch-type cell with a 50-50 mixture of pentane and isopentane as the pressure-transmitting medium.

At present, the only tractable model for describing electron transport in transition-metal systems is the Evans, Greenwood, and Lloyd[12] modification of the standard diffraction model. Recognizing its possible shortcomings,[13] we nevertheless employ this model because of its notable successes[14] and convenient form.

Incorporating the Evans, Greenwood, and Lloyd modification the diffraction model expression[15] for the electrical resistivity in atomic units (N.B. atomic unit of resistivity is $\hbar/\mathrm{Ry}=43.5\ \mu\Omega\,\mathrm{cm}$) is

$$\rho=\frac{24\pi^3}{\Omega_0 k_F^2 E_F}\sum_{ijlm}\alpha_{lm}^{ij} I_{lm}^{ij}\ , \tag{1}$$

where

$$\alpha_{lm}^{ij}\equiv(2l+1)(2m+1)\sin(\eta_l^i)\sin(\eta_m^j)\times e^{i(\eta_l^i-\eta_m^j)} \tag{2}$$

and

$$I_{lm}^{ij}\equiv\sqrt{c_i c_j}\int_0^1 dx\, x^3 P_l(1-2x^2)\times P_m(1-2x^2)S_{ij}^{\rho}(2k_F x)\ , \tag{3}$$

where the resistivity static partial-structure factor

$$S_{ij}^{\rho}(K)=\int_{-\infty}^{\infty} d\omega\frac{\hbar\omega}{k_B T}n\left[\frac{\hbar\omega}{k_B T}\right]S_{ij}(K,\omega)\ , \tag{4}$$

with $n(x)=(e^x-1)^{-1}$, and $S_{ij}(K,\omega)$ is the Van Hove dynamical partial structure factor. The other parameters in these expressions are as follows: Ω_0 is the atomic volume, k_F and E_F the Fermi wave vector and energy, η_l^i the l phase shift evaluated at the Fermi energy for the ith constituent, c_i the concentration of the ith constituent, $P_l(y)$ the lth Legendre polynomial, $\hbar$ is Planck's constant over 2π, k_B is Boltzmann's constant, and T is the absolute temperature.

The dynamical structure factor in Sham-Ziman approximation[16] is

$$S_{ij}(K,\omega)=a_{ij}(K)\delta(\omega)e^{-2W(K)}+\left[n\left[\frac{\hbar\omega}{k_B T}\right]+1\right]\sum_{q\lambda}\frac{\hbar K^2}{2M\omega}[a_{ij}(\vec{K}+\vec{q})\delta(\omega+\omega_{q\lambda})+a_{ij}(\vec{K}-\vec{q})\delta(\omega-\omega_{q\lambda})]\ , \tag{5}$$

where the geometrical partial-structure factor

$$a_{ij}(K)=\frac{1}{\sqrt{N_I N_J}}\sum_{IJ}\exp[i\vec{K}\cdot(\vec{R}_I-\vec{R}_J)]\ , \tag{6}$$

where the I sum in Eq. (6) runs over the position vectors $\vec{R}_I$ of the ith constituent ions and the J sum similarly for the jth constituent. The sum in Eq. (5) runs over the phonon wave numbers $\vec{q}$ and branches λ; M is the ionic mass. Polarization effects are ignored. The multiphonon terms cancel the Debye-Waller factor $e^{-2W(K)}$ in the one-phonon term in the dynamical structure factor in Sham-Ziman approximation. For convenience, we denote diagonal components of the partial-structure factors with one index, e.g., $S_i=S_{ii}$.

The geometrical structure factors reduce to sums of delta functions in the ordered-crystalline case and in the disordered cases (amorphous and disordered crystalline) they are continuous functions of the scattering vector $\vec{K}$.[17] (If we only include N processes, the diffraction model yields the Bloch-Gruneisen form for the resistivity.[17,5]) The ingredients necessary to compute the PCR are apparent in the above expressions. However, without detailed calculations the required derivatives are not generally available. We will, therefore, make the usual approximations for transition-metal-(TM) based alloys: *TM d phase shift dominant and* $S_{\mathrm{TM}}^{\rho}(2k_F)>>S_{\mathrm{TM}i}^{\rho}(2k_F)$ *for i not TM.* For disordered alloys, one has

$$\rho_d\approx\frac{30\pi^3}{\Omega_0 k_F^3 E_F}C_{\mathrm{TM}}S_{\mathrm{TM}}^{\rho}(2k_F)\sin^2(\eta_2^{\mathrm{TM}})\ . \tag{7a}$$

