PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 29, NUMBER 8 15 APRIL 1984

Size-induced deviations from Matthiessen's rule in gallium single crystals

Robert I. Boughton

Department of Physics and Astronomy, Bowling Green State University, Bowling Green, Ohio 43403

(Received 14 October 1983)

Size-effect data are presented for gallium single-crystal wires oriented for current flow along the b axis. The enhancement of the temperature-dependent resistivity is deduced with the use of straightforward assumptions concerning the common high d/l_b behavior of all theoretical enhancement functions. Comparison is made with the theoretical curves of Sambles *et al.*, wherein an angularly dependent specularity parameter is employed.

INTRODUCTION

Interest in the effects of boundary scattering on electron transport properties in metals has had a long history replete with a number of examples of misinterpretation of theoretical predictions and experimental results (cf. Neighbor and Newbower[1]). Perhaps the most widely misinterpreted statement in the theoretical literature is that attributed to Dingle[2] in his work on boundary scattering for the case of thin wires, where it is asserted that in the case of totally diffuse scattering, over the entire range of variation in the bulk mean free path to dimension ratio l_b/d, the total resistivity of a boundary limited wire never deviates by more than 5% from the Nordheim-rule relation

$$\rho_d = \rho_b + \rho_b l_b/d \tag{1}$$

where ρ_d is the resistivity of the sample of lateral dimension d and ρ_b is the bulk resistivity.

Although the statement is perfectly correct as it stands, predictions based on the relation in Eq. (1) cannot be used to extract meaningful information about the temperature-dependent part of the resistivity in the limit where $l_b \gtrsim d$. The reason is that although the total resistivity is closely described by Eq. (1), the preponderant contribution is due to residual scattering. Hence, under readily attainable conditions, the temperature-dependent part of the resistivity can easily account for only 5% of the total or less, and therefore fall completely within the margin of disagreement between Nordheim's rule and the exact theory as originally quoted by Dingle.

Unfortunately, this fact has passed unnoticed by many experimental investigators who have sought to make "corrections" for the size effect in pure samples so that the resulting "bulk" temperature dependence could be extracted. Experimental evidence that an additional systematic contribution to the temperature-dependent part of the resistivity in thin wires can be attributed to boundary scattering was first obtained by Andrew[3] in mercury and tin, Olsen[4] in indium, and Reich and Forsvoll[5] in tin; and in more detail by Boughton and Yaqub,[6] and by Boughton *et al.*[7] in work on thermal and electrical transport in pure single-crystal gallium wires. The nature of the size-dependent contribution is observed to take the form of an enhanced contribution to the temperature-dependent part of the resistivity at and below temperatures where the bulk mean free path l_b is comparable to the wire's dimension d. In the case of high-purity gallium, where l_b is estimated to be on the order of several centimeters at absolute zero, this condition can be readily achieved for reasonably sized samples in the liquid-helium temperature range. A detailed understanding of the influence of boundary scattering and other phenomena associated with the condition where the ratio of mean free path to dimension is large, such as ballistic carrier transport, has recently become especially important in the design of microphysical structures.

A study of the temperature-dependent part of the resistivity for a series of size-limited wires of varying lateral dimension has been carried out on gallium single crystals oriented along the b axis. The experimental data are used to generate an empirically determined estimate of the enhancement of the temperature-dependent resistivity due to boundary scattering over the Nordheim-rule expression. Comparison is made with the theory of Dingle and with other modifications which incorporate more sophisticated treatment of the specularity of boundary scattering, such as the thin-film theory of Soffer[8] as extended by Sambles *et al.*[9] to wires.

THEORETICAL AND EXPERIMENTAL BACKGROUND

The size effect in wires was first treated in detail theoretically by Dingle.[2] The calculation was carried out

under the simplifying assumptions of (1) the relaxation time approximation and (2) a spherical Fermi surface. The assumption of a circular cross section was made along with the inclusion of a "polish" factor p, which is independent of scattering angle, to accommodate the possibility of specular reflection. It is convenient for comparison purposes to represent Dingle's theory by the following expression:

$$\rho_d = \rho_b + G\left[\frac{d}{l_b}, p\right]\frac{\rho_b l_b}{d} \tag{2}$$

where the enhancement function $G(d/l_b, p)$ depends on the mean free path to diameter ratio l_b/d and on the polish parameter p. Plots of $G(d/l_b)$ for the cases of totally diffuse boundary scattering ($p=0$) and for $p=0.5$ are illustrated in Fig. 1(a).

