Available online at www.sciencedirect.com
ScienceDirect
Scripta Materialia 60 (2009) 799–802
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

Transmission electron microscopy study of an electron-beam-induced phase transformation of niobium nitride

Jonghan Won,[a,*] James A. Valdez,[a] Muneyuki Naito,[b] Manabu Ishimaru[b] and Kurt E. Sickafus[a]

[a] *Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA*
[b] *Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan*

Received 28 October 2008; revised 14 January 2009; accepted 17 January 2009
Available online 2 February 2009

Tetragonal γ-NbN_{1-x} was irradiated with 300 keV electrons at room temperature to fluences from 1.8×10^{24}–5.4×10^{26} e/m^2. The superlattice structure in γ-NbN_{1-x} was observed using transmission electron microscopy and found to disappear at a fluence of 5.4×10^{26} e/m^2. During this process, displaced nitrogen atoms occupy vacant sites on the nitrogen sublattice. The final structure is a δ-phase (B1) structure. A randomized arrangement of N vacancies is responsible for the observed $\gamma \rightarrow \delta$ transformation.
Published by Elsevier Ltd. on behalf of Acta Materialia Inc.

Keywords: Niobium nitride; Phase transformation; Electron irradiation; Transmission electron microscopy; Order–disorder

Niobium nitride, NbN_{1-x} exhibits attractive physical properties such as exceptional hardness [1,2] and superconducting behavior in the case of stoichiometric NbN (critical temperature $T_c = 17$ K) [3,4]. In nitrogen (N) deficient NbN_{1-x}, it is known that N vacancies as well as large variations in the hypostoichiometric composition variable (x) lead to a variety of crystal structures: β-phase (hexagonal: $0.51 < x < 0.55$), γ-phase (tetragonal: $0.15 < x < 0.25$), δ-phase (cubic: $0.02 < x < 0.16$), and ε-phase (hexagonal: $0 < x < 0.08$). Due to the variety of crystallographic phases in this binary Nb–N system, researchers have performed detailed structure/property investigations on Nb–N compounds [5–9]. However, the most of these studies were performed using traditional methods such as high temperature annealing or cooling under vacuum or N_2 atmosphere. Another possibility is to use energetic particle irradiation to induce structural changes, including order-to-disorder (O–D) and crystal-to-amorphous (C–A) phase transformations [10–13]. In the case of the Nb–N system, Skelton et al. [14] reported that phase transformations, such as hexagonal β-Nb_2N to cubic δ-NbN_{1-x} and cubic δ-NbN_{1-x} to hexagonal ε-NbN phase changes, occurred under irradiation with a variety of ions. Traditionally, energetic electron irradiation and concomitant, in-situ transmission electron microscopy (TEM) observation have been shown to be useful methods for studying structural evolution under irradiation [15,16]. In this study, we performed 300 keV electron beam irradiations of γ-phase NbN_{1-x} and found a phase transformation to another crystalline NbN_{1-x} phase, an irradiation-induced transformation not previously observed. In this report, we describe the atomistic structure of this metastable phase and discuss its formation processes.

A commercial niobium nitride (NbN_{1-x}) sputtering target (Kurt J. Lesker Company) with a purity of 99.5% was used as a pristine sample. Grazing incidence X-ray diffraction (GIXRD, Bruker AXS D8 advanced X-ray diffractometer) measurements (results not shown) indicated that the pristine NbN_{1-x} sample is isostructural with γ-$NbN_{0.75}$ with tetragonal lattice parameters $a = 0.439$ and $c = 0.867$ nm. γ-$NbN_{0.75}$ (γ-Nb_4N_3) possesses a crystal structure that is a derivative of the cubic rock salt (B1) structure, but with a tetragonal super unit cell due to ordering of N vacancies along the c-axis (space group I4/*mmm*). According to the previous studies [17–19], the c parameter depends on the N content of the γ-NbN_{1-x} phase, ranging from 0.863 nm for $x = 0.25$ to 0.867 nm for $x = 0.15$. This suggests that the pristine γ-NbN_{1-x} sample used in this study is a sub-stoichimetric composition, but is relatively N-rich with x closer to 0.15 than to 0.25.

