Electron-excitation energy-dependent features in the M-series x-ray spectrum of lanthanum

Robert J. Liefeld, Alex F. Burr, and Merrill B. Chamberlain*
Physics Department, Box 3D, New Mexico State University, Las Cruces, New Mexico 88001
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M-series (14 to 15 Å) x-ray spectra from lanthanum are presented for near-threshold electron excitation. Several structures in the spectra which are not the ordinary characteristic-x-ray lines exhibit very strong intensity and wavelength (energy-position) dependence on the energy of the exciting electrons. Consideration of a sequence of spectra recorded for closely spaced ($\Delta E = 1$ eV) incident electron energies and of the shape of the continuum-limit spectrum from lanthanum for other energies show that the several structures are actually a single feature of the continuous spectrum. This linelike feature exactly follows the energy of the incident electrons and has large intensity resonances in the neighborhoods of the threshold excitation energies of the lanthanum M_5 and M_4 inner levels. The interpretation offered suggests that the observed spectral variations are due to resonances in the cross section for scattering incident electrons into vacant $4f$ levels and that these resonances exist because of the excitation of sets of excited negative-ion bound states involving $3d$ inner-shell electrons. Consequences of the observed spectral variations for valence-band x-ray spectroscopy, appearance-potential spectroscopy, and continuum-limit spectroscopy are discussed.

INTRODUCTION AND BACKGROUND

For several years now an improved soft-x-ray spectroscopic view of the density of states in the filled portion of the valence bands of metals has been obtained by exciting the appropriate valence-band lines with near-threshold-energy incident electrons.[1,2] This technique avoids self-absorption in the sample, avoids excitation of multiple overlying satellites, and has permitted correction for continuum backgrounds by subtraction of continuous spectra recorded for just less than threshold-energy excitation. Attempts to record the shapes of the valence-band lines of lanthanum ($M\alpha$; valence $\rightarrow M_5$), ($M\beta$; valence $\rightarrow M_4$) with the near-threshold-energy technique were frustrated by the appearance, at less than threshold energy, of "line-like structures," which masked the valence-band lines, and which moved in energy position and "resonated" in intensity as the incident electron energy was increased through the $M\alpha$- and $M\beta$-line excitation energies.

The description of the characteristics of these structures, and an explanation of them are the subject of this paper. Earlier meeting papers[3-5(a)] exhibiting some of these spectra referred to the structures as "variable-frequency", or "variable-energy" x-ray lines. A further exposition of the phenomenon and the presentation of similar but more extensive data for the neighboring element cerium will appear in a subsequent paper[5(b)] by Chamberlain, Burr, and Liefeld, and can be found in the Ph.D. dissertation of Chamberlain.[6]

INSTRUMENTATION AND TECHNIQUES

Spectra reported here were all recorded with a vacuum, two-crystal monochromator operated in the (1, +1) configuration. Potassium acid phthalate crystals were used as diffracting elements and the soft-x-ray detector was a flowing-gas (P-10) proportional counter. Spectra were obtained by observing detected intensity as a function of monochromator setting. Elements of the monochromator were angularly stepped in increments ranging from 0.01° to 0.06° ($\Delta\theta_{\mathrm{Bragg}}$) to generate the spectra, with fixed counting time at each position and constant voltage and current in the x-ray-tube source. Isochromats or excitation curves were recorded by observing the detected intensity as a function of x-ray-tube voltage with all the elements of the monochromator fixed and with constant x-ray-tube current. For all spectra, the anode voltage was maintained within 50 mV of a constant dc value with the aid of a calibrated voltbox, potentiometer, and standard cell.

Because of its high reactivity, the lanthanum-metal sample was premachined in an argon atmosphere and transferred after final polishing on abrasive paper under argon into the x-ray tube, which had also been back-filled with argon. The initial high vacuum was obtained with trapped mechanical and diffusion pumps. After a low-temperature (100°C) bake, pumping was transferred to a 400-liter/sec titanium-sublimation and ion pump. X-ray-tube base pressures of $\simeq 10^{-10}$ Torr, and operating pressures in the 10^{-9}-Torr region were achieved even with large, thin, Formvar windows separating the monochromator vacuum ($\simeq 1\times10^{-3}$ Torr) from the x-ray tube and from the gas in the proportional counter ($\simeq 6$ Torr). Currents of up to 100 mA were supplied to the sample over an area of 0.5 in.^{2} by a set of five or six parallel-connected ribbon filaments of thoria-coated irridum. These were placed edgewise to the lanthanum anode, about $\frac{1}{2}$ in. away, with separations of $\frac{1}{8}$ in. so that x-rays from the anode could pass between them into the spectrometer. For most of the spectra reported here a fairly monoenergetic electron bombardment of the anode was achieved by heating the filaments with direct current (< 2 V across the filament). For precise isochromats, and some test spectra, the filaments were heated with half-wave-rectified 60-Hz alternating current and the detector electronics were gated to count only when the voltage drop along the filaments was zero. With this technique the energy spread in the electron beam was less than 0.2 eV.

