

The Critical Voltage Effect in High-Voltage Electron Microscopy

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SUMMARY

In addition to revealing the internal microstructures of materials, the high-voltage electron microscope can also be used to characterize "invisible" features such as electron scattering, site occupancy, and atomic displacement amplitudes on a quantitative basis. The physical basis of the unique "critical voltage effect" is the occurrence of destructive interference between current waves within the specimen at a particular accelerating voltage. Potential applications to studies of random and ordered alloy solid solutions largely depend on the magnitude of the size disparity between solute and solvent atoms.

INTRODUCTION

Research-oriented metallurgists are generally aware that increasing the accelerating voltage of the electron microscope can result in a significant increase in specimen penetration.^{1,2} This ability to examine thick specimens in transmission has been utilized extensively to study the detailed features of microstructures developed during transformation, precipitation, and deformation, using either post-mortem sectioning or dynamic in-situ observations on pre-thinned specimens. At accelerating voltages above the displacement threshold for crystals, electrons in the beam are sufficiently energetic to knock atoms from their lattice sites to create vacancies and interstitials. Study of the agglomeration of vacancies to form planar faults or voids has been a major application of the HVEM for a number of years. Finally, advances in electron microscope lens design and painstaking attention to mechanical and electrical stability have led to the development of very high resolution instruments which should produce atomic-level resolution in the near future.

All these features of high voltage electron microscopy have been discussed in detail in various AIME symposia on metallography, as well as in previous special editions of *Journal of Metals* which were devoted to microscopy.^{3,4} However, there is one additional and unique aspect of high-voltage electron microscopy that is still not generally familiar to materials scientists, namely, the "critical voltage" effect.^{5,6} This phenomenon takes its name from the fact that subtle but characteristic changes occur in the image and corresponding electron diffraction patterns from crystals at certain critical voltages which are determined by the composition, structure, temperature, and other specimen factors. Careful determination of the critical voltage (V_c) can provide quantitative information about departures from randomness in lattice site occupancy, i.e., clustering or short-range order, Debye temperatures, bonding, and charge transfer in alloys. These basic parameters of crystal physics are usually derived from x-ray or neutron scattering studies or elastic wave propagation experiments and are not considered amenable to analysis by electron microscopy.

An important advantage of the critical voltage technique over the other experimental methods is that it is not necessary to work with large single crystals, as the mag-

nifying power of the electron microscope can be used to localize the analysis on small grains ($\sim 1 \mu\text{m}$) or alloy phases, or even selected areas within a larger grain if inhomogeneity in composition is suspected. However, efforts to capitalize on the V_c effect for alloy studies have been handicapped until recently by the lack of a suitable theoretical framework for interpreting such measurements in terms of fundamental parameters.

The purpose of this brief article is to draw attention to the salient features of the V_c effect—particularly in terms of its limitations as well as the type of information which can (or cannot) be derived.

ORIGIN AND OBSERVATIONS OF THE V_c EFFECT

Detailed discussion of the basic electron scattering processes that give rise to the critical voltage effect and the mathematical formalism is beyond the scope of this article.^{7,8} However, the general features may be of interest to some readers, especially those who may already be aware that upon entering a crystalline specimen the energy of the electron beam, i.e., the current flow, is distributed among a series of standing waves. These recombine at the exit surface to form the directly transmitted and diffracted beams which form the various "spots" in the diffraction pattern. The amplitude and symmetry of the various Bloch waves depend on the electron beam energy, i.e., the accelerating voltage of the microscope, as well as the crystallographic orientation, average atomic weight (composition), and temperature of the specimen. At the "critical" voltage, pairs of highly excited Bloch waves may be equal in amplitude but exactly out of phase, leading to complete extinction of the corresponding diffracted beam, and producing related changes in the image.

In terms of diffraction physics, the criterion for the occurrence of V_c is the point of contact between two branches of the dispersion surface at a Brillouin zone boundary. This condition results when the values of the crystal structure factors F_g , F_{2g} , etc., bear a fixed ratio to one another. It is only through the structure factors that V_c depends on crystal parameters such as temperature, composition, short-range order (s.r.o), long-range order (l.r.o.), etc.