* Corresponding author. Tel.: +1 505 903 1033; e-mail: jhwon@lanl.gov

1359-6462/$ - see front matter Published by Elsevier Ltd. on behalf of Acta Materialia Inc.
doi:10.1016/j.scriptamat.2009.01.023

For the electron beam irradiation study, a TEM specimen was prepared in plan-view geometry. This plan-view sample was examined at room temperature in a JEOL JEM 3000F TEM instrument operating at 300 kV. Electron irradiation experiments were carried out by focusing the electron beam onto small regions of electron transparent material (a typical irradiated region was ~100 nm diameter). During these electron beam irradiation experiments, the incident electron flux, measured using a faraday cup, was approximately 1.8×10^{24} e/m^2 s. Irradiations were performed over a range of fluences from 1.8×10^{24}–5.4×10^{26} e/m^2. Irradiations were performed with the electron beam aligned along both low- and high-index crystallographic directions. No crystal-orientation dependences of the structural changes described in this report were observed. Both high-resolution TEM (HRTEM) images and electron diffraction patterns (EDPs) were recorded on imaging plates. These were typically obtained along low-index crystallographic directions. Simulations of EDPs were carried out with SingleCrystal software (CrystalMaker software Ltd.).

To examine irradiation-induced structural changes of γ-NbN_{1-x}, we performed 300 keV electron beam irradiations on this material. Figure 1(a) shows an HRTEM image of the unirradiated specimen, along with its fast Fourier transformation (FFT) diffractogram. Diffraction analysis revealed that the FFT pattern shown in Figure 1(a) is consistent with the tetragonal γ-$NbN_{0.75}$ structure, viewed along a [1 1 0] orientation. The HRTEM image shown in Figure 1(a) shows a doubly-redundant periodicity along the [0 0 1] direction. An HRTEM image obtained after electron beam irradiation to the maximum electron fluence used in this study (5.4×10^{26} e/m^2) is shown in Figure 1(b). It is apparent that the double periodicity fades and disappears after irradiation. Consequently, the first-order reflections in the FFT diagram of Figure 1(b) are significantly diminished in intensity. These results suggest that γ-NbN_{1-x} transforms to another crystalline phase. These results also led us to conclude that the irradiation-induced structure is cubic because the symmetry of the FFT pattern in Figure 1(b) looks remarkably similar to that of a face-centered cubic (fcc) Bravais lattice, viewed along a <1 1 0> direction.

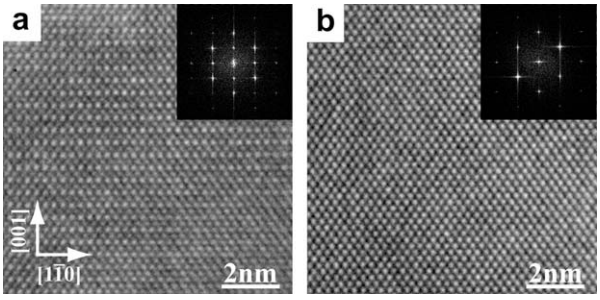

Figure 1. HRTEM images and corresponding FFT patterns (inset) obtained from pristine and electron irradiated NbN_{1-x}. (a) Pristine γ-NbN_{1-x} viewed along a $[1\,1\,0]_\gamma$ direction; (b) NbN_{1-x} following electron beam irradiation using 300 keV electrons to a fluence of 5.4×10^{26} e/m^2 at room temperature. The HRTEM image and the corresponding FFT pattern in (a) clearly show a double periodicity along the $[0\,0\,1]_\gamma$ direction. In the HRTEM image and corresponding FFT pattern in (b), the atomic superlattice and superlattice reflections are completely faded away.

In Figure 2, we compare and contrast experimental EDPs obtained in various low-index crystallographic orientations with simulated EDPs. The experimental EDPs before irradiation are shown in Figure 2(a, c and e) and after irradiation to the maximum electron fluence used in this study (5.4×10^{26} e/m^2) in Figure 2(b, d and f). The simulated EDPs for the pristine γ-phase structure are shown in Figure 2(a', c' and e'), while Figure 2(b', d' and f') show simulated EDPs assuming a cubic δ-phase structure forms upon irradiation (δ-NbN_{1-x} is a B1 rocksalt structure with an fcc Bravais lattice). Before irradiation, the experimental EDPs exhibit superlattice reflections in addition to strong fundamental reflections. During irradiation, the superlattice reflections were observed to gradually decrease in intensity and then vanish completely. For the electron flux conditions used here, the total irradiation time for the superlattice reflections to disappear completely was less than 5 min, corresponding to a fluence of ~5.4×10^{26} e/m^2. The simulated EDPs shown in Figure 2 are in very good qualitative agreement with the experimental EDPs. Thus, we conclude that a $\gamma \rightarrow \delta$ phase transformation was induced by the 300 keV electron beam irradiations.

