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Ultrasonic Measurement of the Temperature Dependence of the Nonlinearity Parameters of Copper*

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The temperature dependence of the nonlinearity parameters of copper single crystals has been measured in the range 77 to 300°K. (Nonlinearity parameters are combinations of third-order elastic constants.) These measurements were made from a quantitative determination of the second-harmonic distortion of pulsed MHz ultrasonic waves propagating in the three principal crystallographic directions. By maintaining a constant detector gap of about five microns with a pneumatically controlled variable-gap capacitive detector, it was possible to measure the nonlinearity parameters relative to their room-temperature values, which were determined by absolute calibration. Typically, the nonlinearity parameters change linearly with temperature by about ten percent. Over this temperature range, the measured values of the nonlinearity parameters are consistent with the assumption that the primary contributor to the third-order elastic constants is the closed-shell repulsive interaction of nearest-neighbor atoms.

I. INTRODUCTION

The recent increase in interest in the nonlinear behavior of crystalline solids has been stimulated in part by the possibility of measuring the third-order elastic constants, which characterize this nonlinear behavior. The third-order elastic constants can be determined from a measurement of the variation of the ultrasonic wave velocity with applied stress[1] or from a measurement of the finite-amplitude distortion of an initially sinusoidal ultrasonic wave.[2] We have chosen the latter technique since it can be readily adapted to measurement at cryogenic temperatures.[3]

For cubic crystals there are known relations among the elastic constants (of all orders) of the macroscopic elasticity theory and the interatomic coupling parameters of (microscopic) lattice theory.[4] With the availability of more and more information on higher-order elastic constants, a quantitative comparison between elasticity theory and the predictions of lattice dynamics will be feasible.

In the case of monovalent noble metals such as copper, the elastic constants can be determined theoretically at 0°K once the internal energy of the crystal is specified. One technique for specifying the energy is given by Wigner and Seitz.[5] It is divided into kinetic energy in the ground electronic state, Fermi energy of the electrons, potential energy between charges, Van der Waals energy of the ions, and exchange energy resulting from overlapping of closed electronic shells. The exchange energy should play an increasingly important role in determining the elastic constants as the order of the elastic constants increases, even though its contribution to the total lattice energy is not very great. In an adaptation of the technique of Wigner and Seitz, Hiki and Granato[6] separated the energy into two terms: the exchange energy between closed shells U_c, and the energy from all other sources U_e. As the atoms are displaced relative to each other, U_c should vary rapidly, while U_e should change slowly and monotonically. This difference between U_c and U_e is important to the determination of the elastic constants, and their temperature dependence, as can be seen from the following special case.

Consider a uniform dilatation of the crystal. The internal energy can be approximated by

$$U = A/r^n - B/r^m, \tag{1}$$

where r is the distance between any pair of adjacent atoms, and the integers n and m satisfy $n > m > 1$. The term A/r^n corresponds to U_c and $-B/r^m$ corresponds to U_e. The elastic constant of order p is obtained from p derivatives of U with respect to r. Thus, the greater the order of the elastic constant, the greater the effect of the (repulsive-force) term U_c, because $n > m$.

In considering the magnitudes of the third-order elastic constants, one can assume central forces and apply symmetry arguments to conclude that

$$\begin{aligned} C_{112} &= C_{166}, \\ C_{123} &= C_{456} = C_{144}. \end{aligned} \tag{2}$$

These relations are analogous to the Cauchy relations among the second-order elastic constants. Hiki and Granato[6] have considered the problem in more detail. Assuming central forces and that only the repulsive-force term U_c is important to the determination of the third-order elastic constants, they conclude that

$$\begin{aligned} C_{111} &= 2C_{112} = 2C_{166}, \\ C_{123} &= C_{456} = C_{144} = 0. \end{aligned} \tag{3}$$

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[6] Y. Hiki and A. V. Granato, Phys. Rev. **144**, 411 (1966).

TABLE I. K_2 and K_3 for [100], [110], and [111] directions.

Direction	K_2	K_3
[100]	C_{11}	C_{111}
[110]	$\frac{1}{2}(C_{11}+C_{12}+2C_{44})$	$\frac{1}{4}(C_{111}+3C_{112}+12C_{166})$
[111]	$\frac{1}{3}(C_{11}+2C_{12}+4C_{44})$	$(C_{111}+6C_{112}+12C_{144}+24C_{166})/9$ $+(2C_{123}+16C_{456})/9$

These relationships were derived under the assumption that the sample be at 0°K and that the zero-point energy be negligible. The effect of temperature is outlined in the Appendix, where only the "high-temperature limit" is considered.