The corresponding expression for N processes in TM-based crystalline alloys for a Debye phonon spectrum is

$$\rho_N \approx \frac{25\pi^3}{\Omega_0 k_F^2 E_F}\left[\frac{2}{Z}\right]^{2/3} \alpha(2k_F)C_{\mathrm{TM}}\left[\frac{T}{\Theta}\right] J_5\left[\frac{\Theta}{T}\right] \times \sin^2(\eta_2^{\mathrm{TM}}) , \tag{7b}$$

where

$$\alpha(K) \equiv 3(\hbar K)^2/Mk_B\Theta ,$$

Z is the electron to atom ratio, Θ is the Debye temperature, and $J_5(X)$ is the Debye integral:

$$J_5(X) = \int_0^X dx\, x^5 n(x)[n(x)+1] . \tag{8}$$

We shall further simplify these expressions by giving the high-temperature limiting terms and by neglecting the inelastic parts of $S^{\ell}_{\mathrm{TM}}(2k_F)$ which can be shown to make negligible contributions to the PCR in disordered alloys. [One cannot invoke this approximation if the temperature coefficient of resistance (TCR) is of interest, since the phonon contributions to the TCR are comparable in magnitude to those contributed by the elastic term.[18]] Thus (for $T > \Theta$)

$$\rho_d \approx \frac{30\pi^3}{\Omega_0 k_F^2 E_F} C_{\mathrm{TM}} a_{\mathrm{TM}}(2k_F) \sin^2(\eta_2^{\mathrm{TM}}) \tag{9a}$$

and

$$\rho_N \approx \frac{25\pi^3}{\Omega_0 k_F^2 E_F} (4Z)^{-2/3} C_{\mathrm{TM}} \alpha(2k_F) \frac{T}{\Theta} \sin^2(\eta_2^{\mathrm{TM}}) \tag{9b}$$

for disordered and N-process crystalline cases, respectively.

We shall now present expressions for the PCR resulting from Eqs. (9). First we note that the experimentally accessible PCR is related to the theoretical quantity $\partial\ln\rho/\partial\ln V \,|_T$ in an isotropic material by

$$\left.\frac{\partial\ln R}{\partial P}\right|_T = \left.\frac{\partial\ln V}{\partial P}\right|_T \left.\frac{\partial\ln(\rho L/A)}{\partial\ln V}\right|_T = -K\left[\left.\frac{\partial\ln\rho}{\partial\ln V}\right|_T - \frac{1}{3}\right] , \tag{10}$$

where $K \equiv -\partial\ln V/\partial P \,|_T$ is the isothermal compressibility. Noting that the Grüneisen constant,

$$\gamma \equiv \left.\frac{-\partial\ln\Theta}{\partial\ln V}\right|_T , \tag{11a}$$

$$\left.\frac{\partial\ln k_F}{\partial\ln V}\right|_T \approx -\tfrac{1}{3} , \tag{11b}$$

and defining

$$m' \equiv \left.\frac{\partial\ln E_F}{\partial V}\right|_T , \tag{11c}$$

Eqs. (9) yield

$$\left.\frac{\partial\ln\rho_d}{\partial\ln V}\right|_T \approx -(m'+\tfrac{1}{3}) + 2\cot\eta_2^{\mathrm{TM}} \left.\frac{\partial\eta_2^{\mathrm{TM}}}{\partial\ln V}\right|_T \tag{12a}$$

and

$$\left.\frac{\partial\ln\rho_N}{\partial\ln V}\right|_T \approx -(m'+1) + 2\gamma + 2\cot\eta_2^{\mathrm{TM}} \left.\frac{\partial\eta_2^{\mathrm{TM}}}{\partial\ln V}\right|_T \tag{12b}$$

for disordered and crystalline (N processes) cases, respectively.

The term $\partial\ln a(2k_F)/\partial\ln V \,|_T$ is not included in Eq. (12a). This term is seen to be small in solids as follows: once the arrangement of ions is frozen-in, the effect of pressure is merely a uniform contraction of ionic spacings with no "rearrangements," which nearly exactly cancels the effect of the expansion of k_F with pressure. Equations (10)–(12) will provide the basis for the discussion of our room-temperature studies of the pressure dependence of the resistivity in a variety of TM-based disordered alloys and their crystalline counterparts.

RESULTS

The relative change in resistance $R(P)/R(0)-1$ is plotted against P for amorphous and crystallized NiP in Fig. 1. These data are typical of the alloys investigated except that all alloys studied did not form metastable crystalline phases. The amorphous phase has the smallest PCR and the largest ρ. The Ni_3P crystalline compound has the largest PCR and the smallest ρ. The intermediate phase, a disordered, metastable Ni_xP alloy,[19] has intermediate values of PCR and ρ. The change in resistance in the alloys studied is linear in P for the range of pressure ($0 \le P \le 8$ kbar) investigated.

