PHYSICAL REVIEW B VOLUME 47, NUMBER 7 15 FEBRUARY 1993-I

Synchrotron x-ray optical properties of natural diamond

Jeyasingh Nithianandam* and J. C. Rife
Dynamics of Solids Branch, Naval Research Laboratory, Washington, D.C. 20375

(Received 15 June 1992; revised manuscript received 15 October 1992)

Reflectance spectrum of a diamond crystal measured between 200.0 and 610.0 eV is presented. The x-ray reflectance spectrum was combined with an earlier ultraviolet optical spectrum of diamond. Extrapolations to these reflectance spectra were calculated using a set of Lorentz oscillators. These reflectance values were used in obtaining the spectral dependence of the optical dielectric function of diamond via a Kramers-Kronig transform. The accuracy of these optical constants and the reflectance extrapolations were verified using optical sum rules. The refractive index of the diamond is found to be greater than unity near 287.0 eV.

Diamond is one of the simplest and most important systems in condensed matter. It has a combination of desirable physical properties that make it a valuable material for practical applications in electronics and optics.[1,2] Diamond thin films could be grown on various substrates by processes such as chemical vapor deposition and ion implantation methods. A study of the optical properties of diamond near the carbon *K* edge would be valuable in understanding its electronic structure and the nature of electron states due to impurities and defects in diamond. The x-ray optical constants of diamond could be useful in the design of optical components like antireflection coatings, x-ray multilayer mirrors, and optical windows. The optical properties of diamond in the visible and ultraviolet spectral regions have been studied in detail by reflectance and electron-energy-loss methods.[3–5] The optical properties of diamond in the x-ray spectral region are not available due to difficulties in obtaining very thin freestanding single-crystal diamond films. X-ray optical experiments near the carbon *K* edge using synchrotron x-ray radiation are difficult to perform, due to the severe contamination of the surfaces of optical elements in x-ray beam lines. We present here synchrotron x-ray reflectance measurements on a natural diamond crystal and our results on the spectral dependence of the dielectric function of diamond obtained using a Kramers-Kronig analysis of the reflectance data.

The reflectance measurements on a natural diamond were performed at the Naval Research Laboratory soft x-ray beamline X24C of the National Synchrotron Light Source. A high-resolution grating-crystal monochromator (GCM) and a versatile ultrahigh-vacuum (UHV) reflectometer were used in these measurements.[6,7] The optical elements in the beamline, namely, two paraboloidal mirrors and the gratings, were cleaned in an oxygen glow discharge. The oxygen-glow-discharge cleaning reduced the carbon contamination on the surfaces of these optical elements and improved the flux of x rays at the carbon *K* edge. Two gold-coated gratings, each with 2400 grooves per mm, were used at a 2.5° blaze angle to monochromatize the incident x rays. The pair of gratings used in combination doubled the resolving power, suppressed higher orders, and reduced zero-order scattered light. The energy resolution of the monochromator was between 0.1 and 0.25 eV near the carbon *K* edge. The monochromatic x rays at the exit slit of the beamline were 90% polarized with the electric vector in the horizontal plane.

The reflectometer chamber was at a pressure of 2×10^{-9} Torr. This UHV chamber could be rotated about the incident x-ray direction for performing both *s*- and *p*-polarization reflectance measurements. The reflectometer provides for independent rotation of the sample holder and the detector. The sample was kept at room temperature. A GaAsP photodiode detector was used with an electrometer to measure the intensity of the x rays. The electrometer provided a dynamic range of seven orders of magnitude. The reflectance measurements were made by first measuring the incident-beam intensity from the monochromator and then the reflected intensity from a sample as a function of photon energy. The reflectance spectrum was normalized to the circulating electron-beam current in the storage ring. The reflectance spectrum of the sample was also normalized using the monochromator transmission spectrum.

The monochromator transmission plots have two prominent dips near the carbon *K*-edge region. These features are due to residual carbon contamination in the beamline optical elements. The energy positions of these two dips were determined by a method described below. The *s*- and *p*-polarization reflectance spectra of a freshly cleaved highly ordered pyrolytic graphite were measured immediately after recording a monochromator flux plot. The prominent π^* peak in the graphite *K*-edge reflectance spectrum was set at an energy value of 285.35 ± 0.15 eV.[8] The energy positions of the carbon contamination dips in this monochromator flux plot were determined as 285.0 and 291.0 eV. These values were used in the calibration of the photon-energy scale in subsequent measurements. The photon-energy scale was calibrated to better than ±0.15 eV by this procedure.