The consequences of destructive interference are only apparent within $\pm 5\%$ of V_c , which can range from 30 kV to 3,000 kV (Table I). Under favorable conditions, V_c can be measured to $\pm 0.5\%$. Examples of changes in the image and diffraction pattern very near V_c are illustrated in Figures 1 and 2.*

The diffraction process and the physics of the dependence of structure factors on crystal parameters are completely decoupled, and the former is quite accurately understood. For applications of the V_c effect, it is necessary to have a model for the dependence of structure factors on crystal para-

*The critical voltage can also be measured using convergent beam diffraction techniques in HVEMs modified to operate in this mode. See references 19 and 20 for theoretical and experimental papers on this method.

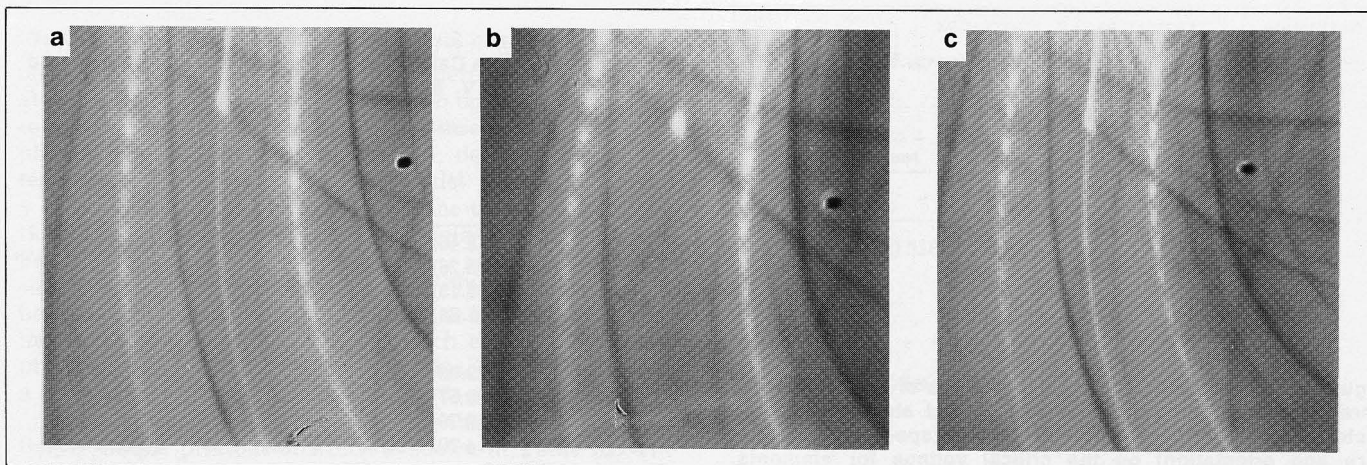


Figure 1. Illustration of the disappearance of the 400 bend contour in Fe-30%Cr at the critical voltage (285 kV). (a) 299 kV; (b) 285 kV; (c) 275 kV.

meters. In the following section, we give a heuristic description of models of the structure factor tailored to interpretation of V_c data.

APPLICATIONS OF THE V_c EFFECTS

Although V_c can be measured quite precisely, the experimenter usually has available the temperature variation of only one or two critical voltages at (for alloys) one or two compositions. Hence, the need for a few-parameter model of the structure factor. Such a model was immediately available to interpret elemental V_c data, but a model was not at first available to interpret alloy data.

Elements

The structure of the theory for elements is illustrated in Figure 3. Note that the item in any box is directly influenced by items connected by lines leading into the box. For example, the structure factors are determined by the lattice parameters, the mean-square displacements (commonly represented by $\langle \mu^2 \rangle$), and the atomic scattering factors, f . The atomic scattering factors depend on the detailed electron distribution of each atom.

What is not shown in Figure 3 is the relative sensitivities of the influences. It turns out that V_c is particularly sensitive to variations in F_g at low scattering angles (corresponding to rearrangement of outer atomic electrons), so the temperature variation of V_c can give highly accurate values of low-angle atomic scattering factors at reciprocal lattice points as well as the crystal Debye temperature, Θ_D ; or if Θ_D is regarded as known (from x-ray diffraction data), only room temperature V_c data are needed. Deviations of measured values of f at low angles from free-atom computed values give insight into the rearrangement of outer atomic electrons in the crystalline environment. Many such determinations exist in the literature; two examples are given in Table II.

