constitutive equations exactly and computed the very complex expressions for ξ_x and ξ_y numerically. However, we have found that ξ_x and ξ_v change dramatically when seemingly justified approximations are introduced. The only approximation we have made is the constitutive equations themselves, since they only approximately describe what happens in a real semimetal.

[10]S. Rodriquez, Phys. Rev. **130**, 1778 (1963).

[11]See also R. A. Gordon, Ph.D. thesis (Brown University, 1972) (unpublished), where this equivalence was also noted. It should also be pointed out that Quinn in Ref. 2 applied the formalism of Kontorovich to bismuth. Since the present paper utilizes the collision-drag theory, a mere comparison of our results and those of Quinn would not be meaningful. Instead, one would have to decide which of the two approaches is the correct one in the case of compensated semimetals. In the present paper we did not intend to answer this fundamental question.

[12]See for instance A. L. Jain and S. H. Koenig, Phys. Rev. **127**, 442 (1962).

[13]In Ref. 2 Quinn used $m_e = 0.01m$ and $m_h = 0.2m$, instead of our $m_e = 0.1m$ and $m_h = 0.2m$. For these values one has $\omega_{ce}\tau_e \gg 1 \gg \omega_{ch}\tau_h$, a condition necessary for the propagation of weakly damped helicons. We have also computed ξ_y for $m_e = 0.01m$, and $m_h = 0.2m$, however the good agreement with the experimental data was lost and ξ_y vs B_0 still did not show a maximum. In addition we have plotted $|\xi_+| = |\xi_x + i\xi_y|$ vs B_0 (as is done in Ref. 2). This quantity also does not exibit a maximum, the reason being that the initial rise of ξ_y with magnetic field is much steeper than the initial decrease of ξ_x.

[14]We would like to emphasize here that, although the local magnetoconductivity tensors in the quantum regime are identical to those in the classical regime, we anticipate a significant difference in the collision-drag forces in the two regimes.

PHYSICAL REVIEW B VOLUME 8, NUMBER 2 15 JULY 1973

Higher-Order Elastic Constants of Copper and Nickel Whiskers*

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(Received 8 January 1973)

The deviations from Hooke's law in whiskers in elastic uniaxial tension experiments are related to higher-order elastic constants. We derive this relation for an arbitrary crystal system and whisker-tension-axis orientation to fourth order in the strain. The deviations from Hooke's law are experimentally found for copper and nickel whiskers. The results are compared with other methods of determining third-order elastic constants.

I. INTRODUCTION

The higher-order elastic constants are of interest in determining the mechanical properties of materials. They can be measured ultrasonically, either by the effect of pressure on the velocity of ultrasound or by the generation of harmonics during the passage of ultrasound through a crystal.[1-3] They can also be measured in a "static" test, by observing the deviations from Hooke's law in elastic materials.[4] So far this latter method has been used only in fused-quartz fibers and in "whiskers." It is this static method that is treated in this paper.

In static tests the accuracy is usually much less than in the ultrasonic methods, but higher strains are available, so that semiquantitative estimates of fourth-order elastic constants can be made. There is also some question about the effects of dislocations and other defects on the results of ultrasonic tests.[5] In these static tests it is doubtful that dislocations can play a large role, since the large uniaxial stress (of the order of 10^8 N/m^2) would move any dislocations out of the crystal.

Section II treats the theory of these static experiments, extending the theory of Murnaghan[6] to arbitrary crystal symmetry and arbitrary crystallographic orientation of the fiber axis and to third power in the applied stress. A particularly simple form is derived for both the quadratic and cubic terms of a generalized Hooke's law for fibers. Section III treats a modification of the experimental procedure of Powell and Skove[4] and Sec. IV reports new results for copper and nickel whiskers.

II. THEORY

We assume that all the work required to deform the fiber is stored in the body as elastic energy, and that none of this energy is dissipated. If we expand the stored energy function Φ in terms of the Lagrangian strain $\vec{\vec{\eta}}$, $\Phi(\vec{\vec{\eta}})$ can be written as

$$\Phi(\vec{\vec{\eta}}) = \Phi_0 + \left(\frac{\partial\Phi}{\partial\eta}\right)_{\vec{\vec{\eta}}} + \frac{1}{2}\left(\frac{\partial^2\Phi}{\partial\eta^2}\right)_{\vec{\vec{\eta}}^2} + \frac{1}{6}\left(\frac{\partial^3\Phi}{\partial\eta^3}\right)_{\vec{\vec{\eta}}^3} + \cdots , \tag{1}$$

where

$$\left(\frac{\partial\Phi}{\partial\eta}\right)_{ij} = \left(\frac{\partial\Phi}{\partial\eta_{ij}}\right)_{\vec{\vec{\eta}}=0} ,$$

$$\left(\frac{\partial^2\Phi}{\partial\eta^2}\right)_{ijkl} = \left(\frac{\partial\Phi^2}{\partial\eta_{ij}\,\partial\eta_{kl}}\right)_{\vec{\vec{\eta}}=0} ,$$

$$(\vec{\vec{\eta}}^2)_{ijkl} = \eta_{ij}\eta_{kl} ,$$

etc., and

$$\eta_{ij}=\frac{1}{2}\sum_k\left[\left(\frac{\partial x_k}{\partial a_i}\right)\left(\frac{\partial x_k}{\partial a_j}\right)-\delta_{ij}\right] .$$

At equilibrium, zero strain, and room temperature we take $\Phi_0=0$. Equilibrium implies $(\partial\Phi/\partial\vec{\vec{\eta}})_{\vec{\vec{\eta}}=0}=0$.