Variation of the resistivity ρ of these alloys with temperature has been determined at one atmosphere.[15] Figure 2 shows the results for the NiP phases, whose pressure dependences are shown in

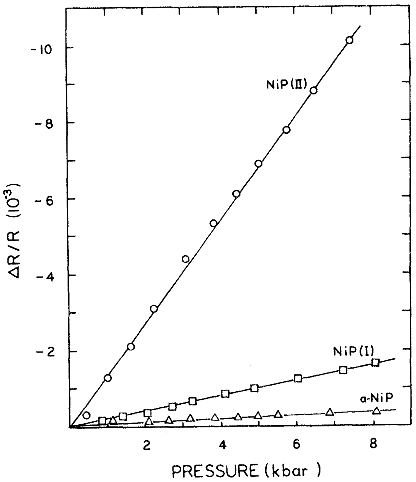

FIG. 1. Relative change in resistance with pressure for amorphous (a) and crystalline (I and II) NiP.

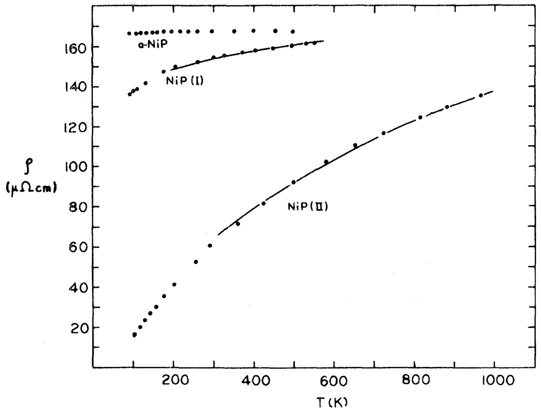

FIG. 2. The temperature dependence of the electrical resistivity of amorphous (a) and crystalline (I and II) NiP.

Fig. 1. The curves are of the type described by Mooij and strongly imply that standard transport theory fails to describe the temperature dependence of these high-resistivity alloys. (The position that Mooij phenomena implies failure of standard theory is not universally accepted. See, for example, Chakraborty and Allen.[20])

The PCR and ρ values at room temperature for the five alloys used in this study, in their amorphous and crystalline forms, are presented in Table I. The disordered phases have considerably larger ρ and significantly smaller PCR magnitudes than the corresponding crystalline phases in most cases. Moreover, the PCR and ρ values of these alloys, which differ widely in composition, suggest a general decreasing trend in the magnitude of the PCR with increasing ρ. In order to further investigate this trend, data for amorphous metals [$Pd_{82-x}V_xSi_{18}$ (Ref. 21), $Fe_{80}B_{20}$ (Ref. 22), $Fe_{78}Mo_2Bo_{20}$ (Ref. 22), $Fe_{40}Ni_{40}P_6B_{14}$ (Refs. 22 and 23), and $Be_{40}Ti_{50}Zr_{10}$ (Ref. 22)], from the recent literature, and data for related crystalline metals[24]

TABLE I. Resistivity and pressure coefficient of resistance of five alloys in their amorphous and crystalline phases.

Systems	Resistivity ($\mu\Omega$ cm)	Pressure coefficient (10^{-3} kbar^{-1})
NiP ($Ni_{77}P_{23}$)		
Amorphous	142	−0.044
Crystalline (I)	77	−0.25
Crystalline (II)	51	−1.74
FeP ($Fe_{78}P_{22}$)		
Amorphous	141	−0.58
Crystalline	60	−0.91
*B*Ni2 ($Ni_{69}B_{14}Si_8Cr_6Fe_4$)		
Amorphous	126	−0.12
Crystalline	51	−1.65
B ($Ni_{63}Cr_{12}Si_8Fe_4$)		
Amorphous	122	0
Crystalline	105	−0.22
2826*A* ($Fe_{32}Ni_{36}Cr_{14}P_6B_{12}$)		
Amorphous	144	−0.50
Crystalline (I)	138	−0.25
Crystalline (II)	94	+0.89

(pure Fe, Pd, and Ni, and the FeNi alloy series), are plotted in Fig. 3 along with our data.

Approximately equal numbers of points to the left and right of 120 $\mu\Omega$ cm are shown in Fig. 3. The points to the right of 120 $\mu\Omega$ cm fall into a relatively narrow range of PCR values (0 to -0.6 kbar^{-1}), while the points to the left of 120 $\mu\Omega$ cm span a range of values at least an order of magnitude larger. (The solid lines form an envelope for the data but have no theoretical basis.) Figure 3 suggests that the trend seen in Table I is general.