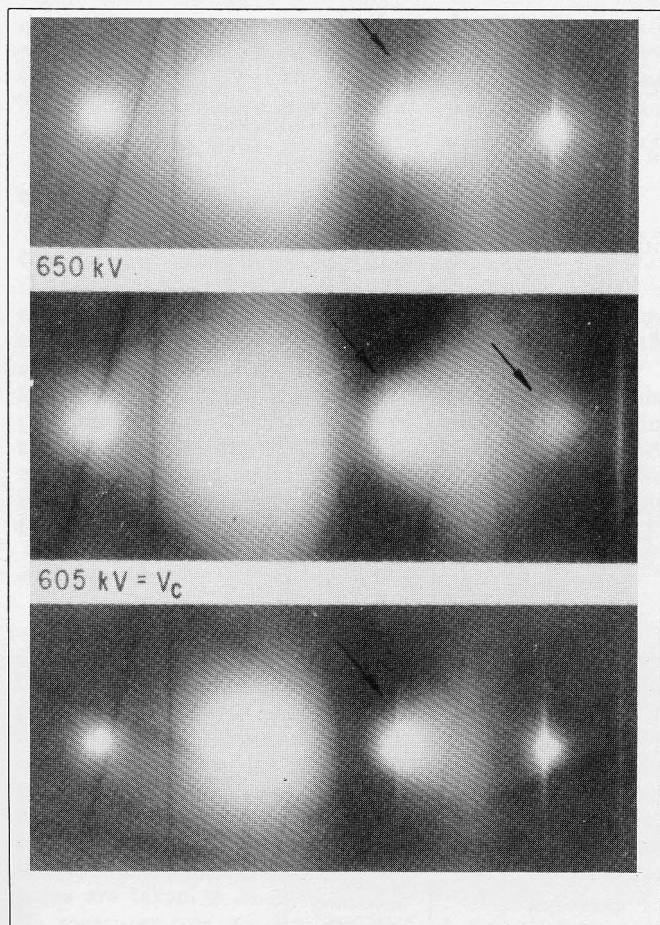


Figure 2. Illustration of the change in the symmetry of the Kikuchi lines for Cu at the critical voltage.

Table I: Representative Values of V_c at 300K

	kV	
	222	004**
fcc		
Al (395 K)*	436	911
Co (380 K)	279	555
Ni (390 K)	297	589
Cu (320 K)	316	602
Ag (220 K)	54	221
Au (185 K)	0	110
bcc	220	004
Cr (495 K)	264	~1298
Fe (425 K)	304	~1294
Mo (380 K)	35	789
W (315 K)	0	660
hcp	00.4	22.2
Mg (330 K)	678	310
Ti (355 K)	236	
Co (380 K)	286	
diamond cubic	333	440
Ge (290 K)	925	1028

* Debye Temperature Θ_D in K
 ** Indices of diffracting planes

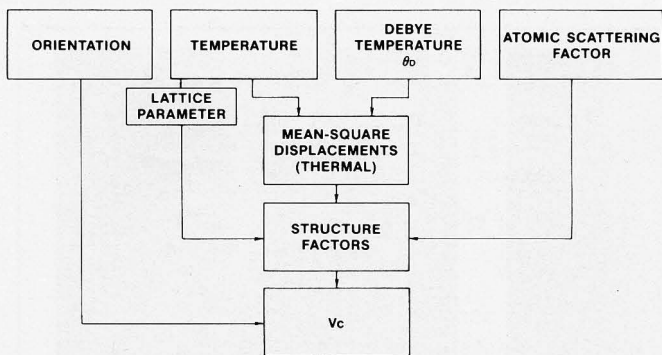


Figure 3. Schematic illustration of influence of intrinsic crystal parameters (Debye temperature — θ_D and atomic scattering factor — f_e) and experimental parameters (specimen temperature and orientation) on the critical voltage for elements. Measurements of V_c at several temperatures have now provided accurate values of θ_D and f_e for most elements.