The temperature-dependent part of the resistivity can be presented in terms of a difference in the value of the function G at values of its argument corresponding to the mean free path at the temperature of interest and at $T=0$ K:

$$\Delta\rho_d = \rho_d(T) - \rho_d(0)\,,$$
$$\Delta\rho_d = \Delta\rho_b(T) + \left[G\left[\frac{d}{l_b(T)}\right] - G\left[\frac{d}{l_b(0)}\right]\right]\frac{\rho_b l_b}{d}\,. \tag{3}$$

Any theory which produces an enhancement that varies with $l_b(T)$ thus predicts a contribution to the temperature-dependent part of the resistivity due to boundary scattering.

In Dingle's theory, the enhancement effect is relatively small and in fact decreases with increasing polish, never exceeding approximately a 20% change. Clearly, the commonly used approximation that Nordheim's rule is valid implies that the function G is a constant and consequently no contribution to $\Delta\rho_d$ can be expected in that case. Several variations of Dingle's theory have been put forward, each elaborating on one of the simplifying assumptions listed above. MacDonald and Sarginson[10] considered wires of square cross section with results that differ from those of Dingle by only a scaling factor. The effect of alternative Fermi surface topology in the intense size-effect limit ($l_b > d$) was treated by Boughton and Neighbor.[11] Recently, Sambles *et al.*[9] adapted to round wires the treatment of angularly dependent specular scattering originally applied by Soffer[8] to the thin-film case. A plot of the enhancement function $G(d/l_b)$, obtained by Sambles *et al.*, is shown in Fig. 1(b) for various values of their "roughness" parameter $H \equiv h/\lambda_e$, where h = rms asperity height and λ_e is the Fermi wavelength of the electrons. The above authors point out that since G now varies over a considerable range, relatively large contributions to the temperature-dependent part of the resistivity [sometimes referred to as size-induced deviations from Matthiessen's rule (SIDMR)] are predicted. In contrast to Dingle's treatment, in most realistic cases this theory predicts an increasing enhancement as the roughness parameter is reduced. In what follows, the enhancement functions predicted by these models will be compared with those obtained empirically from experimental data on gallium single crystals. Since sufficiently extensive calculations have been carried out only for round wires and the cross-sectional shape of the wire is of negligible importance when compared with the influence of roughness, this distinction will be ignored in what follows.