The entire study of the lanthanum-*M*-series emission for near-threshold excitation was repeated, with identical results, after the monochromator was dissassembled, moved to a new location, and reassembled.

LANTHANUM-*M* SPECTRA–PRESENTATION AND DESCRIPTION

The principa. results of this study are contained in some 40 emission spectra, each recorded for a

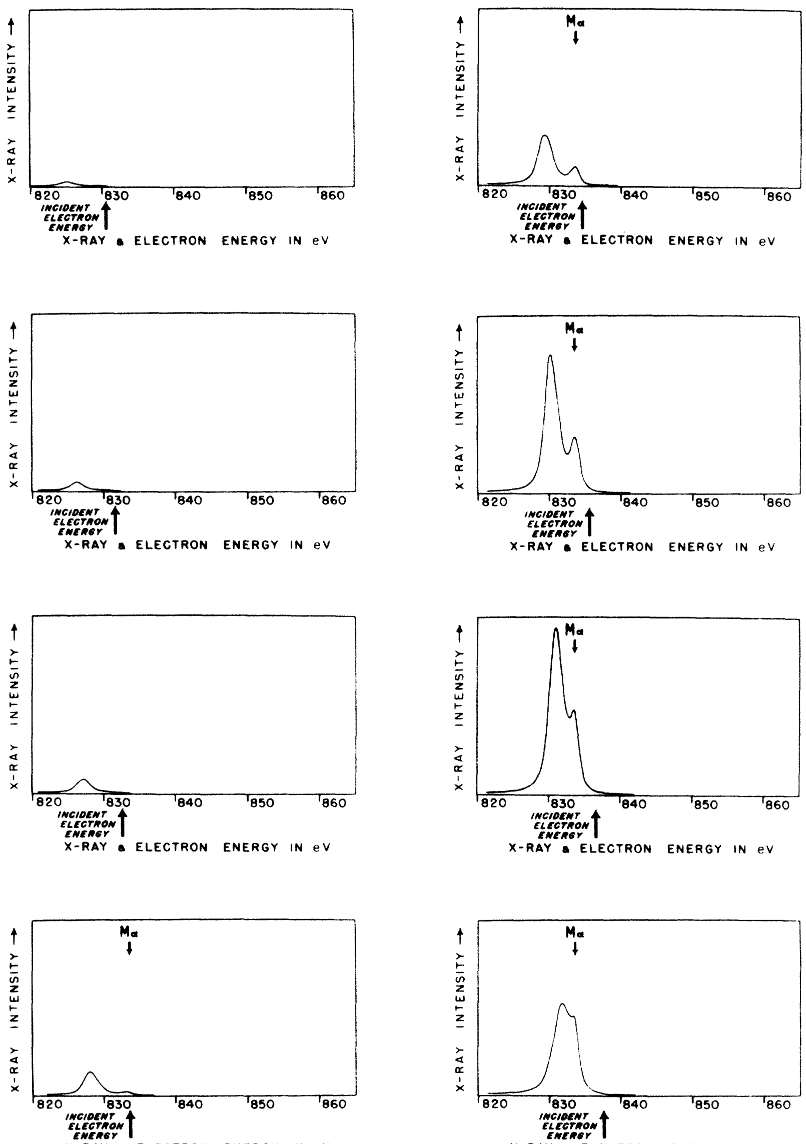

FIG. 1. Lanthanum *M* spectra for incident-electron energies from 830.5 to 837.5 eV.