A type-Ia diamond crystal of 0.21 cm thickness was used in the reflectance measurements. It had a square-shaped (100) surface with approximately 0.75-cm edges. The color of the diamond was yellow. The yellow color of the diamond is due to the presence of platelet nitrogen impurities in the sample.[2] The diamond crystal was cleaned by boiling in a solution of concentrated sulfuric, nitric, and perchloric acids in a special fume hood. The diamond sample was rinsed in deionized water. The root-mean-square (rms) roughness height of the diamond was determined as 0.62 nm with a WYKO profilometer. The s-polarization reflectivity of the clean diamond crystal surface was measured at 5.0° grazing angle of incidence as a function of photon energy between 200.0 and 610.0 eV. The reflectance spectrum of the diamond sample is shown in Fig. 1. The reflectance near the diamond K absorption edge has a steplike increase in value. The reflectance of the diamond sample was measured at a fine energy spacing of 0.05 eV in this energy region in order to determine its optical constants accurately.[9]

Scattering due to roughness of a sample surface is important in the soft x-ray range.[10] Surface irregularities lower the specular reflectivity of a sample according to the following Debye-Waller relation:

$$R_r = R_f \exp[-(4\pi\sigma\cos\phi)^2/\lambda^2] \ . \qquad (1)$$

In this expression, R_f is the theoretical reflection coefficient for a smooth surface, ϕ is the angle of incidence measured from the surface normal, λ is the wavelength of incident x rays, and σ is the rms roughness of the surface with a reflectance of R_r. The Debye-Waller correction factor in Eq. (1) was applied to the reflectance spectrum of diamond in Fig. 1 before evaluating the Kramers-Kronig integral.

The complex amplitude reflectivity function

$$r(E) = \sqrt{R(E)}\exp(i\xi(E))$$

describes a linear causal response. A Kramers-Kronig dispersion relation that links $\xi(E)$ and $R(E)$ is given by

$$\xi(E_0) = -(E_0/\pi)P\int_0^\infty \ln R(E)/(E^2-E_0^2)dE \ . \qquad (2)$$

Here, $R(E)$ is the measured reflectance of a sample surface, $\xi(E)$ is the phase shift upon reflection from the sample, and P denotes the Cauchy principle value. The phase shift was obtained from the measured reflectance spectrum by a numerical evaluation of the Kramers-Kronig dispersion relation. These phase-shift and reflectance values were substituted in the Fresnel's reflectivity equation to obtain the complex dielectric function of diamond as a function of photon energy. The Fresnel's equation for complex s-polarization amplitude reflectivity r_s is given by the following relation:

$$r_s = -(a - ib - \cos\phi)/(a - ib + \cos\phi) = \sqrt{R_s}\exp(i\xi) \ . \qquad (3)$$

The parameters a and b are given by the following equations:

$$a = (1-R_s)\cos\phi/(1+R_s-2\sqrt{R_s}\cos\xi) \ , \qquad (4)$$

$$b = -2R_s\cos\phi\sin\xi/(1+R_s-2\sqrt{R_s}\cos\xi) \ , \qquad (5)$$

$$a^2-b^2 = n^2-k^2-\sin^2\phi \ , \qquad (6)$$

$$ab = nk \ . \qquad (7)$$

Here, n and k are the real and imaginary parts of the refractive index.[11]