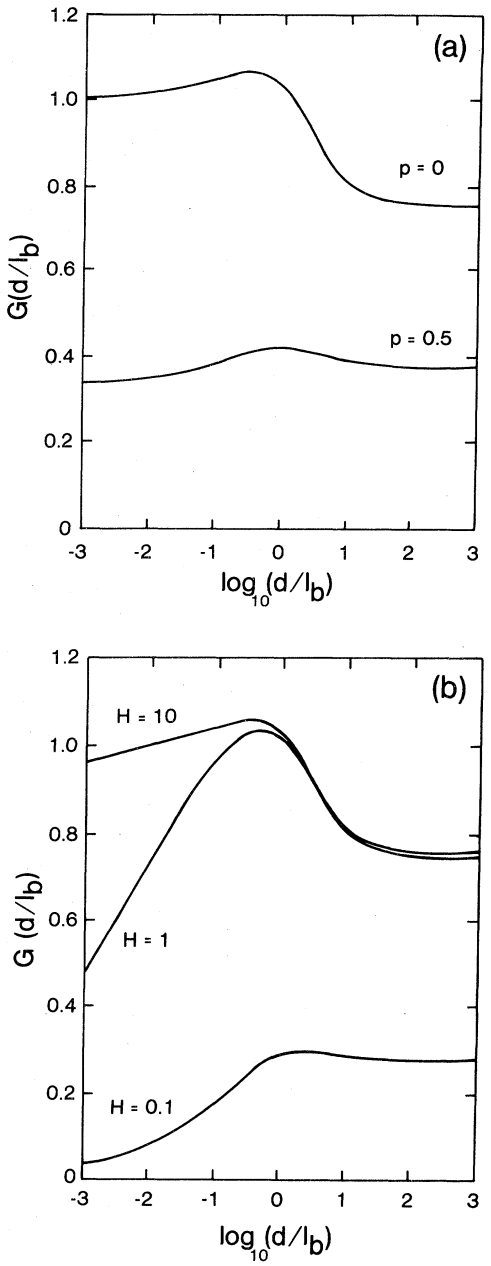

FIG. 1. (a) The function $G(d/l_b)$ plotted vs $\log_{10}(d/l_b)$ according to the theory of Dingle for $p=0$ and $p=0.5$. (b) The function $G(d/l_b)$ plotted vs $\log_{10}(d/l_b)$ according to the theory of Sambles *et al.* for $H=10$, 1.0, and 0.1.

The samples used in the present study were fabricated with square cross section and mold grown by seeding from the super-cooled melt using well-known techniques.[12] Gallium expands upon solidification, so that the surface characteristics of the mold material are faithfully reproduced on the sample surface. For the larger samples the

mold channels were constructed using highly polished Plexiglas spacers. Channel walls for the smaller samples were cut from thin sheets of Mylar, so the possibility exists that the surface polish was not uniform throughout the study. Potential probes are grown as an integral part of the crystal specimen to avoid the introduction of impurities and damage to the specimen when electrical contacts are made. The stock used is 99.9999+% pure gallium provided by Alcoa. All crystals were confirmed to be oriented to within $\pm\frac{1}{2}°$ of the b[010] axis of the orthorhombic lattice by Laue back-reflection x-ray techniques. In all, specimens of five different cross-sectional sizes ranging from 0.250 to 1.26 mm square were measured. The sample dimensions were determined by means of micrometer calipers and a traveling microscope when necessary. To avoid strain due to differential thermal contraction, the samples were attached to a single-crystal-gallium backing plate oriented in the same direction.

Electrical resistivity measurements were made over the temperature range of 1.2 to 7.2 K by means of a self-balancing superconducting Lindeck bridge circuit with a rf superconducting quantum interference device (SQUID) null detector. The sample was supported in a vacuum space on a temperature-controlled holder. The experimental set-up is similar to that employed by Boughton *et al.*,[7] and the reader is referred to that paper for further details. The relative accuracy in the measurement of the absolute resistance approaches 0.1%. The geometrical details of the samples under study along with the corresponding residual resistivity are summarized in Table I. Residual resistivities are obtained by extrapolation of a plot of $\rho_d(T)$ vs T^3 from 1.2 K and above to absolute zero. The error associated with this procedure is also estimated in Table I.

RESULTS

The electrical resistivity of each of the samples studied exhibits a rather characteristic temperature dependence. It is well established[7] that dilute gallium based alloys follow an approximate T^3 temperature dependence in the low-temperature limit. When plotted against T^3, the temperature-dependent part of the resistivity $\Delta\rho$ for the size-limited samples in this study exhibits enhancement due to boundary scattering. A plot of $\Delta\rho$ vs T^3 for all five specimens is shown in Fig. 2. The effect of the enhancement due to boundary scattering is manifested below about 5 K by the reversal in the curvature of the plot as the temperature is reduced. For smaller sample dimension, the inflection occurs at a higher temperature (cf. arrows in Fig. 2). This behavior is consistent with the results obtained with dilute alloys where the inflection point migrates to lower temperatures as the residual bulk mean free path is reduced. An empirical correspondence between the ratio l_b/d and the position of the enhancement inflection can therefore be demonstrated. The question still exists, however, as to whether the bulk resistivity is indeed well described by a T^3 power-law dependence, or that this behavior is particular to the contribution to the temperature-dependent part of the resistivity due to impurity scattering. In order to extract the quantitative behavior of the enhancement function, it is first necessary to correct for the contribution of the temperature-dependent bulk resistivity. Although it can be regarded as an approximate procedure, the following method has been adopted. In general terms, a common feature of all enhancement functions is the asymptotic approach to a constant value in the limit that $d \gg l_b$, that is, as the temperature increases for fixed d. This property implies that at higher temperatures boundary scattering can contribute a constant term of either sign and of variable magnitude to the resistivity in addition to the residual contribution. The fact that in the high-temperature limit the size-effect contribution becomes constant, moreover, implies that the observed temperature dependence of size-limited samples should reflect that of the bulk metal in this regime. A plot of $\log_{10}(\Delta\rho)$ vs $\log_{10}(T^3)$ is shown in Fig. 3 for the largest sample measured in this study. It is evident that above a T^3 value of nearly 100 K^3 ($T=4.6$ K) the slope of the plot steepens, and in fact approaches a value which closely corresponds to a T^5 power-law dependence. The best estimate of the magnitude of the contribution is $\Delta\rho_{b1}=2.72\times10^{-14}T^5$ Ω cm, as obtained from the data for the largest sample.

