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X-Ray *K*-Absorption Fine Structure of Niobium and Copper at Cryogenic Temperatures

THOMAS A. BOSTER
Physics Department, Oklahoma City University, Oklahoma City, Oklahoma

AND

JOHN E. EDWARDS
Physics Department, Ohio University, Athens, Ohio

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The x-ray *K*-absorption fine structure of niobium and copper has been investigated at 300, 77, and 4.2°K to determine the fundamental dependence of fine-structure variations on the Debye temperature and the location of scattering potentials. The increase in the amplitude of the fine-structure fluctuations with a lowering of absorber temperature and the dependence of fine-structure temperature variations on the Debye temperature were found to agree with recent theory. No significant change was found in the energy positions of the fine structure as the temperature of the two absorbers was lowered.

INTRODUCTION

THE absorption coefficient on the high-energy side of the x-ray *K*-absorption edge is not a linear function of energy. Absorption irregularities on the high-energy side of the *K* edge are found to extend several hundred eV beyond the *K* edge.[1] The value of the absorption coefficient fluctuates quite rapidly at energies close to the *K* edge, but at higher energies the fluctuations are less rapid and diminish in amplitude until at several hundred eV from the *K* edge the fluctuations vanish. These fluctuations are referred to as x-ray fine structure.

The object of this research was to investigate the x-ray *K*-absorption fine structure of niobium and copper at 300, 77, and 4.2°K to determine any plasmon oscillation energy shifts in the fine structure when the niobium was in a superconducting state and to determine the fundamental dependence of fine-structure temperature variations on the Debye temperature of the two metals according to recent theory.[2,3] Niobium was chosen because it has a high superconducting transition temperature of 9.2°K and a low Debye temperature of 252°K. Copper was chosen because it is the basic metal used in most theoretical studies of x-ray fine structure and because it has a relatively high Debye temperature of 339°K.

Although many experimenters have worked in the region from room temperature up to the melting point of the metal, only a few have done work at cryogenic temperatures.[4,5] Preliminary experimental work associated with this research[6] indicated that the fluctuations in niobium fine structure were significantly increased as the temperature of the absorbing foil was lowered from 300 to 4.2°K.

THEORY

The fundamental theories on x-ray absorption fine structure have been presented in two review articles by Parratt[7] and Azároff.[8] Although Kronig,[9] Hayasi,[10] Sawada,[11] and Vishnoi[12] have formulated theories which apply to basic x-ray absorption fine structure, the recent theory of Kozlenkov,[13] which is based on the earlier work of Kostarev,[14] applies more directly to the temperature effect in x-ray absorption fine structure. A very important feature of Kozlenkov's theory is that Shmidt[3] has been able to apply it directly to determine a temperature dependence which agrees quantitatively with some experimental results.

Kozlenkov's theory is based on the interference between the ejected photoelectron wave and the scattering potentials created by the nearest-neighbor atoms, next-nearest-neighbor atoms, etc. The atoms are pictured as being arranged in concentric spheres about the atom ejecting the photoelectron wave. Kozlenkov calls these spheres of radii r_s coordinating spheres. Therefore, the propagation of the ejected photoelectron wave through the crystal lattice can be represented by a wave function resulting from a superposition of the initial photoelectron wave and the waves scattered by the neighboring coordinating spheres. It should also be noted that Kozlenkov's theory incorporates the quantum-mechanical phase shift of the primary wave relative to the wave scattered by the neighboring atoms in the coordinating spheres.

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[1] R. L. Kronig, Z. Physik **70**, 317 (1931).

[2] A. I. Kozlenkov, Izv. Akad. Nauk SSSR, Ser. Fiz. **25**, 957 (1961); **27**, 364 (1963).

[3] V. V. Shmidt, Izv. Akad. Nauk SSSR, Ser. Fiz. **25**, 977 (1961); **27**, 384 (1963).

[4] G. N. Ronami and O. P. Sharkin, Izv. Akad. Nauk SSSR, Ser. Fiz. **27**, 835 (1963).

[5] F. W. Lytle, Develop. Appl. Spectr. **2**, 285 (1963).

[6] T. A. Boster and J. E. Edwards, Bull. Am. Phys. Soc. **10**, 607 (1965).

[7] L. G. Parratt, Rev. Mod. Phys. **31**, 616 (1959).

[8] L. V. Azároff, Rev. Mod. Phys. **35**, 1012 (1963).