different incident-electron energy in the region of the lanthanum M_5 (832-eV) and M_4 (849-eV) excitation energies. Considerable effort has been expended to find a way to display these spectra which clearly shows their dependence on incident-electron energy and which facilitates interpretation. Superposition, even with careful labeling and color encoding is not very satisfactory. A three-dimensional plot, with x-ray intensity plotted versus both the x-ray-photon energy and the x-ray-tube voltage is much better.[7] This display and an animated movie[8] produced by filming separate graphs of the individual spectra made for easy visualization of their energy-dependent features. Perusal of these displays leads directly to the idea that the structures whose intensity and energy position vary with incident-electron energy are, in fact, one structure that "tracks" ($\Delta E_{\text{photon}} = \Delta E_{\text{electron beam}}$) the incident-electron energy and resonates in two regions roughly centered on the $M\alpha$- and $M\beta$-line excitation energies. The $M\alpha$ and $M\beta$ characteristic lines are also seen to excite normally at their proper excitation energies.

A presentation similar to the animated film is effected by collating multiple prints of the spectra and producing a "flip-card-movie" book of them by registration and binding. So that the reader may enjoy the insight offered by such a device, 32 of the lanthanum spectra, recorded for x-ray tube voltages of 830.5–864.5 V, are presented in Figs.

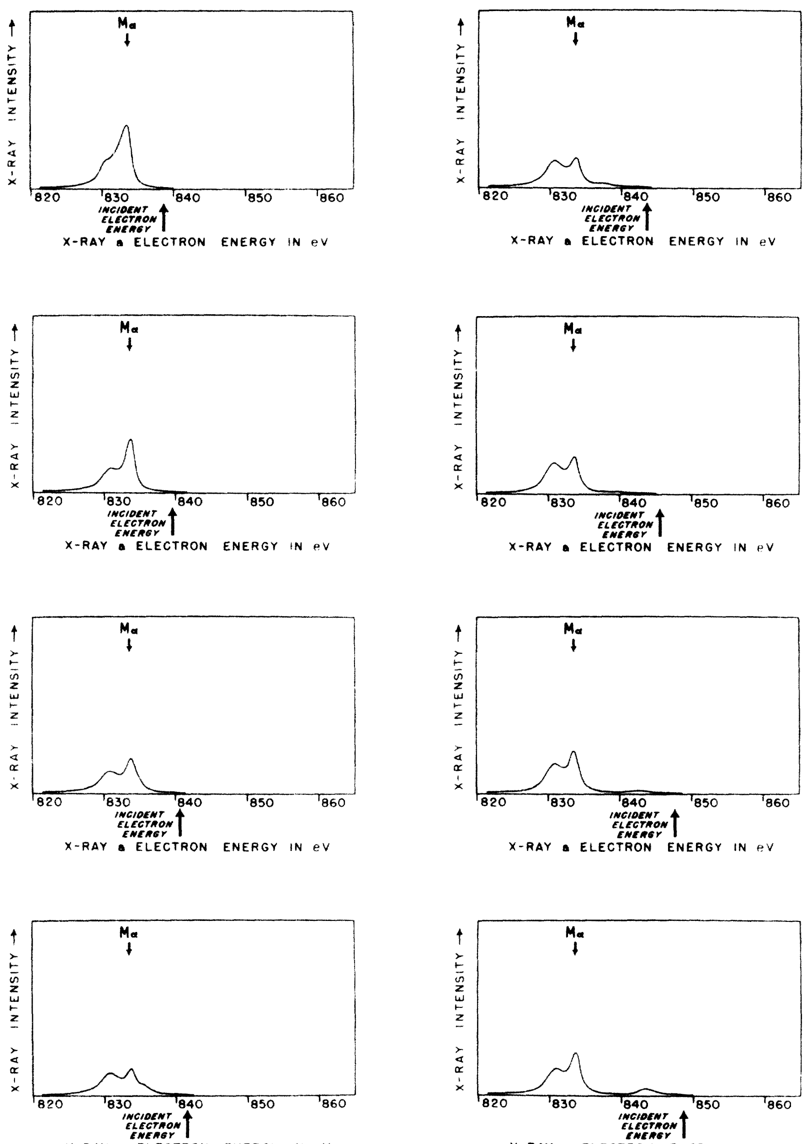

FIG. 2. Lanthanum M spectra for incident-electron energies from 838.5 to 848.5 eV.