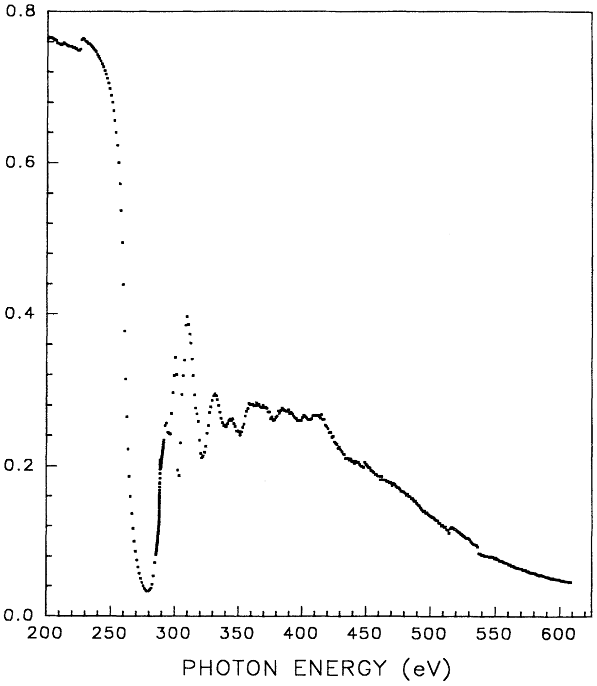

FIG. 1. Reflectance of a yellow color type-Ia natural diamond measured at 5.0° grazing incidence and s polarization using x rays from a synchrotron source is shown.

The Kramers-Kronig integral in Eq. (2) is over all photon energies, but the reflectance spectrum in Fig. 1 is over a limited energy region. A method was developed to form a reflectance data set for diamond over a wide photon-energy scale for the Kramers-Kronig analysis and is described below. The soft x-ray reflectance of diamond in Fig. 1 was first corrected for the loss of reflectivity due to surface roughness using Eq. (1). The optical spectra of diamond in the ultraviolet region obtained from earlier reflectance and electron-energy-loss experiments[3,4] were combined with our soft x-ray reflectance spectrum of diamond. Extrapolations to the s-polarization ultraviolet and soft x-ray reflectance spectra could be calculated with a model complex dielectric function for diamond. In this model, a set of Lorentz oscillators was used to synthesize a model complex dielectric function.[12] A nonlinear least-squares program based on this model was used to obtain fits to the ultraviolet reflectance spectrum of diamond below 30.0 eV (Refs. 3 and 4) and to our soft x-ray reflectance of diamond between 500.0 and 600.0 eV. A reflectance extrapolation between 30.0 and 229.0 eV and a reflectance extrapolation above 600.0 eV were calculated with the parameters of the Lorentz oscillators determined from the model fits to the experimental diamond reflectance spectra.[3,4] The parameters of the Lorentz oscillators used in these reflectance extrapolations are given in Table I. The reflectance extrapolations made at high photon energies with these Lorentz oscillators provide the correct E^{-4} dependence for reflectance.[12] The extrapolated reflectivity spectrum of the diamond is shown in Fig. 2(a).

TABLE I. Values of the Lorentz oscillator parameters of the model dielectric functions for diamond, which were used in the calculations of reflectance extrapolations from 30.0 to 229.0 eV and above 600.0 eV are given. These values were determined from the model fits to a diamond ultraviolet reflectance spectrum (Ref. 3) and our soft x-ray reflectance spectrum from 500.0 to 600.0 eV.

Oscillator strength eV^2	Width of oscillator eV	Energy position eV
	Reflectance extrapolation from 30.0 to 200.0 eV	
265.0	3.1	10.9
145.0	3.6	8.4
330.0	45.5	18.4
46.0	12.5	291.3
	Reflectance extrapolation above 600.0 eV	
510.0	108.7	235.7
984.7	206.2	274.9

A Fortran program that uses a fast Fourier transform (FFT) algorithm to evaluate the Kramers-Kronig integral was developed.[13,14] The FFT method of evaluation of the dispersion integral involves several subtleties. This program could process 2^{17} points and it minimizes the aliasing effects inherent in the FFT analysis.[14] The reflectance spectrum of the diamond extrapolated up to a photon energy of $E_u = 7250.0$ eV was used in the numerical computations of the dispersion integral with this FFT program. The phase-angle shift $\xi(E)$ as a function of photon energy was derived from this analysis. The phase-angle-shift values obtained by this analysis have to be corrected due to incomplete spectral information above E_u. The phase-shift corrections were calculated for photon energies below 800.0 eV and this method is described below. The E_0^2 factor in the denominator of Eq. (2) could be neglected in comparison with E, since $E \geq 7250.0$ eV and $E_0 \leq 800.0$ eV. The reflectance of the diamond sample in this energy region is described by the expression

$$R(E) = R_u(E_u/E)^4 \; . \tag{8}$$

The reflectance value R_u at $E_u = 7250$ eV is known from the reflectance extrapolation calculated with the Lorentz