For the second-order elastic constants of copper, Hiki and Granato[6] could compare their conclusions and experimental results with the experimental results of Overton and Gaffney.[7] For the third-order constants, however, only room-temperature data were available at that time.[8,9] These data tended to support the assumption that the third-order, and higher-order, constants are determined primarily by the exchange energy. Direct comparison between theory and experiment could not be made, however, until the low-temperature uniaxial stress measurements of the third-order elastic constants were made by Salama and Alers.[10] These results disagreed with the conclusions drawn from the theory of Hiki and Granato. The present measurements of the nonlinearity parameters (which are linear combinations of third-order elastic constants) help to clarify this situation for copper.

II. EXPERIMENTAL TECHNIQUE

When an ultrasonic wave propagates through a nonlinear medium, harmonics of the initially sinusoidal ultrasonic wave are generated.[11] Measurement of the absolute value of the amplitude of the second harmonic and of the fundamental gives sufficient information to calculate the magnitude of the coefficient of the first nonlinear term in the equation of motion.

A pure longitudinal wave propagating along the three principal directions in a cubic crystal is described by[7]

$$\rho\frac{\partial^2 U}{\partial t^2}=K_2\left(\frac{\partial^2 U}{\partial a^2}+3\frac{\partial U}{\partial a}\frac{\partial^2 U}{\partial a^2}\right)+K_3\frac{\partial U}{\partial a}\frac{\partial^2 U}{\partial a^2}, \tag{4}$$

where U is the particle displacement, ρ is the mass density in the unstrained state, a is the Lagrangian coordinate measured along the direction of propagation, and the quantities K_2 and K_3 are linear combinations of second- and third-order elastic constants, respectively. Values of K_2 and K_3 for the three principal directions are given in Table I. The growth of the second harmonic with propagation is predicted by the solution of Eq. (4), which can be written

$$U=A\,\sin(ka-\omega t)-\left(\frac{3K_2+K_3}{8K_2}\right)A^2k^2a \times\cos 2(ka-\omega t)+\cdots. \tag{5}$$

Measurement of the fundamental amplitude A and the second-harmonic amplitude gives sufficient information to calculate K_3 since the other quantities are known. Repetition of such measurements would in principle allow one to determine the temperature dependence of K_3; however, a relative measurement is more precise in the present experiment.

A. Apparatus

The basic system, which is electrically similar to the one used by Gauster and Breazeale,[12] is shown in Fig. 1. A pulsed sinusoidal ultrasonic wave is generated by a quartz transducer. This ultrasonic wave and its harmonics are detected by a capacitive detector which is an improved version of the one used by Gauster and Breazeale.[12] The 30-MHz and 60-MHz amplifiers are i.f. amplifiers which selectively amplify either the fundamental or the second-harmonic component. Since the present detector[13] is in a cryostat physically separated from the i.f. amplifiers, it proves to be advantageous to match the impedance of the transmission line to the 50-Ω input impedance of the i.f. amplifiers. This both reduces errors caused by impedance mismatch and eliminates the preamplifier used by Gauster and Breazeale.[12] To compensate for the effect of differential thermal expansion, this detector spacing is pneumatically adjusted between three and ten microns. By monitoring the capacitance with a bridge, the spacing can be held constant to ±0.1% as the temperature is changed. Since the characteristics of the transmission line used are observed to remain constant to within the accuracy of measurement over the temperature range 77–300°K, it is now possible to make measurement of the nonlinearity parameters relative to their room-

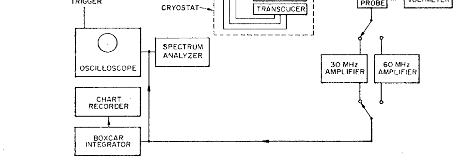

FIG. 1. Cryogenic measurement system.

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temperature values. The calibration apparatus shown in Fig. 1 can be used at room temperature to make an accurate calibration by a substitution technique. Measurements at lower temperatures can then be made relative to the room-temperature value, with an increase of precision since it is no longer necessary to calibrate at each temperature.

The display of the electrical signal on the oscilloscope is a standard technique; however, it proves convenient to be able to monitor the Fourier components of the received pulse with the spectrum analyzer as a means of deciding when the pulse is long enough and uniform enough to approximate the propagation characteristics of an infinite plane wave. The inclusion of the boxcar integrator to average out the effects of random noise results in an increase of sensitivity greater than a factor of 10.