1–4. Voltage increments between spectra are 1 V, except between 841.5 and 847.5, where there are three steps of 2 V each. Copy each page three or four times, cut out and collect individual spectra, stack sequentially, and bind at the top. Flipping through the stack will then show clearly the characteristics of the energy-tracking and intensity-resonating structure or "line." The most obvious of these, which are also detectable by scanning Figs. 1–4 directly, are that the energy position of the peak of this structure is always about 5.5 eV less than the energy of the incident electrons, that the structure almost disappears for a range of incident-electron energies between the $M\alpha$ and $M\beta$ lines, that the structure persists with larger than initial amplitude (for $<M\alpha$ excitation) when the incident-electron energy has been increased well beyond the $M\beta$-line (M_4-level) excitation energy, and that a broader "residual" line remains at the positions where the moving line had its maximum-intensity excursions.

CONTINUOUS-SPECTRUM FEATURE

Evidence that the lanthanum-emission spectrum structure that tracks the incident electron energy and undergoes intensity resonances in the M_5 and M_4 inner-level energy regions is a part of the continuous spectrum comes from two considerations. The first of these is the idea that the only

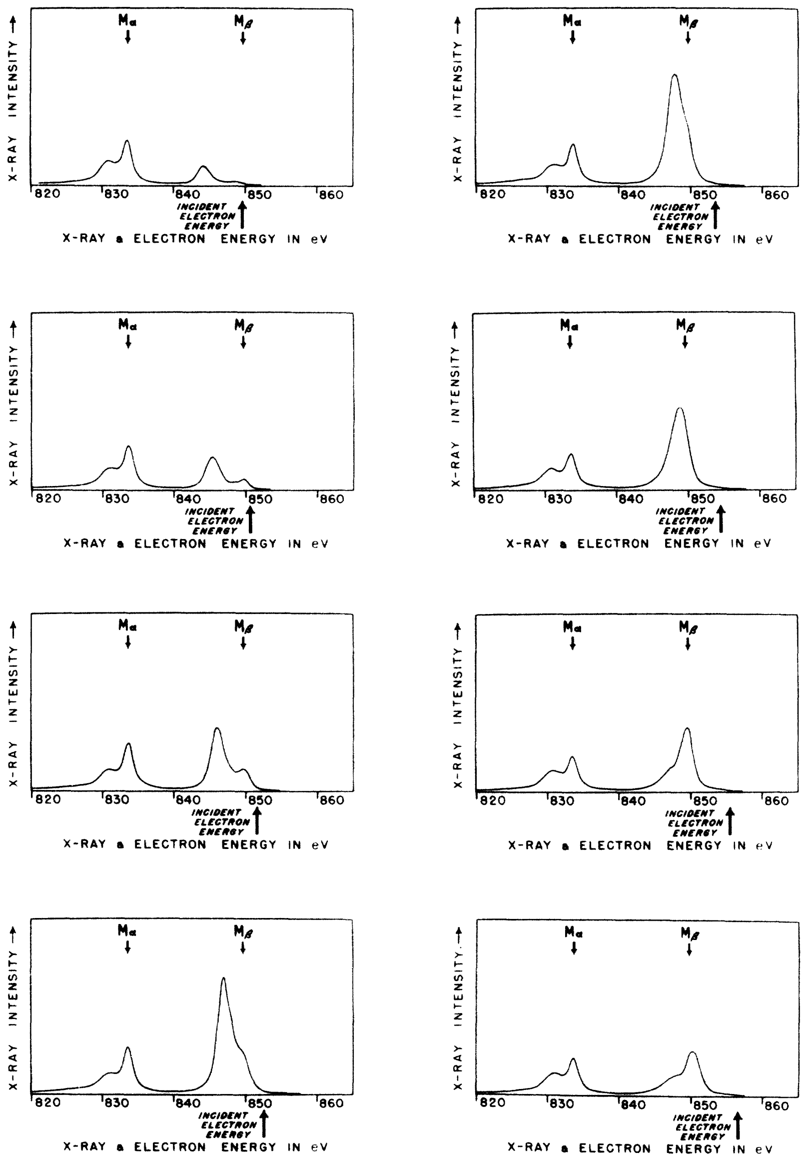

FIG. 3. Lanthanum M spectra for incident-electron energies from 849.5 to 856.5 eV.