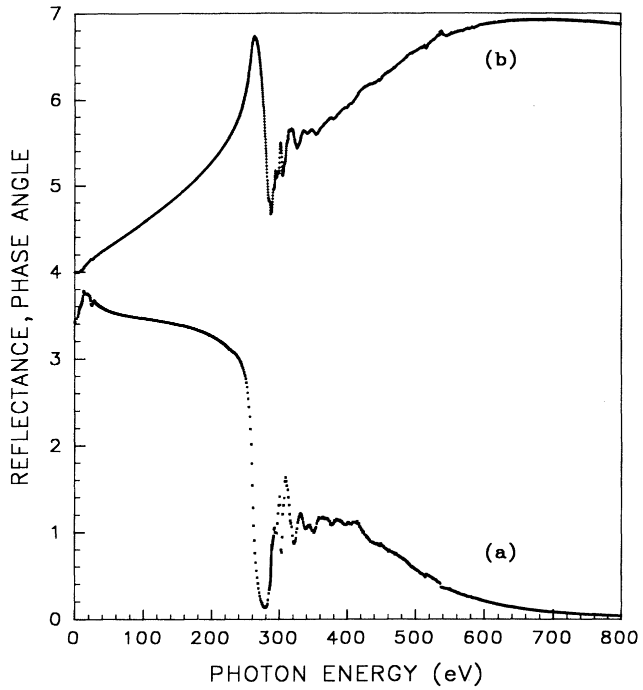

FIG. 2. (a) Extrapolations to the x-ray reflectance of diamond at lower and higher energies are shown. The reflectance values below 30.0 eV were obtained from an earlier electron-energy-loss experiment (Ref. 4). The reflectance extrapolations from 30.0 to 229.0 eV and above 600.0 eV were calculated with a set of Lorentz oscillators whose parameters are given in Table I. (b) The phase-angle shift that occurs due to the reflection of the incident beam from the diamond is shown. This phase-shift function is in radians and it was derived from a Kramers-Kronig transform of the extrapolated reflectance data. The phase-angle values were corrected for the lack of spectral information at higher energies, as discussed in the text. The phase-angle values are shifted vertically by 4.0 units.

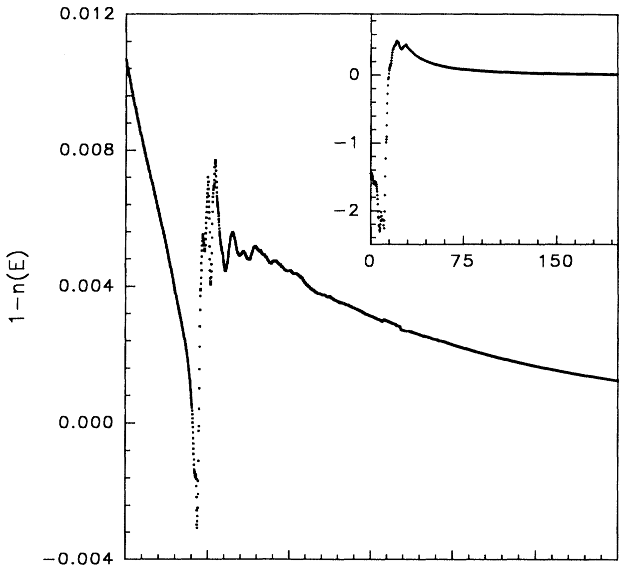

FIG. 3. The variation of the function $\delta = 1 - n(E)$ with photon energy for diamond is shown. The function $n(E)$ is the real part of the refractive index of the diamond sample. The inset shows the refractive index below the diamond 1s core threshold.