After this term is subtracted from the resistivity for each sample, it is possible to test for additional contributions from the bulk. Let us assume that the temperature-dependent part of the resistivity for a sample of size d is given by

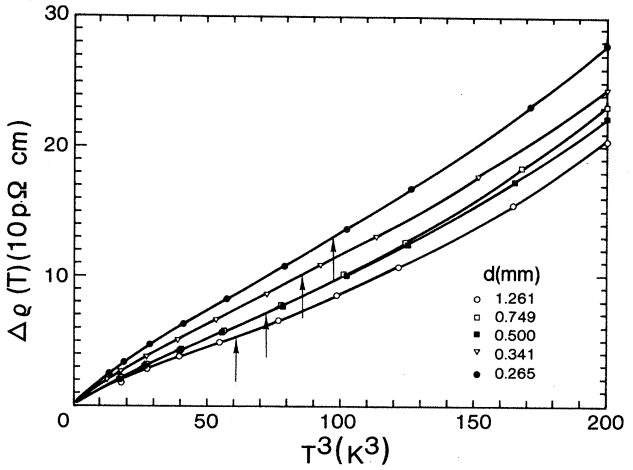

FIG. 2. Temperature-dependent part of the resistivity $\Delta\rho$ vs T^3 for all samples.

TABLE I. Lateral dimensions and residual resistivity of the samples studied.

Sample	Mold surface	Lateral dimension (nm)	ρ_0 (pΩ cm)
1	Plexiglas	1.261	56.0±0.1
2	Plexiglas	0.749	119.0±0.2
3	Mylar	0.500	153.8±0.3
4	Mylar	0.341	206.0±0.5
5	Mylar	0.265	230.5±0.5

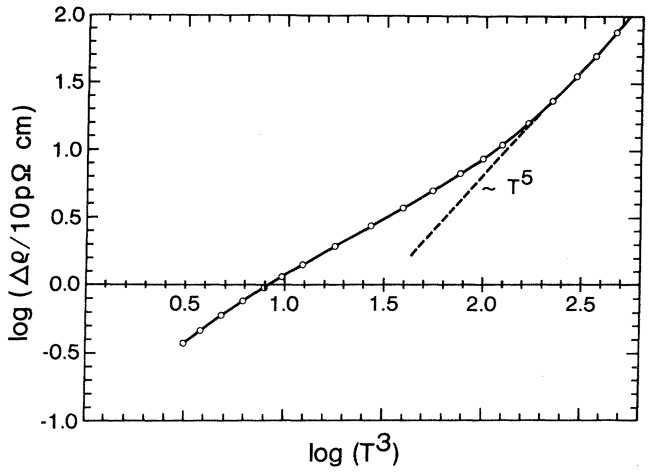

FIG. 3. $\mathrm{Log}_{10}(\Delta\rho)$ vs $\log_{10}(T^3)$ for the 1.261-mm-diameter sample.

$$\phi_d \equiv \Delta\rho_d - \Delta\rho_{b1} = \Delta\rho_{b2} + \left[G\left[\frac{d}{l_b(T)}\right] - G\left[\frac{d}{l_b(0)}\right]\right]\frac{\rho_b l_b}{d}, \quad (4)$$

where

$$\Delta\rho_{b1} = 2.72\times10^{-14}T^5\ \Omega\,\mathrm{cm}\ .$$

If the additional bulk term $\Delta\rho_{b2}$ is proportional to c_2T^n, then, a plot of $\Phi(T)\equiv\phi_d/T^n$ vs T^{-n} should yield an intercept equal to c_2, the coefficient of the additional bulk term. It should be noted that the size-dependent term in Eq. (4) is implicitly temperature dependent through the bulk mean free path factor, $l_b(T)$. Since a cubic power-law dependence is expected on other grounds, a plot of ϕ_d/T^3 vs T^{-3} was made and is displayed in Fig. 4. To within experimental error, the common intercept c_2 in Eq. (4) is determined to be zero for all samples measured.