Murnaghan,[6] using the principal of virtual work, has derived the relationship between the stress per unit *initial* area $\vec{\vec{T}}$ and the strain $\vec{\vec{\eta}}$:

$$T_{ij}=\sum_k J_{ik}\left(\frac{\partial\Phi}{\partial\eta_{kj}}\right) , \tag{2}$$

where J_{ik} is a component of the Jacobian matrix between the initial and final coordinates of a point in the body. The derivatives of Φ at zero strain are

$$C^x_{ijkl\ldots}=\left(\frac{\partial\Phi^n}{\partial\eta_{ij}\,\partial\eta_{kl\ldots}}\right)_x ,$$

where n is the order of the derivative and x is the thermodynamic coordinate held constant in the measurement of $C^x_{ijkl\ldots}$, which in these experiments is the temperature T. Thus $\Phi=\rho_0 F$, where ρ_0 is the initial density and F the Helmholtz free energy per unit mass. It is convenient to use the contracted index notation in which $11\to 1$, $22\to 2$, $33\to 3$, $23\to 4$, $13\to 5$, $12\to 6$. In this convention,

$$\begin{aligned}&\eta_{ij}=\tfrac{1}{2}(1+\delta_{ij})\eta_I ,\\ &C^T_{IJ\ldots}=\rho_0\left(\frac{\partial^n\Phi}{\partial\eta_I\,\partial\eta_J\cdots}\right)_T ,\end{aligned} \tag{3}$$

where δ_{ij} is the Kronecker δ. Tensor coordinates will be denoted by lower-case indices, and coordinates in the contracted notation will be denoted by upper-case indices. We will have occasion to use the compliances

$$S_{IJ}=(C^{-1})_{IJ} .$$

We assume the uniaxial tension to be applied along the x_3 ($\langle 001\rangle$) axis of the sample, and the relation between initial coordinates of a point in the body (a_i) to be related to the final coordinates (x_i) by an expansion in terms of the applied force per unit initial area (P) by

$$\begin{aligned}x_1&=(1+\sigma_1P+\sigma_{11}P^2+\sigma_{111}P^3+\cdots)a_1\\&\quad+(1+\sigma_6P+\sigma_{66}P^2+\sigma_{666}P+\cdots)a_2,\\ x_2&=(1+\sigma_2P+\sigma_{22}P^2+\sigma_{222}P^3+\cdots)a_2\\&\quad+(1+\sigma_6P+\sigma_{66}P^2+\sigma_{666}P^3+\cdots)a_1,\\ x_3&=(1+\sigma_3P+\sigma_{33}P^2+\sigma_{333}P^3+\cdots)a_3\\&\quad+(1+\sigma_5P+\sigma_{55}P^2+\sigma_{555}P^3+\cdots)a_1\\&\quad+(1+\sigma_4P+\sigma_{44}P^2+\sigma_{444}P^3+\cdots)a_2,\end{aligned} \tag{4}$$

where the σ_I's are expansion coefficients which will be related to the second-, third-, and fourth-order elastic constants. Using this coordinate transformation, the elements of the strain tensor are, to third order in P,

$$\eta_I=\sigma_IP+\sigma_{II}P^2+\sigma_{III}P^3+\eta_I'P^2+\eta_I''P^3,$$

where the η_I' and η_I'' have been separated for convenience and are listed in Table I. Using (1) and (3) and the expansion for η (the Einstein summation convention is used in this paper; whenever terms with repeated lower-case alphabetical indices appear they are summed from 1 to 3; whenever terms with repeated upper-case alphabetical indices appear they are summed from 1 to 6),

$$\Phi=\tfrac{1}{2}C_{IJ}\eta_I\eta_J+\tfrac{1}{6}C_{IJK}\eta_I\eta_J\eta_K+\tfrac{1}{24}C_{IJKL}\eta_I\eta_J\eta_K\eta_L ,$$

and

$$\begin{aligned}\frac{\partial\Phi}{\partial\eta_I}&=C_{IJ}\eta_J+\tfrac{1}{2}\{C_{IJK}\sigma_JP[\sigma_KP+2(\eta_K'+\sigma_{KK}P^2)]\}\\&\quad+\tfrac{1}{6}C_{IJKL}\sigma_J\sigma_K\sigma_LP^3,\end{aligned}$$

to third order in P.

For uniform uniaxial tension in the $\langle 001\rangle$ direction, the stress per unit initial area is given by $T_I=P\delta_{3I}$. To first order, the relation between stress and strain (2) becomes

$$P\delta_{3I}=C_{IJ}\sigma_JP .$$

Multiplying through by $(C^{-1})_{KI}$ summing on I,

$$(C^{-1})_{K3}=\sigma_K,$$

which gives the obvious identification

$$\sigma_K=S_{3K} .$$

To second order, we then have

$$P\sigma_{3I}=(\sigma_3P^2+P)\sigma_{3I}+C_{IJ}(\sigma_{JJ}P^2+\eta_J')+\tfrac{1}{2}C_{IJK}\sigma_J\sigma_KP^2 .$$

Multiplying through by $(C^{-1})_{KI}$, and summing, we find

$$\sigma_{LL}=-S_{3L}S_{33}-\eta_v'P^{-2}-\tfrac{1}{2}C_{IJK}S_{LI}S_{3J}S_{3K} .$$

For experimental reasons, a nonlinearity parameter δ is defined:

$$\delta_{001}\equiv\sigma_{33}(S_{33})^{-2}=-\tfrac{3}{2}-\tfrac{1}{2}(S_{33})^{-2}C_{IJK}S_{3I}S_{3J}S_{3K},$$

where the subscript 001 indicates the tension is

TABLE I. Elements of strain matrix.

$\eta_1'=\frac{1}{2}(\sigma_1^2+\sigma_6^2)+2\sigma_5^2$	$\eta_1''=\sigma_1\sigma_{11}+\sigma_6\sigma_{66}+4\sigma_5\sigma_{55}$
$\eta_2'=\frac{1}{2}(\sigma_2^2+\sigma_6^2)+2\sigma_4^2$	$\eta_2''=\sigma_2\sigma_{22}+\sigma_6\sigma_{66}+4\sigma_4\sigma_{44}$
$\eta_3'=\frac{1}{2}\sigma_3^2$	$\eta_3''=\sigma_3\sigma_{33}$
$\eta_4'=\sigma_3\sigma_4$	$\eta_4''=\sigma_3\sigma_{44}+\sigma_4\sigma_{33}$
$\eta_5'=\sigma_3\sigma_5$	$\eta_5''=\sigma_3\sigma_{55}+\sigma_5\sigma_{33}$
$\eta_6'=\frac{1}{2}\sigma_6(\sigma_1+\sigma_2)+2\sigma_4\sigma_5$	$\eta_6''=\frac{1}{2}\sigma_6(\sigma_{11}+\sigma_{22})+\frac{1}{2}\sigma_{66}(\sigma_1+\sigma_2)+2(\sigma_4\sigma_{55}+\sigma_5\sigma_{44})$

applied to the sample along the ⟨001⟩ crystallographic direction. It is possible to rotate this result to allow for cases when tension is applied along other crystallographic directions. For a crystal whose long axis has a direction cosine with respect to the crystallographic axes a_{3i}, the nonlinearity parameter δ'_{001} is given by

$$\delta'_{001} = -\tfrac{3}{2} - \tfrac{1}{2}(S'_{33})^{-2} C_{IJK}\,\alpha_I \alpha_J \alpha_K ,$$

where

$$\alpha_K = a_{3i} a_{3j} S_{ij,K} ,$$

$$S_{IK} = (2 - \delta_{ij}) S_{ij,K}$$

(not summed on i, j)

$$S'_{33} = a_{3i} a_{3j} a_{3k} a_{3l} S_{ijkl} .$$

To third order in P, the relation between stress and strain is

$$P\delta_{3I} + (\sigma_{33}P^3 - \sigma_3^2 P^3 + P)\,\delta_{3I} + C_{IJ}\sigma_{JJJ}P^3 + \eta''_J + C_{IJK}\sigma_J P(\eta'_K + P^2\sigma_{KK}) + \tfrac{1}{6} C_{IJKL}\sigma_J\sigma_K\sigma_L P^3 .$$