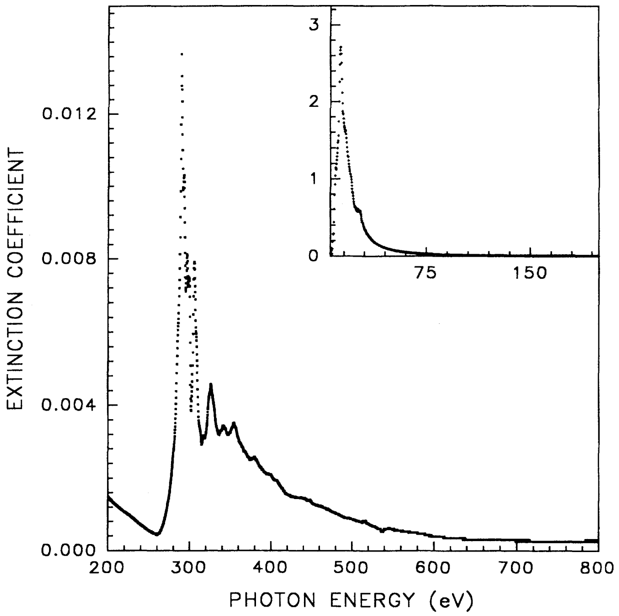

FIG. 4. The variation of the extinction coefficient of diamond, $k(E)$, with photon energy is shown. The inset shows our extinction coefficient values below the diamond 1*s* core threshold and they are in agreement with the extinction coefficient function of diamond in Ref. 4.

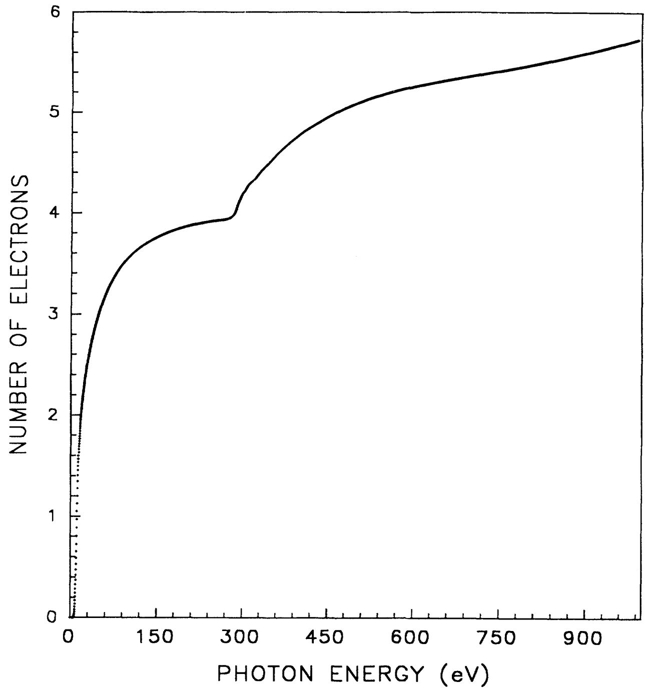

FIG. 5. The number of electrons that effectively participate in the optical process calculated with the classical *f*-sum rule.

oscillators. The Kramers-Kronig integral in Eq. (2) was modified using these approximations and it was evaluated from E_u to infinity. The spectral dependence of the corrected phase-angle shift is shown in Fig. 2(b) for energies below 800.0 eV.

The extinction coefficient $k(E)$ and the function $\delta=1-n(E)$ for diamond were determined from Eqs. (4) to (7) using $\xi(E)$ and $R(E)$. The spectral dependence of $\delta(E)$ and $k(E)$ are shown in Figs. 3 and 4. The ultraviolet optical constants derived from these analyses agree with previous electron-energy-loss values.[4] The function $\delta(E)$ in Fig. 3 has negative values near 287 eV. It has a lowest value of -0.0031 at 287.4 eV. We note that a similar variation of $\delta(E)$ has been reported for amorphous carbon.[1,15] The negative value of $\delta(E)$ is associated with a large increase of the diamond reflectance at lower energies relative to its reflectance near 285.0 eV, as seen in Figs. 1 and 2(a).

The accuracy of the optical constants of diamond and the reflectance extrapolations were verified with various optical sum rules.[16,17] The number of electrons that effectively participate in an optical process is given by the following *f*-sum rule:

$$N_{\mathrm{eff}}=(8\pi\epsilon_0 m_0 A/h^2e^2N_A\rho)\int_0^\infty E\epsilon_2(E)dE\ , \qquad (9)$$

where ϵ_0 is the permittivity of free space; m_0 and e are the rest mass and a charge of an electron, respectively; N_A is Avogadro's number; A is the atomic weight; and ρ is the density of diamond. The integral in Eq. (9) was evaluated and the variation of the oscillator strength N_{eff} with the photon energy is shown in Fig. 5. We find that the oscillator strength of four valence electrons is nearly exhausted by 285.0 eV and it has a value of 5.74 at about 1000.0 eV. The classical *f*-sum rule in Eq. (9) has slow convergence and it has to be calculated over a large energy range to obtain an accurate value for the oscillator strength. In order to overcome this difficulty, Leveque[16] introduced an augmented *f*-sum rule that has a rapid convergence. It is given below:

$$N'_{\mathrm{eff}}(W)=(8\pi\epsilon_0 m_0 A/h^2e^2N_A\rho)\left[\int_0^W E\epsilon_2(E)dE + W^2\epsilon_2(W)\right] . \qquad (10)$$