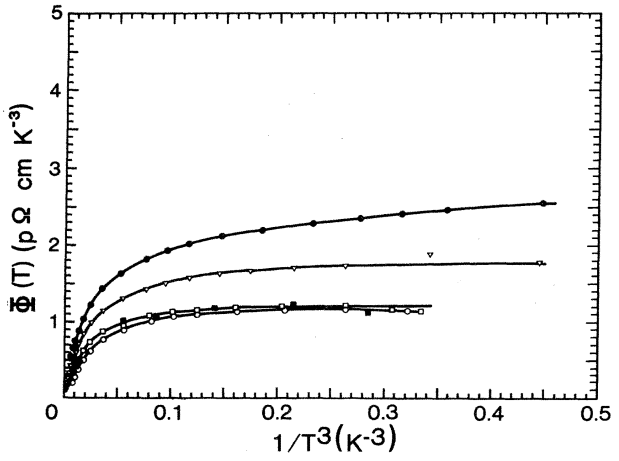

FIG. 4. The quantity $\Phi(T)\equiv\phi_d(T)/T^3$ plotted vs T^{-3} for all samples. Legend: ○—1.261 mm; □—0.749 mm; ■—0.500 mm; △—0.341 mm; ●—0.265 mm diameter.

This result suggests that the T^3 term observed in previous alloy studies is due solely to the influence of impurity scattering, and furthermore that the almost naive assumption of a Bloch-type T^5 dependence appears to adequately describe the behavior of the bulk resistivity for the pure metal, even though this power law is never quite attained in impurity-dominated specimens at higher temperatures.

The behavior of the enhancement function produced by boundary scattering can then be determined by plotting the function

$$\Delta G = G\left[\frac{d}{l_b(T)}\right] - G\left[\frac{d}{l_b(0)}\right] = \frac{\phi_d d}{\rho_b l_b}$$

vs d/l_b. In order to obtain the necessary values of ΔG, an accurate determination of the material constant $\rho_b l_b$ must be made. Previous determinations using residual resistivity plots by Cochran and Yaqub[13] and by Boughton[14] yield values of 8.2×10^{-12} $\Omega\,\mathrm{cm}^2$ and 7.3×10^{-12} $\Omega\,\mathrm{cm}^2$, respectively, for b-axis gallium. These studies, however, did not take into account the possibility that $G(d/l_b)$ might be a variable function and thus take on values that are significantly different than unity. It is pointed out by Sambles and Preist[15] that this determination can be readily carried out using higher-temperature data. It is made feasible in the regime where $d/l_b \gg 1$ by the fact that all metal surfaces should correspond to high values of roughness H (or polish $p=0$) in this limit. The typical plot of $\Delta\rho_d(T)$ vs d^{-1} at some high temperature where $d \gg l_b$ can therefore be used to determine the product $\rho_b l_b$. In such a case the enhancement function takes on the unique value 0.75. In the present study, however, the electron mean free path is so long, even at the highest temperatures attained, that the largest value of d/l_b obtained for any sample in the present study lies between 1 and 10. It is nevertheless still possible to take advantage of the commonality of the enhancement functions for roughness values exceeding 1.0. In the decade $1 \le d/l_b \le 10$ the function $G(d/l_b)$ when plotted versus $\log_{10}(d/l_b)$ has an approximate slope of -0.02 per decade for $H > 1.0$.