As before, we multiply by $(C^{-1})_{MI}$ and sum, getting

$$\sigma_{MMM} = (S_{33}^2 - \sigma_{33}) S_{M3} - P^{-3}\eta''_M - C_{IJK} S_{MI} S_{3J}(P^{-2}\eta'_K + \sigma_{KK}) - \tfrac{1}{6} C_{IJKL} S_{MI} S_{3J} S_{3K} S_{3L} .$$

It is again convenient to define a nonlinearity parameter ζ for a sample whose axis lies along the ⟨001⟩ direction. This ζ is a combination of the second-, third-, and fourth-order elastic constants, whereas δ is a combination of the second- and third-order constants:

$$\zeta_{001} \equiv \sigma_{333}(S_{33})^{-3} = -2(1 + 2\delta_{001}) + \tfrac{1}{2}(S_{33})^{-3} C_{IJK} S_{3I} S_{3J} B_K - \tfrac{1}{6}(S_{33})^{-3} C_{IJKL} S_{3I} S_{3J} S_{3K} S_{3L} ,$$

where

$$B_K = C_{LMN} S_{3L} S_{3M} S_{KN} .$$

As before, for other crystallographic directions, ζ'_{001} is found by rotating axes to be

$$\zeta'_{001} = -2(1 + 2\delta_{001}) + \tfrac{1}{2}(S'_{33})^{-3} C_{IJK}\alpha_I\alpha_J\beta_K - \tfrac{1}{6}(S'_{33})^{-3} C_{IJKL}\alpha_I\alpha_J\alpha_K\alpha_L ,$$

$$\beta_K = C_{MNP}\alpha_M\alpha_N S_{KP} .$$

In tensile experiments it is the extension (ϵ), the change in length of the whisker divided by the length of the whisker, in the direction of the applied force that is determined experimentally. If the force is applied in the ⟨001⟩ direction, ϵ_3 is given by

$$\epsilon_3 = (x_3 - a_3)/a_3 .$$

Along the x_3 axis $a_1 = a_2 = 0$. Thus from (4)

$$\epsilon_3 = \sigma_3 P + \sigma_{33} P^2 + \sigma_{333} P^3 .$$

It is simpler to write ϵ_3 in terms of E_3, Young's modulus for the ⟨001⟩ direction:

$$E_3 = S_{33}^{-1} = \sigma_3^{-1} ,$$

$$\epsilon_3 = (P/E_3) + \delta_{001}(P/E_3)^2 + \zeta_{001}(P/E_3)^2 ;$$

or in an arbitrary direction,

$$\epsilon_3 = (P/E') + \delta'_{001}(P/E')^2 + \zeta'_{001}(P/E')^3 , \qquad (5)$$

where E', ζ'_{001}, ζ_{001} are calculated as before.

These equations have been derived for second order in the special cases of isotropic symmetry by Murnaghan,[6] and of cubic symmetry in the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions by Seegar and Buck.[7] Table II gives expressions for δ and ζ in these directions for the special case of cubic symmetry. These results are somewhat simpler than those of Seegar and Buck and of course are extended to fourth order in the case of ζ.

III. EXPERIMENTAL TECHNIQUE

The method used to determine δ and ζ in these experiments is a modification of the technique of Powell and Skove[4] in which a small low-frequency oscillatory stress is applied in addition to a large stress. The response of the sample to both the static and the oscillatory forces is monitored and those data are then related to the point-wise derivative of the stress-strain curve.

A diagram of the apparatus is shown in Fig. 1. It is a modification of the tensile machine of Brenner.[8] The static force was applied by a large electromagnet acting on two ceramic magnets and the small oscillatory force by a separate smaller electromagnet acting on the same magnets. Two permanent magnets were used to help cancel nonlinearities in the relation between the magnet current and the resulting force. For the large electromagnet these nonlinearities were less than 0.1% and they were less than 0.01% for the smaller electromagnet.

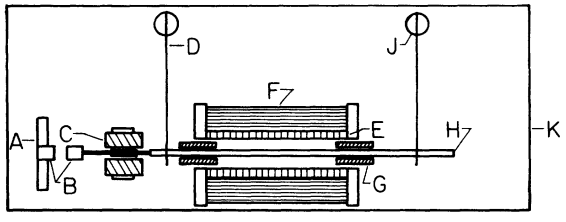

FIG. 1. Top-section view of apparatus: A, mounting block; B, whisker mount; C, differential transformer; D, leaf spring; E, oscillating electromagnet; F, constant electromagnet; G, ceramic magnet; H, quartz rod; J, spring support; K, quartz base plate.

TABLE II. The parameters δ and ζ for special orientations with cubic symmetry.

$$\delta_{001}=\delta_{\text{Isotropic}}=-\tfrac{3}{2}-S_{11}[C_{111}(X^3+\tfrac{1}{2})+3C_{112}(X^3+X^2+X)+3C_{123}X^2],$$

$$\delta_{011}=-\tfrac{3}{2}-\tfrac{1}{2}F^{-2}[C_{111}(Y^3+4S_{12}^3)+3C_{112}(Y^3+2S_{12}Y^2+4S_{12}^2Y)+6C_{123}S_{12}Y^2+3C_{144}S_{12}S_{44}^2+3C_{166}S_{44}^2)],$$

$$\delta_{111}=-\tfrac{3}{2}-\tfrac{1}{2}G^{-2}[(C_{111}+6C_{112}+2C_{123})Z^3+3(C_{144}+2C_{166})S_{44}^2+2C_{456}S_{44}^3],$$