We computed this integral and obtained a value of four valence electrons for N'_{eff} at $W=58.4$ eV and six electrons for N'_{eff} at $W=538.75$ eV.

An inertial sum rule that relates the real part of the refractive index $n(E)$ was used in verifying the accuracy of our optical constants[17] and it is given below:

$$\tau=\int_0^\infty (n(E)-1)dE\Big/\int_0^\infty |n(E)-1|dE=0\ . \qquad (11)$$

This integral was evaluated using the $n(E)$ of the diamond sample and a value of 0.082 was obtained for τ at 800.0 eV. The value of τ is small and our optical constants of diamond are good below 800.0 eV. The reflectivity of diamond at 10.0° grazing incidence was calculated using these optical constants and it is in reasonable agreement with the reflectance of diamond measured at 10° grazing incidence.[18]

In summary, we have presented the grazing incidence synchrotron x-ray reflectance measurements on a natural diamond and obtained its optical constants over a wide energy region. The index of refraction is slightly greater than unity near 287.0 eV. The optical sum rule checks used on the diamond optical constants have shown that the calculated reflectance extrapolations are good. These x-ray optical measurements[18] would stimulate further work on many-body effects at the diamond K absorption edge, electronic structure of diamond, and optical and electronic applications of diamond.

The author thanks M. N. Kabler, J. Long, and J. Butler of NRL; W. Hunter of SFA; and R H. French and E. I. Du Pont Company for informative discussions; and Professor H. G. Maguire for diamond crystals. Part of this research was done at the NSLS in Brookhaven National Laboratory.

---

[*] Present address: Hughes STX Corporation, 4400 Forbes Boulevard, Lanham, MD 20706.

[1] E. Spiller, Appl. Opt. **29**, 19 (1990).

[2] M. Seal and W. J. P. van Enckevort, Proc. SPIE **969**, 144 (1988).

[3] H. R. Phillip and E. A. Taft, Phys. Rev. **127**, 159 (1962).

[4] K. Zappenfeld, Opt. Commun. **1**, 119 (1969).

[5] D. L. Windt, W. C. Cash, Jr., M. Scott, P. Arendt, B. Newman, R. F. Fisher, A. B. Swartzlander, P. Z. Takacs, and J. M. Pinneo, Appl. Opt. **27**, 279 (1988).

[6] J. C. Rife, H. R. Sadeghi, and W. R. Hunter, Rev. Sci. Instrum. **60**, 2064 (1989).

[7] W. R. Hunter and J. C. Rife, Nucl. Instrum. Methods A **246**, 465 (1986).

[8] E. J. Mele and J. J. Ritsko, Phys. Rev. Lett. **43**, 68 (1979).

[9] D. W. Lynch, J. Phys. (Paris) Colloq. **C5**, 21 (1977).

[10] H. G. Birken, C. Kunz, and R. Wolf, Phys. Scr. **41**, 385 (1990).

[11] D. M. Roessler, Brit. J. Appl. Phys. **16**, 1359 (1965).

[12] B. W. Veal and A. P. Paulikas, Phys. Rev. B **10**, 1280 (1974).

[13] C. W. Peterson and B. W. Knight, J. Opt. Soc. Am. **63**, 1238 (1973).

[14] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, 1986), p. 381.

[15] B. L. Henke, P. Lee, T. J. Tanaka, R. L. Shimabukuro, and B. K. Fujikawa, At. Data Nucl. Data Tables **27**, 1 (1982).

[16] G. Leveque, Phys. Rev. B **34**, 5070 (1986).

[17] E. Shiles, T. Sasaki, M. Inokuti, and D. Y. Smith, Phys. Rev. B **22**, 1612 (1980).

[18] J. Nithianandam, J. C. Rife, and H. Windischmann, Appl. Phys. Lett. **60**, 135 (1992).