Table II: X-Ray and Electron Scattering Amplitude and 100 kV Extinction Distance Calculated for Free Atoms and Determined for Crystals From V_c Measurements*

Reflection	f_x		f_e		$\xi_g \text{ \AA}$	
Fe (bcc)						
110	(18.46)	18.42	(2.97)	3.01	(270)	286.7
200	(15.26)	15.22	(2.11)	2.12	(395)	411.8
211	(13.15)	13.28	(1.68)	1.67	(503)	534.6
220	(11.64)	11.91	(1.41)	1.39	(606)	657.6
Cu (fcc)						
111	(22.06)	21.75	(2.89)	3.02	(242)	285.8
200	(20.67)	20.44	(2.60)	2.68	(281)	326.3
220	(16.79)	16.69	(1.91)	1.93	(416)	472.5
311	(14.79)	14.76	(1.62)	1.62	(505)	579.0

* f_x for x-rays; f_e for electrons (free atoms) - crystal

Table III: Representative Computer Printout Illustrating Typical Values of Parameters Used in the Calculations

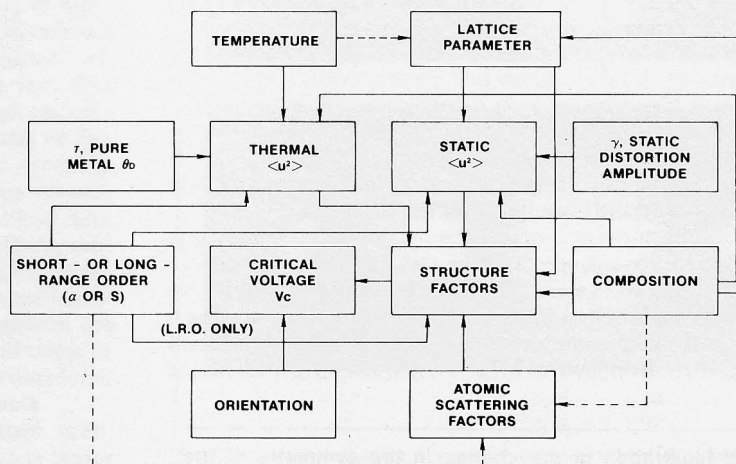
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FOR FE
DEBYE TEMPERATURE= 424.000 (DEG K)
ATOMIC WEIGHT = 55.847
LATTICE PARAMETER= 2.8664 (ANGSTROMS)
FOR SI
DEBYE TEMPERATURE= 300.000 (DEG K)
ATOMIC WEIGHT = 28.086
EFFECTIVE LAT PAR= 2.4872 (ANGSTROMS)

FIXED ALLOY PARAMETERS
DEBYE TEMP INTERPOLATION PARAMETER (TAU)= 1.0000
STATIC DISPL AMPLITUDE FACTOR (GAMMA) = 1.0000
VEGARD'S LAW DEVIATION PARAMETER (G) = .3023
110 SYSTEMATICS OF BCC

TEMPERATURE = 295.00 (DEG K)
LATTICE PARAMETER = 2.8557 (ANGS)
ETA = .0481
COMPOSITION = .9000 (MOLE F3 OF FE.)
MSD OF FE ATOMS = 1.5831E-02 (ANGS**2)
MSD OF SI ATOMS = 1.5831E-02 (ANGS**2)
THERMAL MSD OF FE AND SI ATOMS = 1.4627E-02 (ANGS**2)
STATIC MSD OF FE ATOMS = 1.2044E-03 (ANGS**2)
STATIC MSD OF SI ATOMS = 1.2044E-03 (ANGS**2)
ALLOY DEBYE TEMPERATURE = 418.36 (DEG K)
SHORT-RANGE ORDER PARAMETERS
ALPHA1 = .000
ALPHA2 = .000
ALPHA3 = .000
CRITICAL VOLTAGE
(1) 3-BEAM ESTIMATE = 341.18 (KV)
(2) RETHE ESTIMATE = 309.59 (KV)
(3) 17-BEAM ESTIMATE = 306.73 (KV)
CRITICAL VOLTAGE SENSITIVITIES
DVC/D COMPOSITION = -1.9348E 01 KV
DVC/D TEMPERATURE = -2.1270E-01 KV/DEG C
DVC/D ALPHA = -2.9053E 00 KV
  
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Figure 4. Schematic representation of influences of various crystal parameters on the critical voltage for alloys. Measurements of V_c for a range of compositions, specimen temperature and orientation can yield accurate values of the intrinsic parameters for the alloy systems (τ , γ and f_e^a , f_e^b) and a quantitative value of the state of order (α or S) for particular specimens.