spectral features that should indeed follow or track the energy of the incident electrons are those structures associated with the "high-frequency limit" of the continuous spectrum. The other is the shape of the continuum limit from lanthanum. For the limit itself, of course, $h\nu_{\text{limit}} = eV_{\text{max}} + \phi_{\text{cathode}}$, where V is the dc voltage across the tube. Structures at and near the high-frequency limit of continuous spectra and near the onset of continuous-spectrum isochromats have been studied extensively. Some of the observed structures are to be associated with the density of available states above the Fermi level in the sample, and some are to be associated with the nature of the incident-electron spectrum in the sample.[9] The process is considered as one in which an incident hot electron stops in an available level above the Fermi level and the energy difference is radiated away as a single photon. For this process the shape of the continuous spectrum near the high-frequency limit may be considered as the convolution of the energy spectrum of the incident electrons within the emitting layer of the sample with the product of the density of available final states for such electrons and the matrix element for the transition. Since the initial state of the electron is well represented by a plane wave and its final state is that of a conduction electron, also representable as a plane wave (or by a limited collection of them), the matrix element for the transi-

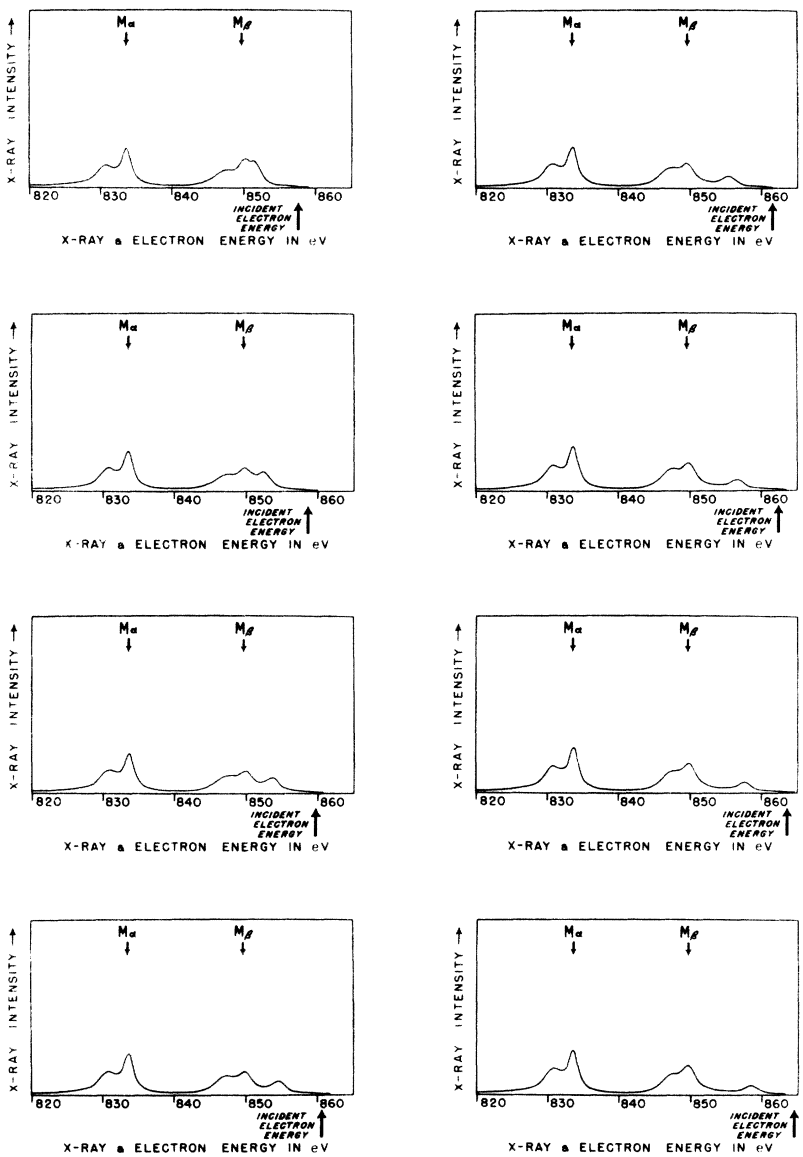

FIG. 4. Lanthanum M spectra for incident-electron energies from 857.5 to 864.5 eV.

tion is usually assumed to be independent of the final electron state energy. Also, for incident-electron energies of less than about 1 keV the high-energy portion of the incident electron spectrum in the emitting layers of the sample is reasonably well characterized by a linelike spike, representing electrons that have lost no energy, (elastically scattered or unscattered), followed by a relatively low ledge representing electrons that have been inelastically scattered. Characteristic loss features are also present but are of secondary importance. Thus, for at least a few volts from the high-energy limit of a continuous spectrum, or from the onset of a continuum isochromat, for low-energy electrons, spectral shape is reasonably well taken[10] as the scanning of the density of states close to the Fermi level by the linelike spike of the incident-electron spectrum. The low ledge of inelastically scattered electrons only causes a tilt in the spectra.