B. Samples and Bonds

The copper single crystals used in the present experiment are three of the ones used by Gauster and Breazeale for measurements at room temperature.[14] They were grown by F. W. Young, Jr., Solid State Division, Oak Ridge National Laboratory, from American Smelting and Refining Co. 99.999% copper by a Bridgeman technique. One sample each of the three principal orientations was used. Dislocation effects were reduced by irradiation with fast neutrons.[15] The total dose was 10^{17} to 10^{18} neutrons/cm^2. Sample end faces were lapped optically flat and parallel to within approximately 10 sec of arc. Sample orientations checked by Laue backreflection x irradiation were accurate to better than 1 deg.

The only bond found satisfactory over the full temperature range 77–300°K was the adhesive from a cellulose tape. The tape is applied to the sample and warmed under water. The backing is then gently peeled off and the transducer applied. These bonds were found to be thin and fairly uniform if applied carefully.

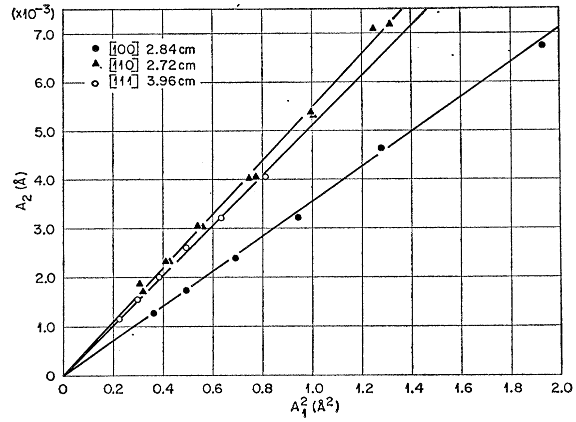

FIG. 2. Second-harmonic amplitude versus the square of the fundamental amplitude at 30 MHz in copper crystals.

TABLE II. Measured values of room temperature K_3 for [100], [110], and [111] directions in copper.

Direction	K_3 (10^{12} dyn/cm^2)
[100]	−13.9
[110]	−31.2
[111]	−25.7

C. Measurements

Low-temperature measurements are made in the following manner. The 30-MHz ultrasonic pulse and its second harmonic are amplified, detected, and recorded at room temperature for a particular setting of the circuit parameters. A calibration run is made. For other temperatures the circuit parameters are held constant. Thus, the system is controlled so that the output of either amplifier is given by

$$V_{\text{out}} = \text{const} \times A V_b , \tag{6}$$

where A is the amplitude of the ultrasonic wave component under consideration and V_b is the bias voltage of the detector. In going from a reference temperature T^R to a different temperature T it is convenient to hold the fundamental amplitude constant by suitably adjusting the drive voltage to the quartz transducer while keeping the detector bias constant. The change in the nonlinearity parameter is then determined from the change in second harmonic in going from T^R to T. The simplest way to determine this change is to adjust the bias voltage, while at T, so that for the second-harmonic signal

$$V_{2\text{out}}{}^T = V_{2\text{out}}{}^R , \tag{7}$$

where the superscript R refers to the reference temperature. Then the second-harmonic amplitude of the ultrasonic wave at temperature T is given by

$$A_2{}^T = A_2{}^R (V_b{}^R / V_b{}^T) . \tag{8}$$

Thus, $A_2{}^T$ can be measured relative to its value at T^R. By incorporating Eq. (8) into the second-harmonic amplitude

$$A_2 = A^2 k^2 a \left(\frac{3K_2 + K_3}{8K_2} \right) \tag{9}$$

expressed in Eq. (5), and taking into account other changes with temperature, one can write

$$\frac{K_3}{K_3{}^R} = \frac{K_2}{K_2{}^R} \left[1 + \frac{\beta}{1+\beta} \left(\kappa^2 \frac{V_b{}^R}{V_b} \frac{K_2}{K_2{}^R} - 1 \right) \right] , \tag{10}$$

where the superscript R indicates the value of the

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[14] W. B. Gauster and M. A. Breazeale, Phys. Rev. **168**, 655 (1968).