The variation of the enhancement function $G(d/l_b)$ with sample size in this region is relatively small and can be corrected for. Let d_1 be the size of the largest sample. It is assumed that the enhancement function can be expanded to first order for fixed l_b as

$$G\left[\frac{d}{l_b}\right] = G\left[\frac{d_1}{l_b}\right] + [G'(\kappa)]_{\kappa_1}\left[\frac{d}{l_b} - \frac{d_1}{l_b}\right] = G(\kappa_1) + [G'(\ln\kappa)]_{\kappa_1}\left[\frac{d}{d_1} - 1\right], \quad (5)$$

where $\kappa = d/l_b$. The resulting correction to the enhanced resistivity is

$$\phi_d = [G'(\ln\kappa)]_{\kappa_1}\frac{\rho_b l_b}{d_1} + \frac{\rho_b l_b}{d}\{[G(\kappa)]_{\kappa_1} - [G'(\ln\kappa)]_{\kappa_1}\}\ . \quad (6)$$

For the given parameters of gallium and given the behavior of the enhancement function of Dingle and Sambles *et al.*, the slope of a ρ_d vs d^{-1} plot in this region un-

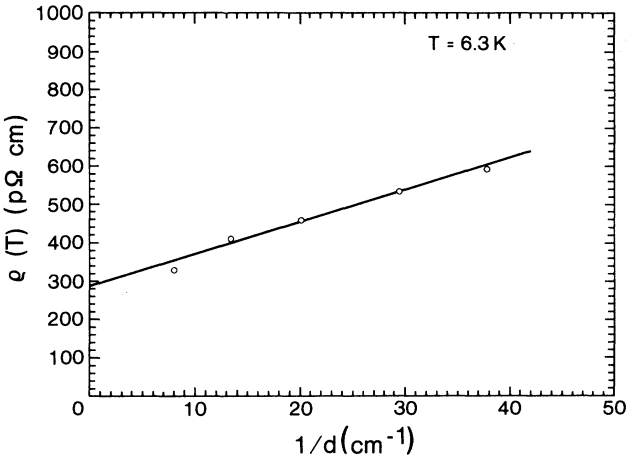

FIG. 5. Plot of ρ_d vs d^{-1} for all samples at $T=6.3$ K.

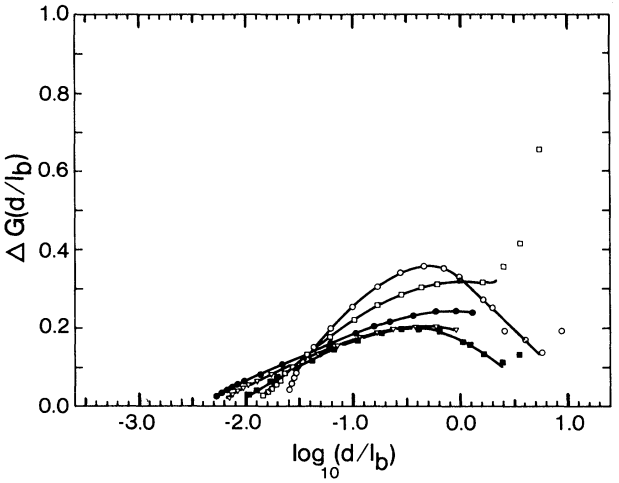

FIG. 6. Plot of $\Delta G(d/l_b)$ vs $\log_{10}(d/l_b)$ for all samples (same legend as in Fig. 2).

derestimates the $\rho_b l_b$ product by approximately 9% and the intercept overestimates the value of $\rho_b(T)$ by about 2%. Since for realistic values of the roughness (polish) all enhancement functions have essentially the same slope, the accuracy of the correction for this variation is not crucial.

The ρ_d data for the fixed temperature of $T=6.3$ K are plotted versus d^{-1} in Fig. 5. This particular temperature was chosen since it is the highest available to interpolate reliably for all samples. By means of a least-squares analysis, the slope is determined to be $S=8.34$ pΩ cm^2, and the intercept $I=284.4$ pΩ cm. In order to obtain accurate values of $\rho_b l_b$ and $\rho_b(T')$, the following iteration process was carried out. A preliminary value of $\rho_b l_b$ is obtained by assuming the asymptotic value for the slope of ρ_d vs d^{-1} as 0.75 $\rho_b l_b$. The approximate mean free path l_b at this temperature is then obtained by dividing by the value of $\rho_b(T')$ obtained from the intercept. For the largest sample ($d=0.1261$ cm), the value of κ is evaluated and the corresponding value of the enhancement function $G(\kappa)$ obtained. The quantity S is then set equal to $G(\kappa)\rho_b l_b$ and a new more refined value of $\rho_b l_b$ is obtained. The procedure is repeated until convergence is achieved.