[9] R. L. Kronig, Z. Physik **75**, 191 (1932); **75**, 468 (1932).

[10] T. Hayasi, Sci. Repts. Tôkoku Univ. **33**, 123 (1949).

[11] T. Shiraiwa, T. Ishimura, and M. Sawada, J. Phys. Soc. Japan **13**, 847 (1958).

[12] A. N. Vishnoi and B. K. Agarwal, Proc. Phys. Soc. (London), **89**, 799 (1966).

[13] A. I. Kozlenkov, Izv. Akad. Nauk SSSR, Ser. Fiz. **28**, 794 (1964).

[14] A. I. Kostarev, Zh. Eksperim. i Teor. Fiz. **19**, 413 (1949).

One result of the Kozlenkov-Shmidt theory[2,3] is that the variable part of the absorption coefficient is given by

$$\bar{\mu}=\sum_s A_sN_s\sin(2kr_s+2\eta_1)\times\exp\left\{-\frac{15.4mEr_s^2}{k_BM\Theta v_0^{2/3}}\left[F\left(\frac{T}{\Theta}\right)+\frac{1}{2}\right]\right\}, \quad (1)$$

where A_s is the amplitude at the point of the central atom of the wave scattered by an atom of the sth coordinating sphere, N_s is the number of atoms in the sth coordinating sphere, k is the wave number of the electron ejected from the central atom, r_s is the radius of the sth coordinating sphere, η_1 is the phase of the scattered wave, m is the mass of the electron, E is the energy of the ejected electron, k_B is Boltzmann's constant, M is the mass of the atom, T is the temperature of the absorber, Θ is the Debye temperature, v_0 is the volume per atom, and

$$F(T/\Theta)=(e^{\Theta/T}-1)^{-2}+\tfrac{1}{3}(T/\Theta)f_D(T/\Theta), \quad (2)$$

where

$$f_D\left(\frac{T}{\Theta}\right)=3\left(\frac{T}{\Theta}\right)^3\int_0^{\Theta/T}\frac{e^xx^4}{(e^x-1)^2}dx, \quad (3)$$

and x represents the value of $\hbar\omega/k_BT$. It is seen in Eq. (1) that the strongest contribution to the absorption coefficient will come from the coordinating spheres having smaller radii. At high energy, the E in the exponential term in Eq. (1) will reduce the amplitude of the fluctuation in the absorption coefficient. The one-half term in the exponential in Eq. (1) accounts for the zero-point quantum-mechanical oscillations of the atoms in the absorber lattice. This suggests that large amplitude fluctuations in $\bar{\mu}$ would not be seen even if the absorber was at 0°K. The $F(T/\Theta)$ function indicates that elements with high values of Debye Θ should exhibit less temperature variation at the lower temperatures. At low temperatures, where the outer coordinating spheres become a little more significant as scattering potentials, one would expect additional structure to be present.

EXPERIMENTAL

The x-ray K-absorption spectra in this research were obtained with a bent-crystal (Cauchois-type) spectrograph. The geometry of the spectrometer and the location of its component parts are shown in Fig. 1. The α-quartz crystal was bent to a radius of curvature of 101.7 cm.

A 0.8-mm-thick α-quartz crystal was used to investigate niobium. The Bragg diffraction was from the $31\bar{4}0$ planes which have a d spacing of 1.1802 Å. In the vicinity of the K edge of niobium, this geometry results in a dispersion of about 65 eV/mm.

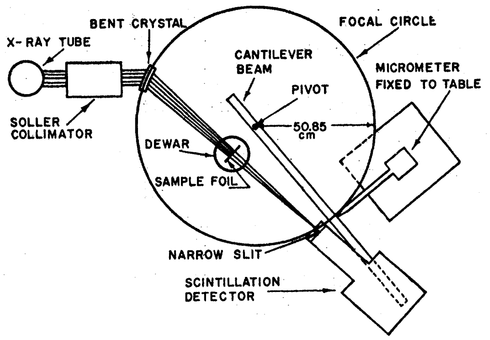

FIG. 1. X-ray spectrometer.

The same type crystal was used to investigate the copper region. However, previous work[15] indicated that a thinner 0.2-mm α-quartz crystal would increase the yield of monochromatic x rays at copper K-edge energies. In the investigation of copper the Bragg diffraction was from the $10\bar{1}0$ planes of the α-quartz crystal which make an angle of 15° 45′ with the $31\bar{4}0$ planes. The $10\bar{1}0$ planes have a d spacing of 4.2461 Å and this results in a dispersion of about 54 eV/mm in the vicinity of the K edge of copper.