$$\zeta_{001}=\zeta_{\text{Isotropic}}=-2(1+2\delta_{001})+S_{11}^{-1}\{C_{111}(\tfrac{1}{2}B_1+X^2B_2)+C_{112}[(X^2+2X)B_1+(3X^2+2X+1)B_2]$$
$$+C_{123}(X^2B_1+2XB_2)\}-S_{11}[\tfrac{1}{3}C_{1111}(X^4+\tfrac{1}{2})+\tfrac{4}{3}C_{112}(X^4+X^3+X)+C_{1122}(X^4+2X^2)+2C_{1123}(2X^3+X^2)],$$

$$\zeta_{101}=-2(1+2\delta_{101})+4F^{-3}\{C_{111}(\tfrac{1}{2}Y^2\beta_1+S_{12}^2\beta_3)+C_{112}[(\tfrac{3}{2}Y^2+2S_{12}Y+2S_{12}^2)\beta_1+(\tfrac{1}{2}Y^2+2S_{12}Y)\beta_3]$$
$$+C_{123}(2S_{12}Y\beta_1+\tfrac{1}{2}Y^2\beta_3)+C_{144}(\tfrac{1}{4}S_{44}^2\beta_3+S_{12}S_{44}\beta_5)+C_{166}(\tfrac{1}{2}S_{44}^2\beta_1+S_{44}Y\beta_5)\}$$
$$-\tfrac{4}{3}F^{-3}[C_{1111}(\tfrac{1}{8}Y^4+S_{12}^4)+C_{1112}(\tfrac{1}{2}Y^4+S_{12}Y^3+4S_{12}{}^3Y)+3C_{1122}(\tfrac{1}{8}Y^4+S_{12}^2Y^2)+3C_{1123}(S_{12}Y^3+S_{12}^2Y^2)$$
$$+\tfrac{3}{2}C_{1144}S_{12}^2S_{44}^2+3C_{1244}S_{12}S_{44}^2Y+\tfrac{3}{4}(C_{1166}+C_{1266})S_{44}^2Y^2+\tfrac{1}{16}C_{4444}S_{44}^4],$$

$$\zeta_{111}=-2(1+2\delta_{111})+\tfrac{9}{2}G^{-3}[(C_{111}+6C_{112}+2C_{123})Z^2\beta_2+(C_{144}+2C_{166})(S_{44}^2\beta_2+2S_{44}Z\beta_4)+2C_{456}S_{44}^2\beta_4]$$
$$+\tfrac{1}{6}G^{-3}[(C_{1111}+8C_{1112}+6C_{1122}+12C_{1123})Z^4+6(C_{1144}+2C_{1166}+4C_{1244}+2C_{1266})S_{44}^2Z^2+(C_{4444}+6C_{4466})S_{44}^4+24C_{1456}S_{44}^3Z],$$

where

$$X=S_{12}/S_{11},\quad Y=S_{11}+S_{12},\quad Z=S_{11}+2S_{12},\quad F=Y+\tfrac{1}{2}S_{44},$$

$$G=Z+S_{44},\quad B_1=-S_{11}^2(2\delta_{001}+3),\quad B_2=S_{11}^2[(C_{111}+2C_{123})(X^3+X^2+X)+C_{112}(5X^3+9X^2+3X+1)],$$

$$\beta_1=C_{111}(\tfrac{1}{4}Y^3+S_{12}^3)+\tfrac{3}{4}C_{112}(Y^3+2S_{12}Y^2+4S_{12}^2Y)+\tfrac{3}{2}C_{123}S_{12}Y^2+\tfrac{1}{4}C_{144}S_{12}S_{44}^2+\tfrac{1}{4}C_{166}S_{44}^2Y,$$

$$\beta_2=\tfrac{1}{9}(C_{111}+6C_{112}+2C_{123})Z^3+\tfrac{1}{9}(C_{144}+2C_{166})S_{44}^2Z,$$

$$\beta_3=C_{111}(\tfrac{1}{2}S_{12}Y^2+S_{12}^2Y-S_{12}^3)+C_{112}(\tfrac{1}{2}Y^3+3S_{12}Y^2+2S_{12}^3)+\tfrac{1}{2}C_{123}(Y^3-S_{12}Y^2+4S_{12}^2Y)+\tfrac{1}{4}C_{144}S_{44}^2(Y-S_{12})$$

$$\tfrac{9}{2}\beta_4=(C_{144}+2C_{166})S_{44}^2Z+C_{456}S_{44}^2,$$

$$\beta_5=C_{144}S_{12}S_{44}^2+C_{166}S_{44}^2Y$$

The transducer for the displacement of the rod (and hence the extension of the whisker) was a differential transformer. The output of the differential transformer was linear in displacement over the range of an experiment to better than 0.01%. The steady displacement was measured with a differential voltmeter and the oscillatory displacement with a lock-in amplifier whose output drove the smaller electromagnet. In no case was the oscillatory force more than 5% of the maximum steady force.

The displacements used in the experiment were small, and extensive thermal and mechanical shielding was necessary. Wherever possible fused quartz was used in the construction of the puller and during measurements the apparatus was enclosed in a styrofoam box. The whole apparatus was mounted from the ceiling, forming a pendulum whose period was about 3 sec.

The puller is essentially a driven harmonic oscillator and its response χ can be described by

$$\chi=K_M\cos(\omega t+\phi)$$
$$=\left[m^2\left(\frac{K_W+K_A}{m}-\omega^2\right)^2+\omega^2R^2\right]^{1/2}\cos(\omega t+\phi). \tag{6}$$

K_W and K_A are the spring constants of the whisker and the apparatus, respectively, ω is the frequency (rad/sec) of the driving force, R is the damping constant, m is the mass of the pulling-rod assembly, K_M is the measured spring constant of the sample-puller system, t is the time, and ϕ is the phase. The term K_M is proportional to the output of the lock-in amplifier. From Eq. (6)

$$K_W=(K_M^2-\omega^2R^2)^{1/2}+m\omega^2-K_A. \tag{7}$$

If K_W is to be measured accurately it is imperative that R and ω be small enough so that the term ω^2R^2 can be neglected. R was found to be less than 20 g/sec. Equation (7) indicates that there is an optimum value for ω for which

$$m\omega^2-K_A=0.$$

Thus the optimum ω is the resonant frequency of the apparatus when no whisker is present. For the present apparatus, the moving mass was 12 g and the resonant frequency about 4 Hz ($\omega\approx 25$ rad/sec). At this frequency ω^2R^2 is indeed negligible with respect to K_M^2 and $K_W=K_M$.