To rationalize the $\gamma \rightarrow \delta$ transformation, consider kinetic energy transfer from incident electrons to target

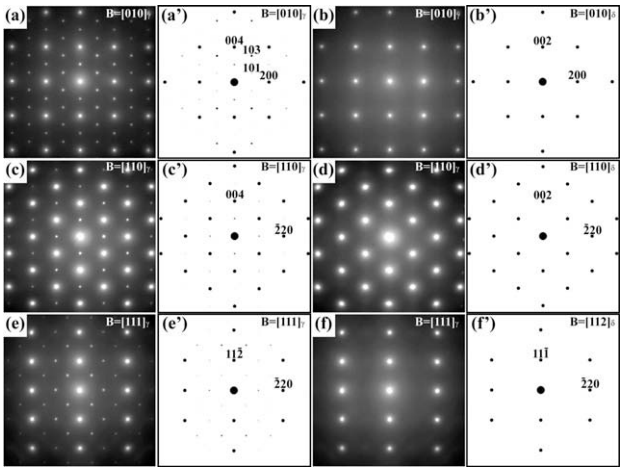

Figure 2. Electron diffraction patterns (EDPs), both experimental and simulated for pristine and irradiated NbN_{1-x}. Electron beam orientations are as follows: (a and b) $[0\,1\,0]_\gamma$, (c and d) $[1\,1\,0]_\gamma$, and (e and f) $[1\,1\,1]_\gamma$, where γ represents the tetragonal unit cell of the pristine γ-NbN_{1-x} phase. EDPs (a, c and e) were obtained prior to prolonged electron irradiation. EDPs (b, d and f) were obtained following 300 keV electron irradiation to a fluence of 5.4×10^{26} e/m^2 at room temperature. Superlattice reflections in (a, c and e) before irradiation are not apparent in (b, d and f) after electron irradiation. (a', c' and e') and (b', d' and f') show simulated EDPs. The incident beam directions in (a', c' and e') correspond to those in (a, c and e) (labeled γ for γ-phase NbN_{1-x}), while (b', d' and f') correspond to $[0\,1\,0]_\delta$, $[1\,1\,0]_\delta$, $[1\,1\,2]_\delta$, where δ represents the cubic unit cell of δ-NbN_{1-x}. Simulated EDPs in (a', c' and e') are based on a pristine, tetragonal γ-NbN_{1-x} structure with 85% N factional occupation in an ordered arrangement on the N sublattice. Simulated EDPs in (b', d' and f') are based on a cubic, δ-NbN_{1-x} with 85% N fractional occupation. The N atoms in the cubic δ-NbN_{1-x} model occupy randomly sites on a face-centered cubic (fcc) N sublattice.