The x-ray tube used in this research was an OEG 50-S manufactured by the Machlett Co. The mechanical part of the photon-counting system is shown in Fig. 1. The monochromatized x ray beam which is focused at the focal circle is intercepted by a narrow slit. The slit can be moved along the focal circle of the spectrometer by a micrometer which has a least count of 0.010 mm. A molybdenum slit (0.038 mm wide) was used in the niobium region and a brass slit (0.114 mm wide) was used in the copper region.

The photon counting system consisted of a thallium-activated sodium iodide crystal, a low-noise photomultiplier tube, and a low-noise preamplifier. The signals were further amplified by a window amplifier. Total variation in the stability of the counted x-ray beam was about 1%.

The resolution of the spectrometer was tested by examining the WLβ1 emission line which has a natural width of 7.1 eV. The uncorrected width of the WLβ1 emission line was found to be 8.4 eV when the 0.038 mm slit was used. The uncorrected width of the WLβ1 emission line was found to decrease to less than 8 eV as the slit width was reduced. Low counting rates made it necessary to maintain the slit width at 0.038 mm. The MoKβ1,3 doublet which has a separation of 17.5 eV and is located 605 eV above the niobium K edge was easily resolved and served as a convenient energy reference.

The "cold-finger"-type Dewar was designed to have a special demountable sample holder which would be contiguous to the liquid helium chamber. At atmospheric pressure (with a full outer chamber of liquid

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[15] T. A. Boster and J. E. Edwards, J. Chem. Phys. 36, 3031 (1962).

nitrogen) the Dewar would hold the 5 liters of liquid helium for approximately 24 h. Beryllium windows 0.0432 cm thick were placed over the 1.90-cm-diam opening through which the x-ray beam would pass and 30-μ aluminum foil was placed over the two holes in the copper heat shield which was maintained at liquid nitrogen temperature. A 100-Ω Allen Bradley carbon resistor was mounted in the sample holder next to the thin sample foil to monitor the temperature. During the liquid helium runs the sample temperature was found to be 4.2±0.5°K in all cases.

EXPERIMENTAL RESULTS FOR NIOBIUM

The absorption limit fine structure of niobium at room temperature was obtained by placing the thin niobium foil in a special form attached to a micrometer head. In this way the niobium foil could be rotated out of the beam to obtain an I_0 count and then accurately returned to its original position for the I count. Values of I_0 divided by I resulted in graphs of the $\ln(I_0/I)$ or μx as a function of photon energy.

Graphs were obtained for four different niobium absorber thicknesses of 12.7, 20, 33, and 100 μ. About seven trials were run at each absorber thickness. Although a significant thickness effect was not found, these trials did produce very accurate data on the niobium K edge and fine structure at room temperature. A typical absorption curve for the 33-μ foil is presented in Fig. 2.

After the preliminary room-temperature data had been taken, a 20-μ niobium foil was mounted in the low-temperature Dewar. The count rate of the transmitted beam coming through the 1.90-cm-diam sample holder on the high-energy side of the niobium K edge was about 10^4 counts/min. It was decided to take 2-min counts every 0.01 mm in the region close to the main K edge and every 0.05 mm in the region beyond. Special attention was given to the 0–50-eV region since this is where the plasmon oscillation shifts were expected to occur. Several runs were made through the 1.90-cm-diam sample holder mounted in the Dewar with the niobium foil removed. This was necessary to determine the I_0 spectrum. When the Dewar was filled with liquid helium and positioned in the x-ray beam, it was not possible to remove it every other count to obtain a value of I_0. A total of about 16 h was necessary to finish one complete run.

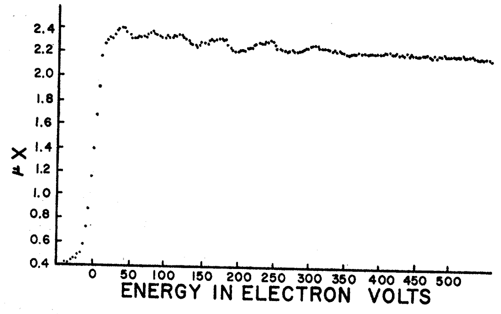

FIG. 2. X-ray K edge and fine structure of niobium at 300°K.