The Cu whiskers were grown in porcelain boats by hydrogen reduction of Cu halides in the manner described by Brenner.[9] X-ray analyses showed that only whiskers whose growth axes were in the ⟨001⟩ direction were produced from CuBr. Both ⟨011⟩ and ⟨001⟩ whiskers in about equal numbers were produced from CuCl, and ⟨111⟩ and ⟨001⟩ whiskers in about equal numbers were produced from CuI. This dependence of the growth axes on

the source material has also been reported by Powell and Skove.[4] Most of the Cu whiskers used in these experiments were grown from the reagent-grade Cu halide. Those whiskers designated as pure, however, were grown from the high-purity (99.999%) Cu halide obtained from Johnson, Matthey, and Co., Ltd., London, England. It is unlikely that the whiskers grown from the high-purity material were much purer, however, since residual-resistivity ratios ($R_{300\,K}/R_{4.2\,K} \approx 70$) were independent of source material.

In addition to the nominally pure Cu whiskers, several doped samples were studied. The Ag-doped whiskers were grown from CuI to which 0.5-mole% AgI had been added. Zn-doped samples were grown from CuBr to which small pieces of metallic Zn had been added. The doped samples were grown in the same manner as the undoped samples.

The Ni whiskers used for this study were also produced by the halide-reduction technique, in the manner described by Bailon.[10] These whiskers were grown in ceramic boats which had been baked out in an attempt to remove volatile impurities. Reagent-grade $NiBr_2$ was used for the growth of Ni samples and only ⟨001⟩ whiskers were found. After growth all the samples were stored in an evacuated desiccator to retard oxidation and contamination.

The whiskers were held in the pulling apparatus with diphenyl carbizide which was melted around the whisker. All whiskers were checked for glue-joint slippage by applying an extension of about 0.5% for about 15 min. Several samples were held at 1% extension for 12 h with no change in the results before and after the long-term stress.

If y represents the output of the lock-in amplifier, then $y \propto d\epsilon/d(P/E)$ or $y \propto 1/K_M$. From (5),

$$y \propto 1 + 2\delta'(P/E') + 3\zeta'(P/E')^2.$$

If y_0 represents the lock-in amplifier output when $P = 0$, it is possible to define a dimensionless parameter M such that

$$M = (y - y_0)/y_0 = 2\delta'(P/E') + 3\zeta'(P/E')^2 .$$

This definition is advantageous since the constant of proportionality between y and K_M is not precisely known, since the whisker cross section is not well known. The only problem that now remains is to relate this result to experimental quantities and to determine y_0.

A least-squares fit of the data was made to the function

$$y = C_1 + C_2 I + C_3 I^2, \tag{8}$$

where I is $i - i_0$, i is the instantaneous current in the large electromagnet, i_0 is the current in this magnet at which the sample is just tight (i.e., at $P = 0$.), y is the instantaneous output of the lock-in amplifier, and C_1, C_2, and C_3 are the fitting parameters determined by the least-squares analysis. It can be shown that

$$y_0 = C_1,$$

$$M = (y - C_1)/C_1,$$

$$\delta = (C_2/C_1) L_0 K_W/2\gamma ,$$

and

$$\zeta = (C_3/C_1)(L_0 K_W)^2/3\gamma^2 ,$$

where $K_W = K_M - K_A$, L_0 is the initial unstretched gauge length of the sample, γ is the response of the differential transformer $\Delta L/\Delta V$, and all the other terms have been previously defined. K_M can be determined from the slope of the force-elongation curve which was taken separately.

The largest uncertainty in the results came from L_0, the sample gauge length measurement and was about 3%. This was due to the difficulty in judging exactly where the glue contact began.

In order to judge the effect of still higher-order elastic constants, a plot of the relation

$$M/I = (y - C_1)/C_1 I = (C_2/C_1) + (C_3/C_1) I$$

was made. The intercept and slope are related to δ and ζ, respectively, and any effect of higher-order constants will show up as a deviation from a straight line. No significant deviations were found, as illustrated in Fig. 2.

IV. RESULTS

The data for each whisker are given in Table III. The uncertainties in δ and ζ are mainly due to the standard deviations to the least-squares fit to (8). The scatter in the data as well as the apparent

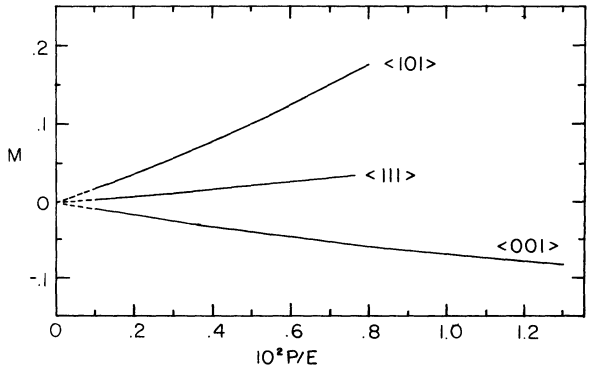

FIG. 2. Plot of the meter reading M (proportional to the slope of the stress-strain curve) divided by the magnet current I (proportional to the applied stress) vs I for a copper whisker. The intercept is related to the third-order elastic constants, the slope to the fourth-order elastic constants, and the linearity of the plot shows that the effect of higher-order constants is negligible.

TABLE III. Values of δ and ζ for each sample.

δ	ζ	ϵ_{max} (%)	Source
A. Copper ⟨001⟩			
-3.5 ± 0.2	27 ± 11	0.76	I[a]
-4.2 ± 0.4	29 ± 21	0.61	I
-4.2 ± 0.3	71 ± 15	1.20	Cl
-4.3 ± 0.2	55 ± 5	1.66	Cl
-4.3 ± 0.7	75 ± 7	1.33	Cl
-4.4 ± 0.3	66 ± 14	1.20	Cl
-4.5 ± 0.2	67 ± 7	1.26	Br[a]
-4.6 ± 0.2	86 ± 10	0.97	Br[a]
-4.9 ± 0.2	89 ± 11	0.82	Br[a]
-5.0 ± 0.5	90 ± 28	0.85	I
-5.1 ± 0.4	128 ± 16	1.07	Cl
-3.9 ± 0.2	27 ± 4	1.88	CuZn
B. Copper ⟨101⟩			
8.3 ± 0.4	182 ± 22	0.8	Cl
9.2 ± 0.6	193 ± 62	0.6	Cl
10.3 ± 0.8	192 ± 73	0.5	Cl
C. Copper ⟨111⟩			
0.9 ± 0.1	101 ± 14	0.66	I
1.4 ± 0.4	95 ± 36	0.70	I
2.2 ± 0.3	41 ± 36	0.54	I[a]
2.6 ± 0.3	4 ± 17	0.56	I
2.7 ± 0.3	-5 ± 8	0.79	I
3.9 ± 0.3	5 ± 20	0.56	I
0.8 ± 0.2	14 ± 4	0.76	CuAg
1.2 ± 0.1	85 ± 13	0.81	CuZn
1.8 ± 0.1	23 ± 5	0.91	CuZn
D. Nickel ⟨001⟩			
-2.3 ± 0.3	11 ± 7	1.3	Br
-2.4 ± 0.2	36 ± 8	1.3	Br
-3.2 ± 0.3	46 ± 10	1.5	Br
-3.7 ± 0.4	142 ± 28	0.5	Br
-4.1 ± 0.6	43 ± 30	0.9	Br