Nb and N atoms. The maximum possible kinetic energy transfer (relativistically corrected) between an electron of mass m and a target atoms of mass M is given by $2E_o(E_o + 2mc^2)/Mc^2$ where E_o is the incident electron beam energy, and c is a speed of light. For $E_o =$ 300 keV, the maximum energy transfer to Nb and N are 9 and 60 eV, respectively. If the displacement threshold energies, E_d, for both Nb and N atoms are in the range 20–60 eV (typical values for ceramics) [20], N atoms are far more likely to be displaced by 300 keV electrons than Nb atoms.[1] We estimate that the "Bragg–Williams" long-range order parameter [21] for N-ordering can be decreased from 1 (ordered structure) to 0 (disordered structure) upon displacing N atoms to a level of ~1/7 dpN (displacements per N atom). This disorder should equate to the complete extinction of superlattice reflections due to ordering of N vacancies in NbN_{1-x}. We observed this complete extinction to occur at a fluence of 5.4×10^{26} e/m^2. Using our electron fluence and assuming this fluence achieves a displacement damage dose of ~ 0.14 dpN (one atom in seven on the N sublattice), we estimate that the displacement cross-section, σ_d, for 300 keV electrons is approximately 2.5 barns. Our cross-section calculation is based on the displacement cross-section analysis presented by Seitz and Koehler [22], who use a relativistic form of the Mott–Rutherford differential scattering cross-section due to McKinley and Feshbach [23]. A 2.5 barn cross-section corresponds to a displacement threshold energy, E_d, for N atoms, of about 44 eV. Though the magnitude of this E_d seems reasonable, it is significantly larger than E_d values found in other similar non-stoichiometric compounds. It has been shown in several non-stoichiometric compounds that the *deficient* chemical species can be characterized by very low E_d values of only a few eV (5.4 eV in VC_{1-x} [24], 7.8 eV in $V_{1-x}O$ [25]; 2.8–8.4 eV in $YBa_2Cu_3O_{7-x}$ [26]). It is important to note that we have not considered reordering effects, specifically radiation enhanced thermal reordering [27], in the analysis described above. However, reordering is probably important since our irradiations were carried out at room temperature. Thus, our displacement threshold estimate, $E_d^N = 44$ eV, is an upper limit (since not all the defects we produce under irradiation are retained). In any case, we are currently investigating the $\gamma \rightarrow \delta$, O–D transformation, at lower electron accelerating voltages and lower temperatures, to determine if E_d^N, is, in fact, lower than our current estimate.

We propose that the observed $\gamma \rightarrow \delta$ transformation is induced by the displacement of N atoms from N lattice sites into "vacant" sites on the N sublattice. Simultaneous with these N sublattice disordering events, the Nb sublattice undergoes small local relaxations from a distorted to a perfect fcc cation sublattice. Together, these anion displacements and cation relaxations account for the $\gamma \rightarrow \delta$ phase transformation. It must be emphasized that Nb atoms need not be displaced in order to induce a $\gamma \rightarrow \delta$ transformation; they need only "relax" into their ideal, fcc lattice positions.

We also can rationalize the observed, irradiation-induced $\gamma \rightarrow \delta$ transformation, by analogy to the thermally-induced $\gamma \rightarrow \delta$ phase transformation, as recorded on the temperature–composition (T–C) phase diagram for the Nb–N binary system (Figure 3) [28]. According to the T–C diagram in Figure 3, γ-NbN_{1-x} transforms to δ-NbN_{1-x} upon heating to 1250–1600 °C, depending on N composition. From a crystallographic perspective, this transformation is enabled by the introduction of Frenkel pair defects on the N sublattice (Frenkel disorder). With increasing temperature, N atoms move gradually from γ-phase, ordered N lattice sites into vacant sites on the N sublattice. When the N sublattice becomes effectively randomized (N vacancies fully disordered), the resultant crystal structure is indistinguishable from the parent rocksalt (B1) crystal structure (assuming local Nb atomic relaxations accompany the N sublattice disordering reactions). At this point, the $\gamma \rightarrow \delta$ phase transformation is complete. The same phase transformation apparently occurs under electron irradiation. Using 300 keV electrons, N atoms are preferentially displaced from their γ-phase lattice sites, while Nb atoms remain, more or less, fixed and undisturbed at their fcc sublattice sites. Eventually, the anion (N) sublattice becomes randomized and the resultant crystal structure mimics the rocksalt (δ-phase) structure. This correspondence between irradiation damage accumulation and T–C phase diagrams has been noted in previous irradiation damage studies (for example, see Ref. [29] for metal alloys and intermetallics; Ref. [30] for oxides). The systems that exhibit O–D transformations that are most