DISCUSSION

The trend in the PCR with ρ exhibited in Fig. 3 is quite striking since a plot based only upon the ordered-crystalline alloys would exhibit no trend and would cover a broad range of positive and negative values as seen in the left-hand part of Fig. 3. This suggests that the PCR values exhibit behavior which is analogous to that of the TCR values in the Mooij correlation: As stated earlier, the standard explanation for the Mooij correlation is that at $\rho \sim 150$ $\mu\Omega$ cm, the electron mean free path l is near the interatomic spacing a and cannot be decreased further; in other words, the Ioffe-Regel condition[4] applies. Another consequence of $l \sim a$ limit is that $\partial \ln\rho / \partial \ln V \sim 0$, so that the Ioffe-Regel condition provides a common explanation for the apparent anomalous effects in both the TCR and PCR of high-resistivity alloys. However, it is also possible that the effect may be a simple consequence of the disappearance of the Gruneisen term in the standard theory for disordered systems [Eq. (12a)]. We attempt to shed some light on these questions by considering some specific examples.

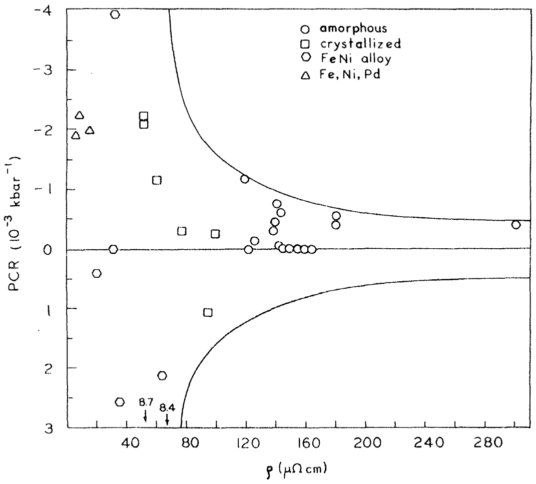

FIG. 3. The pressure coefficient of resistance PCR plotted against resistivity for data from Table I and Refs. 21–24. The solid lines represent the envelope suggested by the data.

Pure transition metals. Although naive considerations suggest that $d\eta_2/\partial \ln V\,|_T < 0$ (for example, a decrease in volume should energetically favor the more compact d orbitals as compared with sp orbitals), band-theory results give $\partial\eta_2/\partial \ln V\,|_T \approx 0$ with $\eta_2 \approx \pi Z_d/10$ in pure ordered-crystalline TM's.[25] Thus, this theory suggests that

$$\left.\frac{\partial \ln\rho}{\partial P}\right|_T \approx -2\gamma K$$

for pure-crystalline TM's. This result agrees well with the experimental findings in these metals.[5] (N.B. The theoretical ideas concerning η_2 above were used to explain dT_c/dP by Ratti, Evans, and Gyorffy[25]; T_c is the superconducting critical temperature in pure TM's.) The small value deduced from the band-theory work for $\partial\eta_2/\partial \ln V\,|_T$ is also consistent with the small values of K found[26] in TM's and suggests that pressurization does not easily alter the d-level occupancy. One expects $\partial\eta_2/\partial \ln V\,|_T \approx 0$ again for pure amorphous TM since the atomic volume of the amorphous phase is very near that for the crystalline phase and the compressibilities K are about the same[27]; thus a much smaller PCR is predicted for pure amorphous TM's. No data exist for such systems because the amorphous phase of pure metals can only be retained at very low temperatures.

Transition-metal alloys. Theoretical predictions for $\partial\eta_2/\partial \ln V\,|_T$ for TM alloys are not available. Thus, one must try to understand the behavior of these alloys by examining the available data alone. The most striking feature of these data is that in many crystalline TM alloys $|\,\partial \ln\rho/\partial P\,|_T\,|$ is considerably larger than $2\gamma K$.[24] Such data imply that $\partial\eta_2/\partial \ln V\,|_T$ values in crystalline TM alloys are large and of either sign, and suggest that the same condition should obtain in the related amorphous TM alloys. This indicates that standard theory fails to explain the trend seen in Fig. 3. and that this trend is therefore a further manifestation of Mooij phenomena.

Another approach to the TM alloys was taken by Lazarus.[21] He implicitly assumed that $\partial\eta_2/\partial \ln V\,|_T$ type contributions to the PCR should be small leading to the conclusion that his observed zero value for the PCR in the $Pd_{82-x}V_xSi_{18}$ was consistent with Ziman theory. Clearly, no firm conclusions can be drawn without better information on $\partial\eta_2/\partial \ln V|_T$ for TM and TM alloy systems.