[a]Denotes high-purity halide used in growth.

relationship between the magnitudes of δ and ζ may be due to the presence of impurities in the samples. To test this hypothesis several doped samples were studied. From Table III it is seen that the magnitude of δ for doped samples tends to be smaller than that for the undoped samples. It is also seen that ζ may be influenced by the presence of doping agents. It does not seem that this explains all of the scatter, however.

It is possible to calculate δ and ζ using the values of the second-, third-, and fourth-order elastic coefficients measured or calculated by others. It turns out that δ is relatively sensitive to small variations in the second- and third-order elastic coefficients. A 1% change in the values of S_{IJ}^T and C_{IJ}^T of Hiki and Granato[2] causes changes of 4, 3, and 10% in the calculated values of δ_{001}, δ_{011}, and δ_{111}, respectively. Salama[11] studied the elastic constants of Cu containing 9-at.% Ni and measured a change of about 5% in the values of both the second- and third-order elastic constants (C_{IJ}^S and C_{IJK}^M). Although the amounts of impurities and doping agents in the present samples are unknown, it appears that the nonlinearity parameters may be appreciably affected by the relatively small impurity concentrations of these whiskers.

TABLE IV. Predicted values of δ and ζ.

δ_{001}	δ_{101}	δ_{111}	ζ_{001}	ζ_{101}	ζ_{111}	Ref.
A. Copper						
-4.4 ± 0.2	8.9 ± 0.7	2.1 ± 0.7	66 ± 25	184 ± 25	20 ± 10	Present
-3.3 ± 1.3	4.8	2.1	···	···	···	a
-4.6 ± 0.2	10.7 ± 0.1	3.8 ± 0.9	70	···	···	b
-2.2 ± 0.3	7.2 ± 0.1	2.7 ± 0.3	35	···	···	c
-6.9	···	···	122	···	···	d
B. Nickel						
-2.8 ± 0.6	···	···	30 ± 20	···	···	Present
-0.7 ± 0.5	···	···	19	···	···	c
-6.6	···	···	119	···	···	d

[a]Powell and Skove (Ref. 4)

[b]Using C_{IJ}^T and C_{IJK}^T of Hiki and Granato (Ref. 2) with the theoretical values of C_{IJKl}^T of Rose (see Ref. d) to predict ζ_{001}.

[c]Using C_{IJ}^T and C_{IJK}^T of Salama (Ref. 11) with the theoretical values of C_{IJKl}^T of Rose (see Ref. d) to predict ζ_{001}.

[d]Using the theoretical values of M. F. Rose [Phys. Status Solidi 17, K199 (1966)].

Figure 3 is a plot of M vs P/E for Cu using the mean values for δ and ζ determined by the present experiments. It was found that ⟨001⟩ and ⟨111⟩ whiskers generally failed at lower stresses than ⟨110⟩. The mean values of δ and ζ are given in Table IV.

Values of δ and ζ were also calculated using the values of the second-, third-, and fourth-order elastic coefficients determined or calculated by other researchers. The results of these calculations are also given in Table IV. The uncertainties in these values of other workers were obtained by using the extreme values of the third-order elastic constants (C_{IJK}^T) given by the individual re-

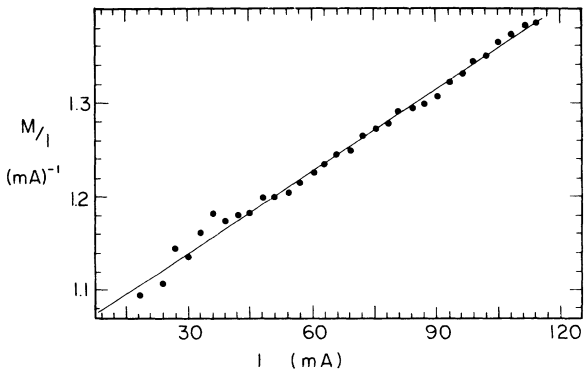

FIG. 3. Plot of the mean data for the three orientations of copper whiskers. The meter reading M is proportional to the slope of the stress-strain curve, and P/E is the applied stress divided by Young's modulus in the direction of the whisker.

TABLE V. Constants needed in conversions.

Constant	Ni	Source	Cu	Source
T	300 K	•••	300 K	•••
ρ_0	8.90 g/cm^3	a	8.92 g/cm^3	a
α	1.68×10^{-5} K^{-1}	b	1.27×10^{-5} K^{-1}	b
$(\partial\alpha/\partial T)_P$	1.2×10^{-8} K^{-2}	c	1.1×10^{-8} K^{-2}	c
C_p	3.85×10^{6} erg/g K	b	4.44×10^{6} erg g K	b
$(\partial C_p/\partial T)_p$	1.4×10^{3} erg/g K^2	c	4.5×10^{3} erg/g K^2	c
$(\partial S_{11}/\partial T)_p$	6.38×10^{-16} cm^2/dyn K	d	3.06×10^{-16} cm^2/dyn K	e
$(\partial S_{12}/\partial T)_p$	-2.99×10^{-16} cm^2/dyn K	d	-1.44×10^{-16} cm^2/dyn K	e
$(\partial S_{44}/\partial T)_p$	5.07×10^{-16} cm^2/dyn K	d	2.35×10^{-16} cm^2/dyn K	e

[a] *Handbook of Chemistry and Physics*, 48th ed., (Chemical Rubber Co., Cleveland, Ohio, 1967), pp. B-108, B-123.

[b] *American Institute of Physics Handbook*, 2nd ed. (McGraw-Hill, New York, 1963), pp. 4–66, 4–67.