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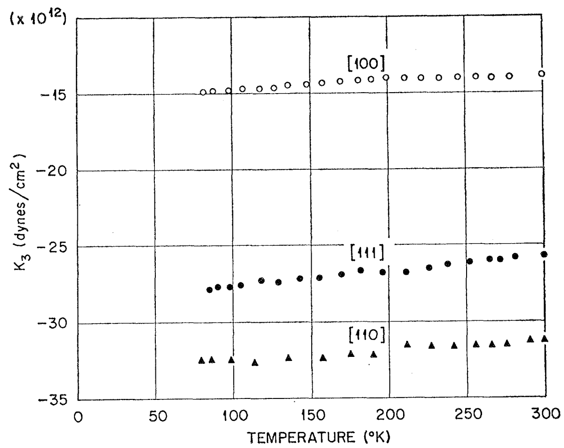

FIG. 3. Temperature dependence of the nonlinearity parameters of copper.

parameter at the reference temperature,

$$\beta=\frac{8}{3}\left[\frac{A_2}{A_1{}^2k^2a}\right]^R \quad \text{and} \quad \kappa=1+\alpha\Delta T,$$

α being the linear expansion coefficient. For the accuracy of this experiment $\kappa^2=1$, so the relative value of K_3 can be determined from

$$\frac{K_3}{K_3{}^R}=\frac{K_2}{K_2{}^R}\left[1+\frac{\beta}{1+\beta}\left(\frac{V_b{}^R}{V_b}\frac{K_2}{K_2{}^R}-1\right)\right]. \tag{11}$$

III. RESULTS

A. Room-Temperature Measurements

The room-temperature values of the nonlinearity parameters were measured to (1) provide a reference value for the relative temperature-dependence measurements and (2) check the reproducibility of measurements by this technique (since the results can be compared with those of Gauster and Breazeale[14]). The reproducibility check is desirable since (1) a modified calibration scheme was used in which a switching arrangement in the sample holder allowed calibration to be made with the sample in place, (2) measurements were made without the preamplifier used previously, and (3) the amplitude of the fundamental is reduced by a factor of 10 below that used previously. A plot of the room-temperature value of the second harmonic amplitude as a function of the square of the fundamental amplitude is given in Fig. 2. The slopes of these curves give the nonlinearity parameters directly when the values of K_2 are known. These nonlinearity parameters are shown in Table II. The values of K_2 used for calculation of these values of K_3 were determined from the results of Overton and Gaffney.[7] These K_3 agree well with those of Gauster and Breazeale.[14] The greatest difference, which occurs for the [110] values, is only 4%. This is well within the previously stated maximum probable error of 10%.

TABLE III. Values of the integers n and m in Eq. (12) for [100], [110], and [111] directions.

Direction	n	m
[100]	1	1
[110]	17	8
[111]	16	9

B. Low-Temperature Measurements

The measured temperature dependence of the nonlinearity parameters is shown in Fig. 3. All measurements were made relative to the room-temperature values given in Table II. Again, the K_2 values were calculated from the results of Overton and Gaffney.[7] The scatter of the data points, which is very small in this case, is an indication of the precision of the measurement. The error of these relative measurements is estimated to be between 2 and 5%.

TABLE IV. Comparison of nonlinearity parameters with the theoretically determined relation $K_3=(n/m)C_{111}$ (units of 10^{12} dyn/cm^2).

Room temperature				77°K				0°K[a]			
	[110] direction $n/m=17/8$				[110] direction $n/m=17/8$				[110] direction $n/m=17/8$		
Expt.[b]	K_3	$(n/m)C_{111}$	% diff.	Expt.[b]	K_3	$(n/m)C_{111}$	% diff.	Expt.[b]	K_3	$(n/m)C_{111}$	% diff.
(a)	−31.2	−29.5	5.6	(a)	−32.5	−32.3	0.6	(a)	33.2	32.1	3.4
(b)	−32.5	−30.4	6.7								
(c)	−32.7	−27.0	19								
(d)	−29.5	−31.9	7.8	(d)	−35.2	−41.4	16.2	(d)	−35.3	−42.5	18.5
	[111] direction $n/m=16/9$				[111] direction $n/m=16/9$				[111] direction $n/m=16/9$		
(a)	−25.7	−24.7	4.0	(a)	−27.8	−26.7	4.0	(a)	28.7	26.9	6.5
(b)	−25.9	−25.4	2.0								
(c)	−29.5	−22.6	26								
(d)	−27.2	−26.7	1.9	(d)	−32.0	−34.7	8.1	(d)	−32.5	−35.6	9.1

[a] Straight-line extrapolation of data to 0°K.
[b] (a) Present experiment; (b) Gauster and Breazeale, Ref. 14; (c) Hiki and Granato, Ref. 6; (d) Salama and Alers, Ref. 10.