Finally, note that if the trend seen in Fig. 3 is a manifestation of the breakdown of standard theory (the most likely case in our view), then the implication is that the elastic (structure scattering) component of ρ "saturates" at approximately the same value of ρ (i.e., 150 $\mu\Omega$ cm) as that for the inelastic (phonon-scattering) component. This follows from the fact that the elastic component contribution to the PCR is dominant in amorphous metals. The inelastic and elastic components of ρ contribute terms of the same order to the TCR; the Mooij correlation, which correlates the TCR with ρ can be explained by means of "saturation" of only the inelastic scattering component of ρ.[7]

---

[1] J. H. Mooij, Phys. Status Solidi A 17, 521 (1973).

[2] N. F. Mott, Philos. Mag. 26, 1249 (1972).

[3] L. W. Shacklette and W. S. Williams, Phys. Rev. B 7, 5041 (1973).

[4] A. F. Ioffe and A. R. Regel, Prog. Semicond. 4, 237 (1960).

[5] J. M. Ziman, *Electrons and Phonons* (Clardedon, Oxford, 1960).

[6] P. J. Cote and L. V. Meisel, *Glassy Metals I,* edited by H. -J. Guntherodt and H. Beck (Springer, Heidelberg, 1981), pp. 141–166.

[7] P. J. Cote and L. V. Meisel, Phys. Rev. Lett. 40, 1586 (1978). See also Ref. 18.

[8] D. Korn, W. Murer, and G. Zibold, Phys. Lett. 47A, 117 (1972).

[9] E. Blasberg, D. Korn, and H. Pfeifle, J. Phys. F 9, 1821 (1979).

[10] A. Brenner, D. E. Couch, and E. K. Williams, J. Res. Natl. Bur. Stand. 44, 109 (1950).

[11] J. Logan and M. F. Ashby, Acta Metall 22, 1074 (1974).

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

[13] See, for example, E. Esposito, H. Ehrenreich, and C. D. Gelatt, Jr., Phys. Rev. B 18, 3913 (1978) or H. N. Dunleavy and W. Jones, J. Phys. F 8, 1477 (1978).

[14] See, for example, R. Evans, G. D. Gaspari, and B. L. Gyorffy, J. Phys. F 3, 39 (1973); or R. Evans, B. L. Gyorffy, N. Szabo, and J. M. Ziman, in *Proceedings of the Second International Conference on Properties of Liquid Metals, Tokyo,* edited by S. Takeuchi (Taylor and Francis, London, 1973), pp. 319–331.

[15] P. J. Cote and L. V. Meisel, Phys. Rev. B 20, 3030 (1979), and references therein.

[16] L. J. Sham and J. M. Ziman, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York 1963), Vol. 15.

[17] G. Baym, Phys. Rev. 135, A1691 (1964).

[18] L. V. Meisel and P. J. Cote, Phys. Rev. B 17, 4652 (1978).

[19] E. Vafaei-Makshoos, E. L. Thomas, and L. E. Toth, Metall. Trans. A 9A, 1449 (1978).

[20] P. B. Allen and B. Chakraborty, Phys. Rev. B 23, 4815, (1981).

[21] D. Lazarus, Solid State Commun. 32, 175 (1979).

[22] R. W. Cochrane, J. O. Strom-Olsen, J. P. Rebouillat, and A. Blanchard, Solid State Commun. 35, 199 (1980).

[23] D. G. Ast and D. J. Krenitsky, Scr. Metall. 10, 247 (1976).

[24] P. W. Bridgman, *The Physics of High Pressure* (Bell, London, 1949); Proc. Am. Acad. Arts Sci. 81, 165 (1952).

[25] V. K. Ratti, R. Evans, and B. L. Gyorffy, J. Phys. F 4, 371 (1974); and, specifically, J. R. Anderson, D. A. Papaconstantopoulos, J. W. McCaffrey, and J. E. Schirber, Phys. Rev. B 7, 5115 (1973); D. A. Papaconstantopoulos, J. R. Anderson, and J. W. McCaffrey, *ibid.* 5, 1214 (1972); R. Evans, V. K. Ratti, and B. L. Gyorffy, J. Phys. F 3, L199 (1973).

[26] See, for example, C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1956), p. 99.

[27] J. J. Gilman (unpublished), technical report of the Materials Research Center, Allied Chemical Corp., as quoted in Ref. 23; see also C. P. Chou, L. H. Davis, and M. C. H. Narasimhan, Scr. Metall. 11, 417 (1977).