The corrected material parameters obtained in this way are $\rho_b l_b = 10.2 \pm 0.5$ pΩ cm^2; $\kappa_1 = d_1/l_b = 3.8$ at $T=6.3$ K; and, $G(\kappa_1)=0.89$ at this temperature. By using the form of $\rho_b = AT^5$ obtained earlier in Eq. (4), the bulk mean free path can be determined at any temperature and the ratio $\kappa = d/l_b$ evaluated.

The resulting plots of ΔG vs $\log_{10}(\kappa)$ for all five samples are exhibited in Fig. 6. It is clear that in samples 2 and 5 the high-temperature data do not reasonably fit any known enhancement function. The error associated with the data in this limit is quite large, approaching $\pm 30\%$. The indication is that the correction for the bulk temperature dependence is slightly in error for these two samples. It is found that the subtraction of an additional T^3 term, on the order of $\Delta\rho_{b2} = 3\times 10^{-15} T^3$ Ω cm, which is presumably caused by a slightly increased amount of impurity scattering, results in reducing these data to a form similar to the data for the other samples. Rather than introduce an extraneous adjustable parameter into the analysis at this point, however, it is better to consider only the data below $d/l_b \sim 1$ where the bulk correction becomes small in evaluating the fit to existing enhancement predictions for these two samples.

The remainder of the samples, however, appear to conform qualitatively rather nicely to the predictions of theory over the entire range of variation in $\log(\kappa)$. The data for sample 1, the largest in the present study, carry the greatest accuracy since the residual contribution that is subtracted is smallest. From the data for this sample, several conclusions can be drawn. The closest fit to theory appears to be the curve obtained by Sambles *et al.*[9] for roughness values in the range $0.464 \leq H \leq 1.0$. In Fig. 7(a), the experimental data for sample 1 are plotted along with several previously published theoretical curves so that the degree of correspondence can be judged. It is clear both from the magnitude of variation and from the curvature of the empirical ΔG plot for values of $d/l_b < 1$ that the simple nonangularly dependent "polish" parameter of Dingle's theory is inadequate to describe the data. The data for samples 3 and 4 in Fig. 7(b) nearly coincide and correspond to a roughness H in the range of 2 to 5. Again, even though the magnitude of variation along the abscissa is comparable, the downward curvature of the plots is in disparity with Dingle's curves for any value of the polish parameter.

It is also worthwhile to consider the data obtained by Morelli[16] on a 2.5-mm-square b-axis sample, even though the range of temperature variation in the measurements did not go beyond 4.2 K. The reduced data for this crystal are presented in Fig. 7(c) using the same material parameters derived in this study. Comparison is made with the $H=0.464$ and $H=0.215$ plots of Sambles *et al.*,[9] where it can be seen that there is a close correlation with the theoretical curves, and so a value of H in this range is indicated. For samples number 2 and 5, the lower-temperature data appear to fit well into the pattern described by samples 1 and 3 and 4, respectively.

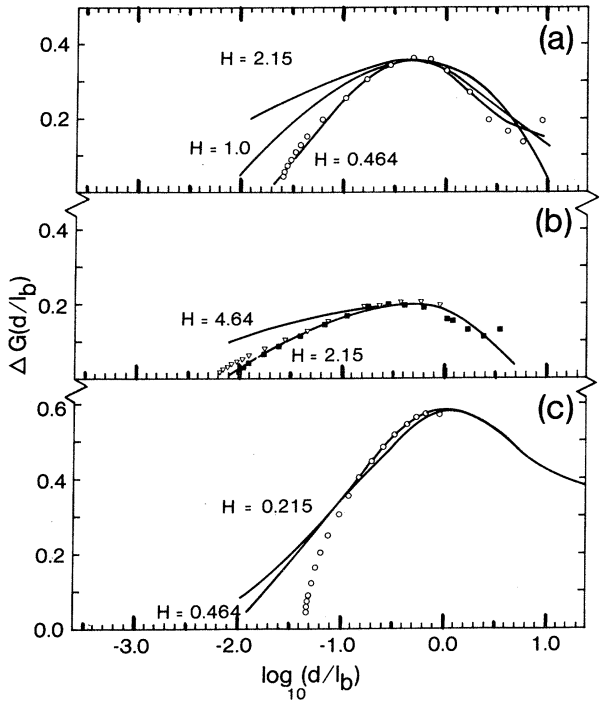

FIG. 7. Comparison of empirically derived enhancement function $\Delta G(d/l_b)$ for (a) ○—1.261 mm; (b) ■—0.500 mm and △—0.341 mm; and (c) ○—2.5 mm diameter (cf. Ref. 16).