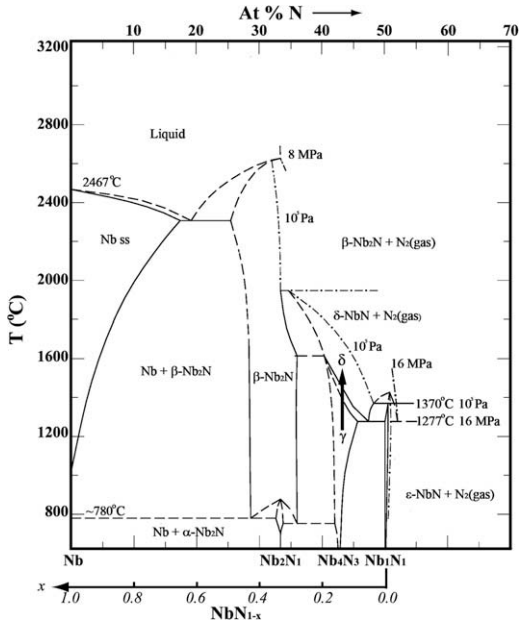

Figure 3. The temperature–composition (T–C) diagram for the Nb–N system according to Ref. [27]. The arrow on the diagrams indicates the temperature–composition region where the thermally-induced $\gamma \rightarrow \delta$ phase transformation is observed. This same transformation was observed in this study, but the transformation was induced by electron irradiation.

[1] The maximum energy transfer to a niobium atom in a 300 keV electron irradiation is actually 27 eV, via a two-stage process of: (1) a head-on electron–oxygen interaction; followed by (2) a head-on oxygen–niobium collision. Obviously, the cross-section for this two-stage process must be very low.

similar to the NbN_{1-x} $\gamma \rightarrow \delta$ transformation observed here are VC_{1-x} [24], $V_{1-x}O$ [25], $Y_1Ba_2Cu_3O_{7-x}$ [26], and Ni_2Al_3 [31]. All of these compounds transform to higher symmetry phases via vacancy disordering on the atom deficient sublattice (C in the case of VC_{1-x}; V in the case of $V_{1-x}O$; O in the case of $Y_1Ba_2Cu_3O_{7-x}$; Ni in the case of Ni_2Al_3). These transformations can be induced either by heating or by energetic particle irradiation. We note that the specific mechanisms for the electron irradiation-induced O–D transformations remain unclear. Several concepts have been proposed in the literature, including subthreshold displacements [32], cooperative displacement and diffusion of the deficient species [33], and crystallographic orientation effects that, in turn, may lead to focusing collisions and related phenomena (see, e.g., Ref. [32]). Regardless of the mechanism(s) at play, the observed $\gamma \rightarrow \delta$ phase transformation is most certainly a consequence of the accumulation of Frenkel pairs on the N sublattice.

In summary, 300 keV electron beam irradiations were performed on NbN_{1-x} at room temperature over a fluence range from 1.8×10^{24}–5.4×10^{26} e/m^2, to test for possible irradiation-induced structural changes. X-ray and electron diffraction measurements indicated that the pristine samples used in these experiments are nitrogen-rich compounds with a tetragonal γ-phase structure (ideal γ-phase has a stoichiometry of $NbN_{0.75}$ (Nb_4N_3) but our pristine samples are approximately $NbN_{0.85}$, based on lattice parameter measurements). Electron diffraction observations revealed that superlattice reflections corresponding to the ordered γ-phase diminished and eventually vanished by an electron fluence of $\sim 5.4 \times 10^{26}$ e/m^2. These results suggest that the tetragonal γ-phase structure is transformed to a cubic δ-phase (rocksalt-type, B1) structure under electron beam irradiation. This hypothesis was confirmed by comparison of experimental and simulated EDPs. This $\gamma \rightarrow \delta$ transformation presumably occurs because N atoms are ballistically displaced by incident electrons into vacant sites on the N sublattice in the N-deficient γ-structure (other mechanisms may also be involved; it was not the intent of this study to establish the mechanism(s) responsible for the transformation). Ballistic knock-on is a stochastic process and eventually the vacant N sites are randomly distributed on the N sublattice. Concurrent with vacancy disordering on the N sublattice, the Nb sublattice undergoes small local atomic relaxations from a distorted lattice, characteristic of the γ-phase, to a perfect fcc lattice. The final irradiation-induced structure is indistinguishable from a cubic rocksalt (B1) structure. We estimate that the displacement cross-section, σ_d, for the N disordering reaction (i.e., Frenkel pair formation) is $\sim$2.5 barns for 300 keV electrons, which leads to an estimate for the N displacement threshold energy, $E_d \sim 44$ eV.

This research was supported by the U.S. Department of Energy (DOE), Office of Basic Sciences, Division of Materials Sciences and Engineering.