Three separate runs at room temperature, liquid nitrogen temperature, and liquid helium temperature were made on niobium out to about 360 eV from the main K-edge. A point-by-point average of these data is presented in Fig. 3. A detailed investigation of the region from 0 to 50 eV did not indicate any energy shifts in the absorption fine structure due to temperature change. This is significant because at 4.2°K the niobium was in a superconducting state and any shift in the plasmon oscillation frequency should have resulted in energy shifts in the absorption fine structure.[16]

EXPERIMENTAL RESULTS FOR COPPER

The absorption-limit fine structure of copper at room temperature was obtained by the same procedure as was used in taking the niobium data at room temperature. A copper-foil thickness of 5.8 μ was selected.

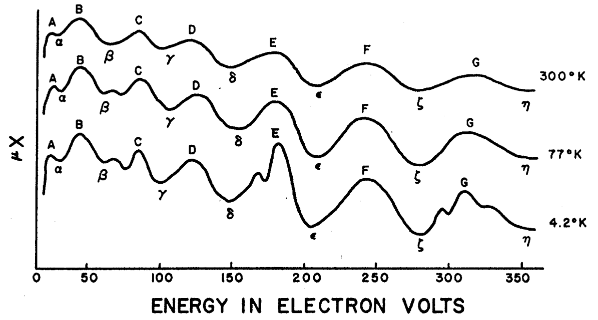

FIG. 3. X-ray fine structure of niobium at 300, 77, and 4.2°K.

Preliminary work indicated that the foil was quite uniform. A typical curve of $\ln(I_0/I)$ or μx as a function of photon energy for the 5.8-μ copper foil is presented in Fig. 4.

After the room-temperature data had been taken the 5.8-μ copper foil was mounted in the sample holder in the low-temperature Dewar. The count rate of the transmitted beam coming through the 1.90-cm-diam sample holder on the high-energy side of the copper K edge was about 4×10^3 counts/min. It was decided to take 5-min counts every 0.05 mm in the region close to the main K edge and every 0.10 mm in the region beyond. The same method of determining a complete spectrum of I and I_0 counts separately was used. A total of about 14 h was necessary to finish one complete run. Three separate runs at room temperature, liquid nitrogen temperature, and liquid helium temperature were made on copper out to about 600 eV from the

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[16] I. I. Soblman and E. L. Feinberg, Zh. Eksperim. i Teor. Fiz. 34, 494 (1958) [English transl.: Soviet Phys.—JETP 7, 339 (1958)].

main K edge. A point-by-point average of these data is presented in Fig. 5.

DISCUSSION

After the niobium data had been carefully studied and the shift in the fine structure of the superconducting niobium was not found, the results were sent to Marton.[17] Since recent theoretical studies[18] indicate that the x-ray–induced plasmon excitation probabilities are much lower than those previously suggested by Sobelman and Feinberg,[16] it is likely that there is no radical shift in the plasmon frequency of electrons in a superconducting metal. Any changes in the plasmon frequency at low temperature will probably result from small changes in the electron concentration resulting from density variation of the metal as a function of temperature. This effect in aluminum has been reported by Leder and Marton.[19]

To analyze the fine-structure data the absorption maxima and minima in Figs. 3 and 5 are designated by capital letters and small Greek letters, respectively. The fine structure is seen to exhibit several variations as the temperature is lowered from 300 to 4.2°K. Although the structure is well defined at 300°K, it becomes much sharper at the lowest temperature; in fact, at 4.2°K the E and G peaks of niobium are split and resolved into two separate peaks. The individual energy positions of the maxima and minima do not seem to shift even though the peaks themselves change shape as the temperature is lowered.

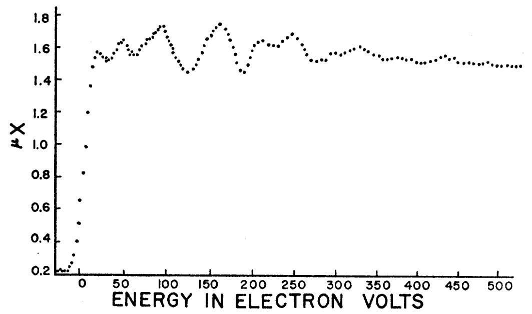

FIG. 4. X-ray K edge and fine structure of copper at 300°K.