CONCLUSION

The data for single-crystal *b*-axis gallium wires compare favorably with the theoretical curves of Sambles *et al.*[9] if the roughness is regarded as an adjustable parameter. It is apparent that the roughness decreases with increasing size, varying from approximately 5 down to 0.5 for various samples in the present study. As mentioned earlier, there is reason to believe that the method of sample preparation could possibly lead to surfaces of higher roughness for the smaller samples. Using a value for the electron wavelength λ_e of 0.378 nm for gallium, these values of H correspond to a variation in the rms asperity factor of from $h=2$ nm for the "roughest" surfaces (smaller samples) down to $h=0.2$ nm for the largest sample.

It is somewhat surprising that the rms asperities are so much smaller than the wavelength of light because even though the Plexiglas mold spacers are "highly polished," no special pains were taken to produce much more than a shiny mirrorlike appearance on the milled surfaces. Thus, although agreement with theory is good with only one adjustable parameter, some doubt must still be cast upon the validity of the results. The Soffer model is unquestionably a much more realistic treatment of the surface scattering problem than the Fuchs-Dingle polish-factor treatments. However, it must also be kept in mind that there remains one serious shortcoming in all current size-effect theories that treat cylindrical wires. The assumption of the relaxation time approximation for electron-phonon scattering is a serious oversimplification. Ehrlich[17] has applied the electron "diffusion" method of Klemens and Jackson[18] to the thin-film problem. The results of that study demonstrate that the SIDMR are much larger than in Fuch's relaxation-time-approximation treatment, especially in the region of $\kappa \approx 1$. It appears worthwhile at this stage in the development of the subject for the application of the electron diffusion model to be made to the case of thin wires. Judging from the results of the treatment of thin films, it is qualitatively apparent that fairly large enhancement functions can be obtained, even for zero polish. The likelihood is great that similarly large enhancements can be expected for thin wires.

[1]J. E. Neighbor and R. S. Newbower, Phys. Rev. 186, 649 (1969).
[2]R. B. Dingle, Proc. R. Soc. London, Ser. A 201, 545 (1950).
[3]E. R. Andrew, Proc. Phys. Soc. London, Sect. A 62, 77 (1949).
[4]J. L. Olsen, Helv. Phys. Acta 31, 713 (1958).
[5]R. Reich and K. Forsvoll, C. R. Acad. Sci. 261, 125 (1965).
[6]R. I. Boughton and M. Yaqub, Phys. Rev. Lett. 20, 108 (1968).
[7]R. I. Boughton, J. J. Polick, and L. Morelli, Phys. Rev. B 17, 1611 (1978).
[8]S. B. Soffer, J. Appl. Phys. 38, 1710 (1967).
[9]J. R. Sambles, K. C. Elsom, and T. W. Priest, J. Phys. F 12, 1169 (1982).
[10]D. K. C. MacDonald and K. Sarginson, Proc. R. Soc. London, Ser. A 203, 223 (1950).
[11]R. I. Boughton and J. E. Neighbor, J. Low Temp. Phys. 7, 241 (1972).
[12]M. Yaqub and J. F. Cochran, Phys. Rev. 137, A1182 (1965).
[13]J. F. Cochran and M. Yaqub, Phys. Rev. 140, A2174 (1965).
[14]R. I. Boughton, Phys. Lett. 74A, 141 (1979).
[15]J. R. Sambles and T. W. Preist, J. Phys. F 12, 1971 (1982).
[16]L. Morelli, Ph.D. thesis, Northeastern University.
[17]A. C. Ehrlich, J. Appl. Phys. 42, 2598 (1971).
[18]P. G. Klemens and J. L. Jackson, Physica (Utrecht) 30, 2031 (1964).