Disordered Solid Solutions

For solid solutions, the structure factors depend not only on the time-varying vibrational (thermal) mean-square atomic displacements (m.s.d.) but also on static m.s.d. due to atomic radius differences. The structure of this more complicated model is shown in Figure 4; details are given in reference 11. In general, the two-model parameters τ and γ may be determined by analysis of the temperature variation of V_c at one composition in a fully disordered alloy. From a theoretical standpoint, τ and γ are expected in the simplest model to have values of unity. This expectation has been used in two ways: γ and τ fitted to a system's V_c data may have deviations from unity which can be interpreted physically, whereas for unknown systems, $\gamma = 1$, $\tau = 1$ gives a best estimate for the sensitivity of V_c to crystal parameters.

A computer program embodying this theory has been written, a sample printout of which is shown in Table III. The program has been used to compute the sensitivity of V_c to composition (via thermal and static m.s.d., lattice parameters and explicitly structure factors; see Figure 4); some examples are given in Table IV. The short-range order dependence of V_c comes from the thermal and static m.s.d. and, in principle, from the atomic scattering factors, although the theory does not encompass this last effect. For alloys with large atomic radius difference, the effect through the static m.s.d. is dominant, especially in f.c.c. alloys (e.g., CuAu, NiAu, CuSn); see Figure 5. Sensitivity of V_c to s.r.o. is generally less in bcc alloys. Some examples of V_c sensitivity to s.r.o. are shown in Table V.

When the atomic radius difference is negligible, the static displacements and s.r.o. (since its effect on thermal m.s.d. is weak) can be dropped from Figure 4, giving a simplified one-parameter (τ) model. An example of such a single-parameter fit to V_c data is shown in Figure 6. The case of FeCr is one in which electron transfer effects (dotted lines in Figure 4) are not obscured by static m.s.d.—this could be an interesting system to examine more carefully. When static m.s.d. are appreciable, one must use a more complicated two-parameter fit to γ and τ . The essential idea is the same, but too complicated to discuss here. See reference 10 for examples.

Ordered Alloys

For ordered alloys, the structure of the theory is similar to that for disordered alloys with short-range order, but with the additional feature that the long-range order parameter explicitly affects the structure factors.¹⁴ Examples of the effect of l.r.o. on V_c are shown in Table VI. Generally, the effect of V_c on l.r.o. is smaller than theory predicts.¹⁵⁻¹⁷ In long-range-ordered structures the effect of S and/or composition on the atomic scattering factors and bonding strengths (not explicitly taken into account by the model) may have a major effect on V_c .¹⁸ That is, the dotted lines in Figure 4 are actually major influences. This will be a fruitful area for future study.

SUMMARY AND DISCUSSION

Diligent readers who have persisted to this point should now be aware of the existence of a unique critical voltage phenomenon and appreciate the manner in which it can be used to obtain quantitative information about alloys. A few may wish to look up some of the key references (especially No. 10) to examine the theoretical aspects in detail and perhaps be inspired to gain access to one of the nation's HVEMs and make some measurements on alloys of special interest. The effort could be very rewarding, especially if pains are taken to do such a study thoroughly, i.e., make V_c measurements at several different temperatures and specimen orientations and for a range of alloy compositions and states of short-range order or clustering.

Table IV: Examples of the Effect of Alloying on V_c *

Solvent	Solute (10 mol.%)
Cu V_c (222) 316 kV	Si 346.0 kV
	Al 345.5
	Ni 316.7
	Au 182.0
Ni V_c (222) 589 kV	Sn 156.0
	Al 620.9 kV
	Cu 591.5
	Fe 586.2
	Mo 533.5
Fe V_c (220) 304 kV	Au 434.5
	Al 320.0 kV
	Si 314.0
	Co 307.0
	Cr 296.5
	Mo 235.0

*Illustrates magnitude and direction of V_c changes with alloying for room temperature measurements.