IV. DISCUSSION

The degree to which the present results agree with the relations among the third-order elastic constants predicted from Eq. (3) can be demonstrated by observing that, according to Eq. (3), all the K_3's are expressible as

$$K_3=(n/m)C_{111}\,, \tag{12}$$

where n and m are integers. The values of these integers for the three principal directions are given in Table III. Using these values of n and m, one can determine the extent to which the measured values of K_3 agree with those predicted under the assumption of central forces and nearest-neighbor interactions [Eq. (12)]. The results are shown in Table IV. The agreement between measured and predicted values is within experimental uncertainty over the entire temperature range for the present experiment. There is better agreement as the temperature is decreased. The values at 0°K are the result of a straight-line extrapolation. In the absence of data at this temperature this appears to be a reasonable procedure, since the effect of the zero-point energy on the magnitude of the third-order elastic constants is assumed to be small. Note that the difference between K_3 and $(n/m)C_{111}$ remains small. It is to be noted that the values of K_3 and $(n/m)C_{111}$ calculated from the data of Salama and Alers[10] differ more than the present results, especially at the lower temperatures. Further data are required to determine the best value of these combinations of third-order elastic constants. It can, however, be pointed out at this time that the present data are consistent with the third-order elastic constants for copper calculated from first principles by considering only nearest-neighbor interactions and assuming a central-force model.

APPENDIX: TEMPERATURE DEPENDENCE OF ELASTIC CONSTANTS

According to the method developed by Leibfried and Hahn[16] the temperature variation of the elastic constants is theoretically determined from calculations based on the free energy. The free energy is chosen because its independent variables, temperature and strain, more simply characterize the state of the crystal than do entropy and strain, which specify the internal energy. Ultrasonic wave propagation in a solid is, however, an adiabatic process, whereas according to the definition of the elastic constants used here[17] the free energy gives the isothermal constants. The difference between the two can be calculated,[18] though, and is small enough compared with present experimental inaccuracies to be neglected.

The free energy per unit cell of a crystal can be written

$$f=V_0\Phi+f^{\text{vib}}\,, \tag{A1}$$

where f^{vib} is the vibrational contribution, V_0 is the unit cell volume, and Φ is the potential energy per unit volume of the crystal at temperature T when all the atoms are situated in their mean positions.[19] Φ is an explicit function only of the lattice parameter and the strain. It is indirectly dependent on T through thermal expansion.[20]

At a reference temperature T_0 let the lattice parameter be r_0. For cubic crystals the expansion of the crystal with temperature change is isotropic. If this change is assumed to be linear, the change with temperature of the third-order constants defined from f can be calculated according to the following scheme. First, the change arising from the potential energy term Φ can be calculated directly:

$$C_{\alpha\beta\gamma}{}^{\Phi}(r)-C_{\alpha\beta\gamma}{}^{\Phi}(r_0)=K(T-T_0)\frac{\partial}{\partial r}C_{\alpha\beta\gamma}{}^{\Phi}(r)\bigg|_{r=r_0}\,, \tag{A2}$$

where K is a constant. Second, because the phonon density of states depends on the strain (nonlinear effect), f^{vib} can be expanded in terms of the strain components η_{ij}

$$f_3{}^{\text{vib}}=f_{ijklmn}\eta_{ij}\eta_{kl}\eta_{mn}\,, \tag{A3}$$

where repeated indices are to be summed over. If the indices of f_{ijklmn} are contracted according to convention to give $f_{\alpha\beta\gamma}$, then $f_{\alpha\beta\gamma}/V_0$ by definition is the vibrational part of the third-order elastic constant. Thus, one can write the change in $C_{\alpha\beta\gamma}{}^{\text{vib}}$ in going from (T_0,r_0) to (T,r) as

$$C_{\alpha\beta\gamma}{}^{\text{vib}}(T,r)-C_{\alpha\beta\gamma}{}^{\text{vib}}(T_0,r_0)=\frac{1}{V_0}[f_{\alpha\beta\gamma}(T,r)-f_{\alpha\beta\gamma}(T_0,r_0)]\,. \tag{A4}$$