The most important feature of the fine structures in Figs. 3 and 5 is the increase in amplitude of the fluctuations as the temperature is lowered from 300 to 77 to 4.2°K. A measure of this increase will allow a direct comparison with the theoretical results of the Kozlenkov-Shmidt theory given in Eq. (1). A simple and direct method of obtaining the amplitude increases is to measure the vertical distance from the top of the maxima to the bottom of the next adjacent minima. This will result in three sets of amplitudes indicated by A-α, B-β, C-γ, etc. Ratios of the individual amplitudes can be calculated from these data. The ratios of the amplitudes corresponding to lowering the temperature from 300 to 4.2°K and 77 to 4.2°K are presented in Figs. 6 and 7. The energy associated with each amplitude A-α, B-β, etc. is taken as the energy at the midpoint between maxima and corresponding minima.

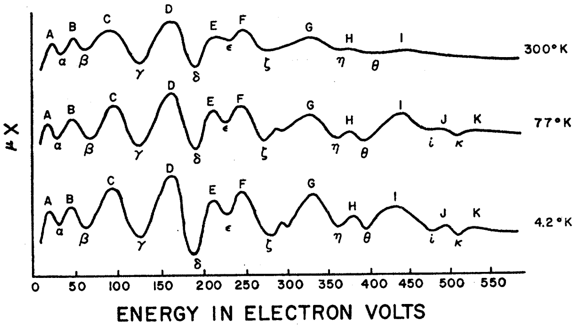

FIG. 5. X-ray fine structure of copper at 300, 77, and 4.2°K.

The temperature dependence of x-ray fine structure in the Kozlenkov-Shmidt theory is satisfied by the negative exponential in Eq. (1). At any given temperature all the parameters are fixed except the energy, which is measured from the main K edge. It is possible to determine the theoretical ratios of maxima-minima amplitudes by substituting the known parameters into the negative exponential for all three temperatures and at each of the midpoint energies. Since the amplitudes A_s associated with larger coordinating spheres are

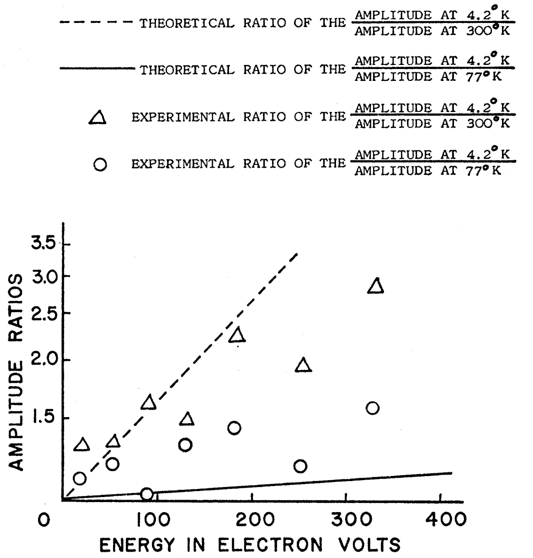

FIG. 6. Experimental and theoretical amplitude ratios for niobium. The experimental points on this semilog graph are taken from Fig. 3. The theoretical estimate of the amplitude ratios results in a straight line on this semilog graph since all terms in Eq. (1) cancel except the temperature-dependent exponential. The two lines represent ratios of exponentials for the 300 to 4.2°K temperature change and the 77 to 4.2°K temperature change.

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[17] L. Marton (private communication) stated that some of his recent unpublished work indicated that there would not be an abnormal shift in the plasmon oscillation frequency in a superconducting metal.

[18] R. A. Ferrell, Bull. Am. Phys. Soc. **10**, 1218 (1965).

[19] L. B. Leder and L. Marton, Phys. Rev. **112**, 341 (1958).