Table V: Examples of the Effect of Short Range Ordering or Clustering on V_c (400)*

Alloy	V_c (kV) ($\alpha^1=0$)	ΔV_c ($\alpha^1=0.2$)
Au ₅₀ Cu ₅₀	237	-69
Ag ₇₅ Mn ₁₅	265	-0.16
Co ₈₅ Fe ₁₅	558	-1.1
Cu ₉₀ Sn ₁₀	464	-120
Cr ₅₀ Mo ₅	867	20.8
Fe ₅₀ Si ₂₀	1342	8.8
V ₈₀ Pd ₂₀	1068	6.4

* α^1 is Cowley-Warren first nearest neighbor occupancy parameter 0 for random solid solution, ± 0.25 for maximum short-range ordering or clustering. Crystal oriented for 400 reflections.

Table VI: Effect of Long Range Ordering on the Critical Voltage

Alloy	S=0*	S=1**
Cu ₃ Au	222	~166
	400	~381
Ni ₃ Fe ¹⁶	222	~272
FeCo ¹⁶	220	~314
Ni ₃ Mo ¹⁷	400	~460

*S=0—random solid solution

**S=1—perfect long range order

The purpose, of course, will be to gain new insight into the fundamental nature of alloys, with a view to discovering new combinations with unusual magnetic, electronic, elastic, or transport properties. One such alloy could improve on or substitute for alloys which utilize components already in short supply.

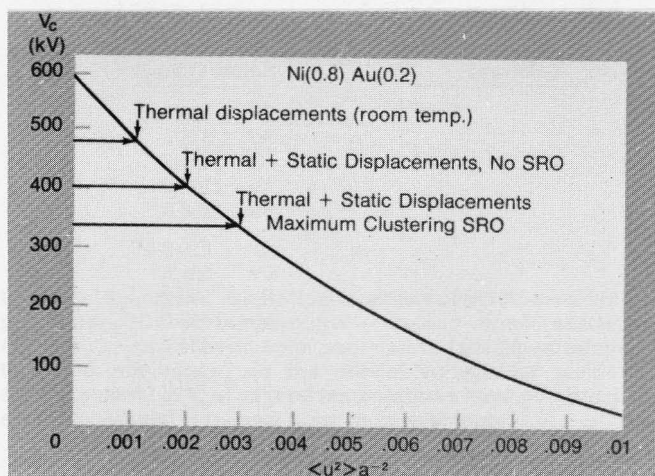


Figure 5. Illustration of the reduction of the V_c for Ni at K (595 kV) due to 1) thermal displacements at room temperature; 2) alloying with 20% Au; and 3) aging to produce maximum clustering.

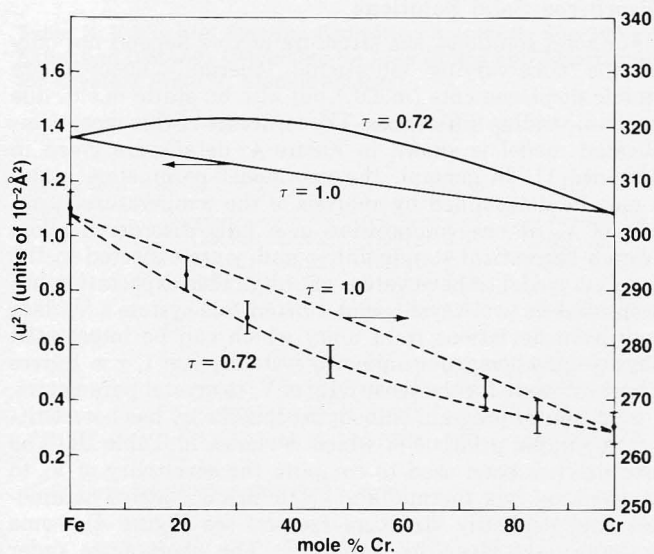


Figure 6. Illustration of the change in V_c with composition for Fe-Cr alloys. The parameter τ is related to the spring constants between adjacent atoms.

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C. Glenn Shirley is senior scientist at the Motorola Semiconductor Research and Development Laboratory, Phoenix, Arizona. He received his BSc (1969) and MSc (1970) from the University of Melbourne (Australia), and his PhD in physics from Arizona State University in 1974. He was a Post-Doctoral Fellow at Carnegie-Mellon University from 1973-76, and a visiting scientist at U.S. Steel Basic Research until he joined Motorola in 1977. His interests include theoretical and experimental analyses of lattice properties of materials, currently with emphasis on electronic properties of thin films. He has published 12 papers in these fields.