[1] B.M. Ennis, A. Madan, W.S. Slaugher, S.A. Barnett, S.X. Mao, J. Appl. Phys. 94 (2003) 6892.
[2] H. Holleck, J. Vac. Sci. Technol. A4 (1986) 2661.
[3] G. Aschermann, E. Friderich, E. Justi, J. Kramer, Z. Phys. 42 (1941) 349.
[4] T. Mitsuoka, T. Yamashita, T. Nakazawa, Y. Onodera, Y. Saito, T. Anayama, J. Appl. Phys. 39 (1968) 349.
[5] Von G. Brauer, R. Esselborn, Z. Anorg. Chem. 309 (1961) 151.
[6] S.-J. Kim, H.F. Franzen, W. Lengauer, J. Less-Common Met. 160 (1990) 193.
[7] N. Terao, Jpn. J. Appl. Phys. 4 (1965) 353.
[8] C.H. de Novion, J.P. Landesman, Pure Appl. Chem. 57 (1985) 1391.
[9] W. Lengauer, P. Ettmayer, Monatshefte für Chemie 117 (1986) 275.
[10] J. Adam, R.A. Dugdale, Nature 168 (1951) 581.
[11] M. Ishimaru, I.V. Afanasyev-Charkin, K.E. Sickafus, Appl. Phys. Lett. 76 (2000) 2556.
[12] M. Tang, J.A. Valdez, P. Lu, G.E. Gosnell, C.J. Wetteland, K.E. Sickafus, J. Nucl. Mater. 328 (2004) 71.
[13] M. Tang, P. Lu, J.A. Valdez, K.E. Sickafus, Philos. Mag. 86 (2006) 1597.
[14] E.F. Skelton, M.R. Skokan, E. Cukauskas, J. Appl. Cryst. 14 (1981) 51.
[15] L.W. Hobbs, J. Am. Ceram. Soc. 62 (1979) 267.
[16] L.M. Wang, Nucl. Instrum. Meth. B 141 (1998) 312.
[17] A.N. Christensen, Acta Chem. Scand. A 30 (1976) 219.
[18] G. Heger, O. Baumgartner, J. Phys. C 13 (1980) 5833.
[19] A.Yu. Chervyakov, V.A. Somenkov, Ya.S. Umanskii, S.Sh. Shil'shtein, V.P. Yanchur, Fizika metallov i metallovedenie 57 (1984) 165.
[20] S.J. Zinkle, C. Kinoshita, J. Nucl. Mater. 251 (1997) 200.
[21] W.L. Bragg, E.J. Williams, Proc. R. Soc. A 151 (1935) 540.
[22] F. Seitz, J.S. Koehler, Solid State Physics, vol. 2, Academic Press, New York, 1956.
[23] W.A. McKinley, H. Feshbach, Phy. Rev. 74 (1948) 1759.
[24] J.D. Venables, R.G. Lye, Philos. Mag. 19 (1969) 565.
[25] P.S. Bell, M.H. Lewis, Philos. Mag. 29 (1974) 1175.
[26] S.K. Tolpygo, J.-Y. Lin, M. Gurvitch, S.Y. Hou, J.M. Phillips, Phys. Rev. B 53 (1996) 12462.
[27] K.-Y. Liou, P. Wilkes, J. Nucl. Mater. 87 (1979) 317.
[28] E.K. Storms, Special Report to the Phase Equilibria Program, Am. Ceram. Soc. Westerville, Ohio, 1989.
[29] M. Nastasi, J.W. Mayer, J. Mater. Sci. Rep. 6 (1991) 1.
[30] K.E. Sickafus, R.W. Grimes, J.A. Valdez, A. Cleave, M. Tang, M. Ishimaru, S.M. Corish, C.R. Stanek, B.O. Uberuaga, Nat. Mater. 6 (2007) 217.
[31] M. Nastasi, L.S. Hung, H.H. Johnson, J.W. Mayer, J.M. Williams, J. Appl. Phys. 57 (1985) 1050.
[32] C.L. Snead Jr., R.C. Birtcher, M.A. Kirk, J. Nucl. Mater. 244 (1997) 273.
[33] M.A. Kirk, M.C. Baker, J.Z. Liu, D.J. Lam, H.W. Weber, in: H.W. Weber (Ed.), High T_c Superconductors, Plenum Publishing Corp., New York, 1988, pp. 59–65.