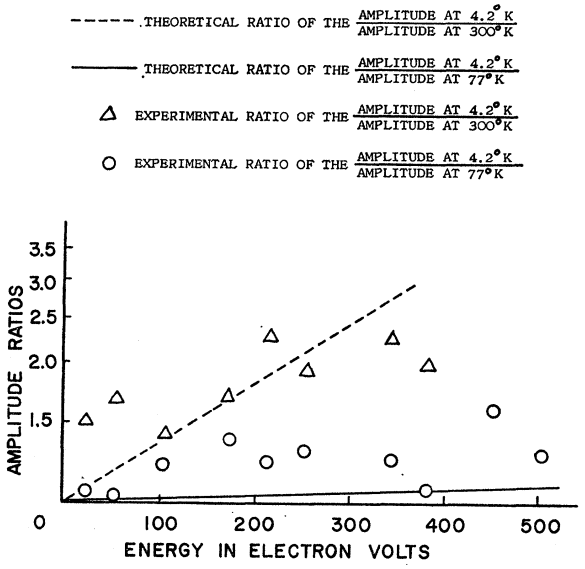

FIG. 7. Experimental and theoretical amplitude ratios for copper. The experimental points on this semilog graph are taken from Fig. 5. The theoretical estimate of the amplitude ratios results in a straight line on this semilog graph since all terms in Eq. (1) cancel except the temperature-dependent exponential. The two lines represent ratios of exponentials for the 300 to 4.2°K temperature change and the 77 to 4.2°K temperature change.

known to be smaller, a good approximation is to use just the first coordinating sphere radius r_s as the nearest-neighbor distance. This approximation is used because the first coordinating sphere is predicted to have the major influence on the fine structure and because the phase values η_1 are not precisely known for the larger coordinating sphere radii. A semilog plot of the ratios of the amplitudes theoretically calculated from the negative exponential attenuating coefficient in Eq. (1) are shown for niobium and copper in Figs. 6 and 7, respectively.

The theoretical ratios in Figs. 6 and 7 indicate that slightly larger amplitude changes are expected in niobium for both temperature changes. This was found to be qualitatively true. At the higher-energy amplitudes the niobium ratio is larger in six out of nine cases. In general, the theoretical estimates of amplitude ratio are too low at the low-energy positions and too high at the high-energy positions. The greatest discrepancy occurs for the ratios corresponding to amplitude change from 77 to 4.2°K, where the experimentally determined ratios are greater than the theoretical in every case. This discrepancy is not noticed in the 300 to 4.2°K range, where the agreement is rather good except at the highest-energy positions. Since niobium has a lower Debye temperature, it was theoretically expected that the amplitude changes in the 77 to 4.2°K region would be greater for niobium than for copper. This is found to agree with experiment. The E-ϵ and G-η ratios for niobium are significantly greater than the ratios for copper in the 77 to 4.2°K region while the corresponding F-ζ and D-δ are about the same.

CONCLUSIONS

Several conclusions can be drawn from the Kozlenkov-Shmidt theory as presented in Eq. (1). The E in the exponential term will reduce the amplitude of the fine-structure fluctuations at high energies. This is seen to be true in niobium and copper where the fine structure terminates at several hundred electron volts from the main K-edge. At low temperatures, where the outer coordinating spheres are more significant as scattering potentials, one would expect additional structure to be present. This additional structure did not appear in the copper data, but the E and G peaks of niobium are clearly split and the additional structure is resolved at the lowest temperature.

The $F(T/\Theta)$ function indicates that elements with high values of Debye Θ should exhibit less temperature variation at the lower temperatures. This was found to be directly applicable in the 77 to 4.2°K region where the niobium amplitude increase was significantly greater than the copper increase. The one-half term in the exponential accounts for the zero-point quantum-mechanical oscillations of the atoms in the crystal lattice. This suggests that large amplitude fluctuations in $\bar{\mu}$ would not be seen even if the absorber were at 0°K, i.e., the exponential function of Eq. (1) at 0°K, where $F(T/\Theta)=0$, still corresponds to a 65% decrease in copper amplitude fluctuations and a 69% decrease in niobium amplitude fluctuations at 150 eV from the main K edge.

There is one way to partially account for the lack of precise agreement between theory and experiment. In Eq. (1), $2mE$ was substituted for $\hbar^2k^2$. If the average inner potential of the crystal W is considered, the substitution would be

$$\hbar^2k^2=2m(E-W), \tag{4}$$

where W is given by

$$W=\frac{h^2}{8md^2}\left(\frac{3N}{\pi}\right)^{2/3}. \tag{5}$$

In Eq. (5), m is the electron mass, d is the lattice spacing, and N is the number of free electrons per unit cell. This substitution would limit the theory to energies greater than W and would prohibit application of the theory to the lowest energy positions. This substitution would also decrease the theoretical value of amplitude attenuation at any given energy. However, W is only about 10–20 eV for most metals and would have a greater effect at the low- and intermediate-energy positions.

From this research it can be concluded that the Kozlenkov-Shmidt theory applies quite well to some areas of the fine structure and is capable of quantitatively estimating temperature effects in x-ray fine structure that were only qualitatively treated in previous work.