[c] Calculated from data in Ref. b.

[d] Calculated from data of W. C. Overton, Jr. and J. Gaffney [Phys. Rev. 98, 969 (1955)].

[e] Calculated from data of G. A. Alers, J. R. Neighbours, and H. Sato [J. Phys. Chem. Solids 13, 40 (1960)].

searchers. No uncertainties were given for the second-order elastic moduli (S^T_{IJ}) and none were assigned. Since the present experiments determined the isothermal nonlinearity parameters, it was necessary to convert the adiabatic and mixed coefficients to the isothermal ones in comparing the present experiments with the results of others.

Thurston has given a general relationship between the adiabatic and the isothermal second-order elastic constants. Powell and Skove[12] have given a similar general expression relating the mixed to the isothermal third-order elastic constants. In contradiction to a statement made by Powell and Skove, no term in their expression is negligibly small for Cu or Ni. Table V contains a list of the constants required in converting the adiabatic and the mixed elastic coefficients to the isothermal coefficients for Cu and Ni. Table VI contains a list of the isothermal pressure derivatives of the second-order elastic constants for Cu and Ni as measured by others.

The data for Ni whiskers are also given in Table V. The uncertainties in δ and ζ were calculated in the manner as for Cu. The experiments were performed prior to those carried out with Cu whiskers, and used the same apparatus as that used by Powell and Skove.[4] This apparatus was not as insensitive to thermal and mechanical influences as the apparatus described above and it did not sensitively determine the point at which the sample became tight. For these reasons, it is felt that the data taken on Ni whiskers may be neither as accurate nor as precise as that taken on Cu whiskers. The results given in Table IV for Ni were calculated in the same manner as for Cu whiskers.

Barsch and Chang[13] have given expressions relating the isothermal pressure derivatives of the three second-order elastic constants and to the third-order elastic constants. These equations together with those for three δ's form a set of six linearly independent equations relating to six third-order isothermal elastic constants for cubic materials to known quantities. Thus it is possible to determine these six elastic constants without using any of the ultrasonic results that utilized uniaxial stress. Table VII contains a list of the isothermal third-order elastic constants for Cu and Ni calculated in this manner. The uncertainties in the third-order constants were obtained by using the extreme values given by the individual researchers. No uncertainties were stated for the isothermal pressure derivatives of the second-order elastic constants. The authors' estimate of $\pm 2\%$ was assigned. No uncertainties were stated for the second-order elastic coefficients and none were assigned. Table VII also includes the isothermal third-order elastic constants for Cu and Ni converted from the mixed values given by other researchers.

In deriving the relations relating ultrasonic changes with pressure and the third-order elastic constants[7] both Thurston and Brugger[1] and Barsch and Chang[13] have apparently assumed that C^M_{IJK}

TABLE VI. Pressure derivatives of the adiabatic second-order elastic constants of Cu and Ni.

$(\partial C_{11}/\partial P)_T$	$(\partial C_{12}/\partial P)_T$	$(\partial C_{44}/\partial P)_T$	Source
A. Copper			
5.94	5.19	2.63	Ref. 2
5.92	5.02	2.36	Ref. 11
6.36	5.20	2.35	a
4.67	3.53	0.85	b
B. Nickel			
6.03	4.87	2.38	Ref. 11

[a] W. B. Daniels and C. S. Smith, Phys. Rev. 111, 713 (1958).

[b] D. Lazarus, Phys. Rev. 76, 545 (1949).

TABLE VII. Isothermal third-order elastic constants.

C^T_{111}		C^T_{112}		C^T_{123}		C^T_{144}		C^T_{166}		C^T_{456}		Ref.
A. Isothermal constants for Cu in units of 10^{12} cm^2/dyn												
−12.4	± 0.3	−8.2	± 0.2	−1.1	± 0.02	−1.0	± 0.4	−7.0	± 0.4	0.70	± 0.9	a
−12.7	± 0.1	−8.2	± 0.2	−0.72	± 0.02	−0.69	± 0.5	−6.7	± 0.3	0.4	± 0.6	b
−13.7	± 0.1	−8.6	± 0.2	−0.65	± 0.02	−0.95	± 0.5	−6.6	± 0.3	0.4	± 0.6	c
−11.7	± 0.1	−6.5	± 0.2	1.54	± 0.02	1.4	± 0.4	−4.8	± 0.3	−1.3	± 0.7	d
−12.8	± 0.2	−8.2	± 0.1	−0.56	± 0.18	−0.05	± 0.09	−7.82	± 0.05	−0.95	± 0.9	e
−14.0	± 0.2	−7.8	± 0.1	−1.9	± 0.2	−1.4	± 0.2	−6.5	± 0.2	−0.2	± 0.1	f
−12.99		−8.11		−1.69		0.87		−7.96		0.70		g
−10.40		−7.70		0.92		...		...		...		h
B. Isothermal constants for Ni in units of 10^{12} cm^2/dyn												
−18.3	± 0.7	−11.5	± 0.5	−0.2	± 0.5	...		...		...		b
−20.4	± 0.4	−10.3	± 0.3	−2.1	± 0.5	−1.4	± 0.6	−9.2	± 0.3	−0.7	± 0.3	f
−10.40		−7.70		0.92		...		...		...		h

[a]Present and Hiki and Granato (Ref. 2).
[b]Present and Salama (Ref. 11).
[c]Present and Daniels and Smith (Ref. a, Table VI).
[d]Present and Lazarus (Ref. b, Table VI).
[e]Converted from data of Hiki and Granato (Ref. 2).
[f]Converted from data of Salama (Ref. 11).
[g]Powell and Skove (Ref. 4) and Granato (Ref. 2).
[h]Theoretical values of Rose (Ref. d, Table IV).

is symmetric with respect to the interchange of any indices, or that

$$C^M_{IJK} = C^M_{IKJ} = C^M_{JKI} = C^M_{JIK} = C^M_{KIJ} = C^M_{KJI} \quad . \tag{9}$$

This is not quite true, and the small differences between the C^M_{IJK} terms can often be calculated from the relation between C^S_{IJK} and C^M_{IJK} given by Brugger. In most cases the difference between the C^M_{IJK} terms are small enough to be neglected. Since only six mixed third-order constants have been reported by other researchers, it is necessary to assume the validity of (9) in order to calculate the isothermal third-order elastic constants from the results of the present experiments.