With the foregoing remarks as background, we now introduce a continuous spectrum (Fig. 5) and a continuum isochromat (Fig. 6) from the lanthanum sample, both recorded at energies well removed from the M_5 and M_4 inner-level excitation energies. Following the usual interpretation that these spectra show the density of empty electron states immediately above the Fermi level in the anode, we note a relatively low density right at the Fermi level followed by a large linelike structure that is due to transitions involving the set of empty $4f$ orbitals.[11] In both spectra the peak of this structure lies about 5.5 eV from the threshold level. Comparison of these continuum spectra with the set of lanthanum-emission spectra presented in Figs. 1–4, and with others for even lower and higher values of incident-electron energy, reveals that it is the $(4f)$ feature of the continuous spectrum that tracks the incident-electron energy (as expected), and that resonates so dramatically in intensity (a newly observed phenomenon) as the incident-electron energy ranges through the M_5 and M_4 inner-level excitation energies. In every case the energy position of the peak of the variable structure is less than the energy of the incident electrons by some 5.5 eV, and the "line" shapes are all similar.

Study of the complete set of lanthanum spectra shows that for incident-electron energies of a few tens of volts less than the M_5-level excitation energy the intensity of the $(4f)$ features decreases, while the remainder of the continuum remains unchanged, except for the shift to higher energies. A minimum in the intensity of the continuum $4f$ structure is observed for incident-electron energies of from 815 to 820 eV, some 10–15 eV less than the M_5 excitation energy. Further, increases in incident-electron energy result in a rapid growth and intensity resonance of the $4f$ structure according to the fashion depicted in Figs. 1–4. For incident-electron energies several tens of volts higher than the M_4 excitation energy, the size of the structure is still decreasing, but it remains larger than it was for several tens of volts below the M_5-level excitation energy.

INTERPRETATION–DISCUSSION AND A SUGGESTED MECHANISM

All of the spectra support an interpretation that the observed phenomena result from resonances in the cross section for scattering incident electrons into the empty $4f$ levels above the Fermi level. Indeed, since the amplitude of the $4f$ structure first decreases prior to resonating in the vicinity of the M_5 energy level, and then decreases

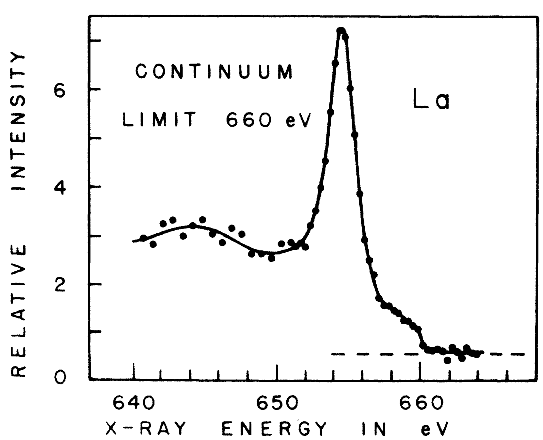

FIG. 5. A continuous spectrum from lanthanum for incident electrons of 660 eV.

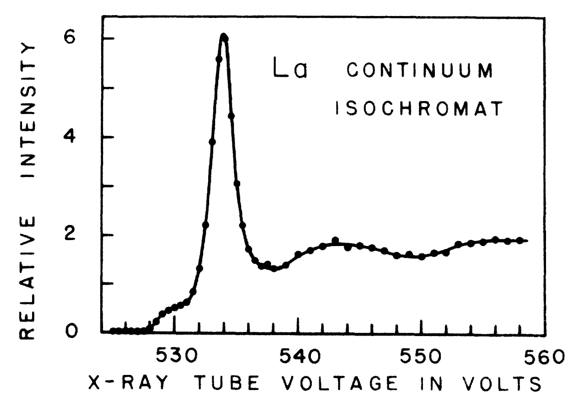

FIG. 6. A continuous spectrum isochromat from lanthanum at 528 eV.

again prior to resonating in the vicinity of the M_4 energy level and falls slowly thereafter, it exhibits most of the energy-dependent characteristics of a classical scattering resonance. The energy position of the resonances and the fact that their intensity ratio is that of the statistical weights of the M_5 and M_4 levels (3:2) suggest that these levels participate directly in the process.