Combining (A2) and (A4) gives the total change in the third-order constant

$$C_{\alpha\beta\gamma}(T,r)-C_{\alpha\beta\gamma}(T_0r_0)=K(T-T_0)\frac{\partial}{\partial r}C_{\alpha\beta\gamma}{}^{\Phi}(r)\bigg|_{r=r_0}+\frac{1}{V_0}[f_{\alpha\beta\gamma}(T,r)-f_{\alpha\beta\gamma}(T_0,r_0)]\,. \tag{A5}$$

Ghate[20] has shown that in the high-temperature limit

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(above approximately one-fourth the Debye temperature) $f_{\alpha\beta\gamma}$ (which depends on the interatomic potential) is linear in temperature. If one defines

$$g_{\alpha\beta\gamma}=\frac{f_{\alpha\beta\gamma}(T,r)-f_{\alpha\beta\gamma}(T_0,r_0)}{T-T_0}, \qquad (\text{A6})$$

one can obtain a temperature coefficient for the third-order elastic constants

$$C_{\alpha\beta\gamma}(T,r)=C_{\alpha\beta\gamma}(T_0r_0)+A_{\alpha\beta\gamma}\times(T-T_0), \qquad (\text{A7})$$

where

$$A_{\alpha\beta\gamma}=K\frac{\partial}{\partial r}C_{\alpha\beta\gamma}{}^{\Phi}(r)\bigg|_{r=r_0}+\frac{g_{\alpha\beta\gamma}}{V_0}. \qquad (\text{A8})$$

In summary, $C_{\alpha\beta\gamma}{}^{\Phi}$ and $g_{\alpha\beta\gamma}$ are independent of temperature by definition. Thus, Eq. (A7) predicts that the third-order constants are linear functions of temperature (above approximately $\frac{1}{4}\Theta$). The slope of a plot of the constants as a function of temperature is the coefficient $A_{\alpha\beta\gamma}$. Future detailed comparison of measured values of this coefficient and the theoretical value as determined from the calculations indicated in Eq. (A7) could conceivably yield important information about interatomic forces.

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Paramagnetic *Ni*Cu Alloys: Electronic Density of States in the Coherent-Potential Approximation*

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The coherent-potential approximation (CPA) is extended to study general band shapes and systems having orbital degeneracy. This permits its application to realistic systems, in particular the *Ni*Cu alloys. The effects of alloying on a highly asymmetric model density of states characteristic of some of the features of the density of states in fcc transition metals are considered in detail. A model Hamiltonian for paramagnetic *Ni*Cu is constructed using a basis of orthogonalized plane waves and tight-binding *d* functions. Orbital degeneracy and hybridization are treated as in paramagnetic Ni. Effects of alloying are assumed to be restricted to the diagonal elemensts of the *d*-*d* block. The model is applicable to the Ni-rich alloys, as is the approximation used to obtain simple solutions of the full CPA equations. The results are consistent with recent photoemission data on *Ni*Cu, and with the "minimum polarity" hypothesis used by Lang and Ehrenreich. They are incompatible with the rigid-band model because the scattering potential of the random alloy is strong compared to the peak widths. Rather than a rigid shift of the density of states, the calculated concentration dependence shows that the main peaks remain stationary while changing magnitude and shape. Decomposition of the total density of states into Ni and Cu contributions confirms that, for the expected position of the Fermi level, the *d* holes are located primarily on Ni sites.

I. INTRODUCTION

In this paper the electronic density of states and other one-electron properties of the *Ni*Cu alloys above their Curie temperatures are studied within the coherent-potential approximation (CPA).[1] The work reported is the first attempt to apply the CPA to a real alloy system.

The CPA, introduced by Soven[1] for the study of electrons in a substitutional alloy, and earlier by Taylor[2] for the formally similar phonon case, has been studied in detail in several recent papers.[3-5]

The CPA results from the self-consistent solution of the usual multiple-scattering version[6] of the Schrödinger equation, within a single-site approximation,[4] in which the properties of all sites but one are averaged over, and that one is treated exactly. It has therefore been found useful in the description of short-ranged scattering in the alloy. The principal advantage of the CPA over other simple approximations results from its self-consistency; the CPA extrapolates away from the limits of low concentration and weak scattering in a physically reasonable way. Effects due to details of the possible local surroundings of a site, are of course averaged over in this approximation. However, we are not interested, in the calculations to be reported, in such refinements as "tails"[7] of localized states.

The idealized model treated in VKE based on a nondegenerate tight-binding band is far removed from a real alloy, but *Ni*Cu proves to be a good candidate for treatment by an alloy theory not very much more

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