From Table VII it is seen that there is some disagreement in the reported values of the third-order elastic constants. It is known that the motion of dislocations is an important factor in studying the elastic constants of bulk samples. This is especially true for soft materials such as Cu. It has been found that if bulk samples are bombarded with neutrons, the damage caused by irradiation is sufficient to prevent dislocation motion. Gerlich[5] has studied LiF and measured changes in the second-order elastic constants when the integrated neutron flux exceeded $10^{17}\, n/\text{cm}^2$. Since the researchers who employed radiation damage used dosages of about this order of magnitude, it seems possible that their determinations of the third-order elastic may be affected by this effect. The results of the present work are in closest agreement with those of Hiki and Granato,[2] who used a prestressing technique to prevent dislocation motion.

The isothermal constants were not calculated from the adiabatic constants given by Gauster,[3] but it is apparent that his results are in very poor agreement with the results of the present work.

The equations for ζ_1, ζ_2, and ζ_3 given in Tables V–VII, respectively, form a set of three linearly independent equations in the 11 fourth-order isothermal elastic constants for cubit symmetry. The uncertainties in the third-order elastic constants preclude saying very much about the individual fourth-order constants, except that their magnitudes are about 10^{14} dyn/cm^2, as expected theoretically.

Conclusions:

Copper: We find good agreement with the third-order elastic constants measured by Hiki and Granato, fair agreement with those measured by Salama, and poor agreement with those measured by Gauster. It is possible that the disagreement with Gauster and Salama is due to the effects of radiation damage on the elastic constants. The fourth-order elastic constants are in order-of-magnitude agreement with the theoretical prediction of Rose.

Nickel: We find fair agreement with the results of Salama for the third-order elastic constants and order-of-magnitude agreement with the theoretical predictions for the fourth-order elastic constants.

*Work supported in part by the National Science Foundation and the U.S. Air Force Office of Scientific Research.

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[1]R. N. Thurston and K. Brugger, Phys. Rev. **133**, A1604 (1964).
[2]Yosio Hiki and A. V. Granato, Phys. Rev. **144**, 411 (1966).
[3]W. B. Gauster and M. A. Breazeale, Phys. Rev. **168**, 655 (1968).

[4]B. E. Powell and M. J. Skove, Phys. Rev. **174**, 977 (1968).
[5]D. Gerlich, J. Holder, and A. V. Granato, Phys. Rev. **181**, 1220 (1969).
[6]F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (Dover, New York, 1967), p. 115.
[7]A. Seeger and O. Buck, Z. Naturforsch. A **15**, 1056 (1960).
[8]S. S. Brenner, J. Appl. Phys. **27**, 1484 (1956).
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PHYSICAL REVIEW B VOLUME 8, NUMBER 2 15 JULY 1973

Electronic Polarizabilities of Very Small Metallic Particles and Thin Films

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(Received 22 January 1973)

This paper presents calculations of the electronic polarizabilities of very small metallic particles and of very thin metallic films. The theoretical model we employ for the metallic particle is simply that of N free electrons trapped by an infinitely deep spherical potential well. The model used for the thin-film problem is that of a system of free electrons constrained to move in the volume enclosed by two infinite parallel planes. Linear-response theory and Poisson's equation are used to calculate the electronic polarizability in terms of the electronic density-density response function. The numerical results provide an idea of just how small, or how thin, a small metallic particle, or thin metallic film, has to be for it to begin to lose its bulk property of being able to screen an externally applied electric field.

I. INTRODUCTION AND SYNOPSIS

The purpose of this paper is to present a model calculation of the electronic polarizabilities α of very small metallic particles and of very thin metallic films. Intimately connected with this problem is the question of the ability of such small or thin metallic systems to screen an externally applied static electric field.

The motivation for these calculations stems from a recently published criticism[1] of the Gorkov-Eliashberg (GE) 1965 prediction[2] that the electronic polarizability of a minute metallic particle should be enormously enhanced with respect to the bulk classical value $\alpha_0 = R^3$, where R denotes the mean radius of the particle. A short résumé of this criticism will serve as a convenient introduction to the formulation of the present problem.

The electric dipole moment $\vec{p}$ developed by an isolated metallic system in response to an externally applied field $\vec{E}_0$ is

$$\vec{p} = \int d^3r\, \vec{r}\, \rho^{in}(\vec{r}) , \tag{1.1}$$

in which $\rho^{in}(\vec{r})$ denotes the induced charge density at the space point $\vec{r}$. Within the framework of linear response,[3] the latter is related to the local electrostatic potential $\Phi(\vec{r})$ by means of the relation

$$\rho^{in}(\vec{r}) = -\int d^3r' \Phi(\vec{r}')\chi(\vec{r}, \vec{r}') , \tag{1.2}$$

where $\chi(\vec{r}, \vec{r}')$ denotes the electronic density-density response function characteristic of the metallic system. $\Phi(\vec{r})$ is given by the solution of the Poisson equation $\nabla^2\Phi(\vec{r}) = -4\pi\rho^{in}(\vec{r})$ or, in view of (1.2), by the solution of

$$\nabla^2\Phi(\vec{r}) = 4\pi\int d^3r' \Phi(\vec{r}')\chi(\vec{r}, \vec{r}') . \tag{1.3}$$

In terms of $\Phi(\vec{r})$, $\vec{p}$ is

$$\vec{p} = -\int d^3r \int d^3r' \vec{r}\, \Phi(\vec{r}')\chi(\vec{r}, \vec{r}') . \tag{1.4}$$

Thus given the appropriate boundary conditions on $\Phi(\vec{r})$, Eqs. (1.3) and (1.4) enable $\vec{p}$, and hence α, to be calculated from the knowledge of the characteristic response function $\chi(\vec{r}, \vec{r}')$.

Now GE were specifically concerned with metallic particles sufficiently minute that the discreteness of their conduction-electron energy levels would have to be taken into account. For such small (but still macroscopic) particles, GE assumed that one would be able to calculate their polarizabilities just as though each behaved as a macroscopic "atom." In terms of the above formulation this meant that GE introduced the drastic assumption that the local field $\vec{E}(\vec{r}) = -\vec{\nabla}\Phi(\vec{r})$ could be identified at every point with the applied field $\vec{E}_0$, so that, for example, in Eq. (1.4) one could write $\Phi(\vec{r}) = -\vec{E}_0 \cdot \vec{r}$. It would then follow[1] from (1.4) that

$$\vec{p} = \vec{E}_0 \Omega \chi_p \tag{1.5}$$

or $\alpha = \Omega\chi_p$, where χ_p denotes the static electronic