It is suggested that intermediate bound states are involved in which incident electrons are "captured" by lanthanum atoms to form negative-ion bound states. In these states a $3d$ electron and the incident electron are in bound orbitals around the vacancy produced in the $3d$ shell. These states then decay radiatively, with one electron returning to the $3d$ vacancy and the other going to a $4f$ orbital above the Fermi level. In short, the cross section for scattering incident electrons into the $4f$ levels of the solid is enhanced via a mechanism involving the production of negative-ion bound states from $3d$ electrons and $4f$ orbitals.

Quite independent of whether or not the suggested mechanism is valid, however, it is evident that the observed intensity variations of a spectral feature that is a portion of the continuous spectrum is a significant phenomenon that directly effects a variety of spectroscopies. In particular, as mentioned earlier, it frustrates attempts to observe valence-band line shapes for near-threshold-energy (or any other) excitation, because the continuum feature intensity resonances overlay and mask the valence-band lines.[12] Also, the "appearance-potential" spectroscopy, in which the presence of particular elements is detected by observing the onset of characteristic-x-ray-line production as a function of incident-electron energy, is considerably complicated by the continuum-resonance effect. Another consequence is that extra "lines" will be found in the x-ray spectra of elements exhibiting this effect. Specifically, the residual "bumps" on the low-energy sides of the lanthanum $M\alpha$ and $M\beta$ lines exist for any incident-electron energy well above threshold energy. They are explainable as continuum enhancement at those positions by virtue of the fact that, though the incident-electron energy is much higher, there are some electrons in the tail of the incident-electron distribution in the sample that have just the right energies to interact with the atoms as described above.

Last, the resonance effect of the continuous-spectrum feature reported in this paper is direct evidence that the cross section for scattering incident electrons into empty levels above the Fermi level can be strongly energy dependent, with respect to particular final-state symmetries. This fact seriously complicates continuum-limit spectroscopy of empty electron levels above the Fermi level. For incident-electron energies well removed from particular inner-shell-excitation energies, the continuum-limit spectroscopy may still provide a nearly correct view of the relative density of states above the Fermi level, but supporting information on the energy-dependent behavior of the matrix elements for the transitions involved is needed.

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*Now at Air Force Materials Laboratory, Wright-Patterson AFB, Dayton, Ohio 45433.

[1]Robert J. Liefeld, in *Soft X-Ray Band Spectra*, edited by Derek J. Fabian, (Academic, London, 1968).

[2]S. Hanzeley and R. J. Liefeld, National Bureau of Standards Spec. Publ. No. 323 (U. S. GPO, Washington, D. C., 1971).

[3]A. F. Burr and R. J. Liefeld, Bull. Am. Phys. Soc. 13, 576 (1968).

[4]A. F. Burr and R. J. Liefeld, Dev. Appl. Spec. A 7, 121 (1969).

[5](a) M. B. Chamberlain, A. F. Burr, and R. J. Liefeld, Bull. Am. Phys. Soc. 15, 560 (1970); (b) Phys. Rev. A (to be published).

[6]M. B. Chamberlain, Ph.D. Dissertation (New Mexico State University, 1970) (unpublished).

[7]By Spacial Data Systems, Inc., Goleta, Calif.

[8]"Some M Series X-Ray Emissions from Lanthanum", Lie-Burr Films.

[9]For discussions of these aspects see, for example, Robert R. Turtle and Robert J. Liefeld, Phys. Rev. B 7, 3411 (1973).

[10]This has been the usual argument by authors analyzing the shape of continuous spectra and continuum isochromats. We use it here as background only, because, as will be seen, the entire body of data presented here shows that the constant-matrix-element assumption is invalid in certain instances.

[11]Lanthanum atoms are generally characterized as having no electrons of $4f$ orbital symmetry, so all the $4f$ orbitals are empty and lie above the Fermi level in the metal.

[12]A much fainter example of this effect has been observed in studies of the first-transition-group elements and has been reported in Ref. 2.