United States Patent [19]

Erickson et al.

[11] **3,920,989**

[45] **Nov. 18, 1975**

[54] **ION SCATTERING SPECTROMETER UTILIZING CHARGE EXCHANGE PROCESSES**

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[73] Assignee: **Minnesota Mining and Manufacturing Company,** St. Paul, Minn.

[22] Filed: **Sept. 20, 1974**

[21] Appl. No.: **507,713**

[52] **U.S. Cl.** **250/307;** 250/309; 250/294

[51] **Int. Cl.²** **H01J 37/00**

[58] **Field of Search** 250/294, 307, 309, 396

[56] **References Cited**

UNITED STATES PATENTS

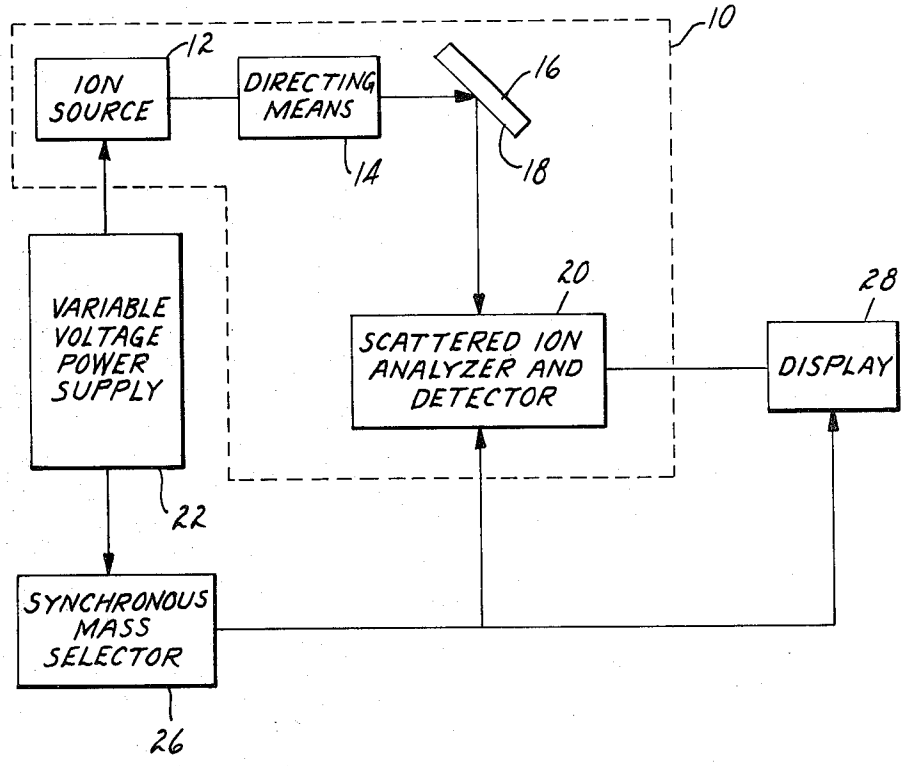
3,480,774	11/1969	Smith	250/309
3,665,182	5/1972	Goff	250/307
3,665,185	5/1972	Goff	250/294

Primary Examiner—James W. Lawrence
Assistant Examiner—B. C. Anderson
Attorney, Agent, or Firm—Alexander, Sell, Steldt & DeLaHunt

[57] **ABSTRACT**

An ion scattering spectroscopic method and apparatus wherein an oscillatory variation in the yield of ions scattered from solid surfaces provides information indicative of electron exchange processes associated with particular electronic states in the atom, which states vary with the electronic environment surrounding the atoms. The apparatus includes means for directing a beam of ions having a known mass and a known charge state toward a solid target surface such that an ion impinges thereon and scatters therefrom. During the impingement, the energy of the incident ions is varied over a range of predetermined primary ion kinetic energies. Ions having a given primary kinetic energy prior to impingement lose a given fraction of that energy upon elastic scattering from an atom of given atomic mass on the target surface. Accordingly, ions scattered from atoms of a single atomic mass are continuously detected by synchronously "tracking" the acceptance energy of an analyzer with the variation in the kinetic energy of the incident ions. A signal indicative of the yield of ions scattered from atoms having a single atomic mass is thus produced and when plotted as a function of incident primary ion kinetic energy, forms a spectrum wherein particular electronic states may be discerned.

10 Claims, 10 Drawing Figures



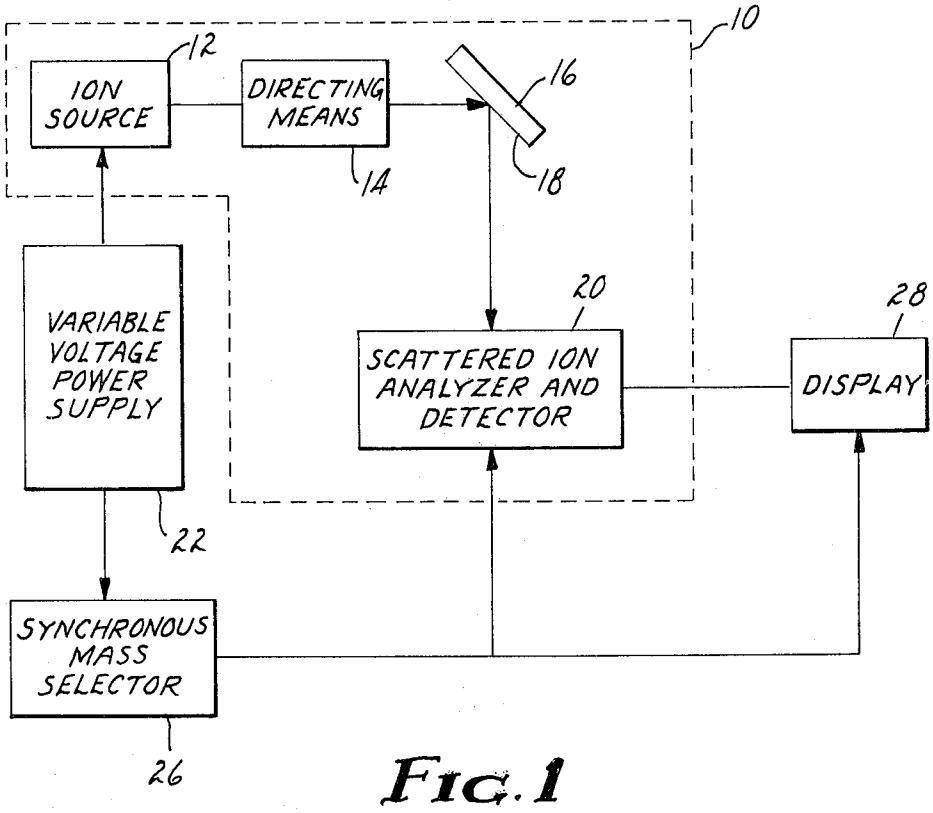
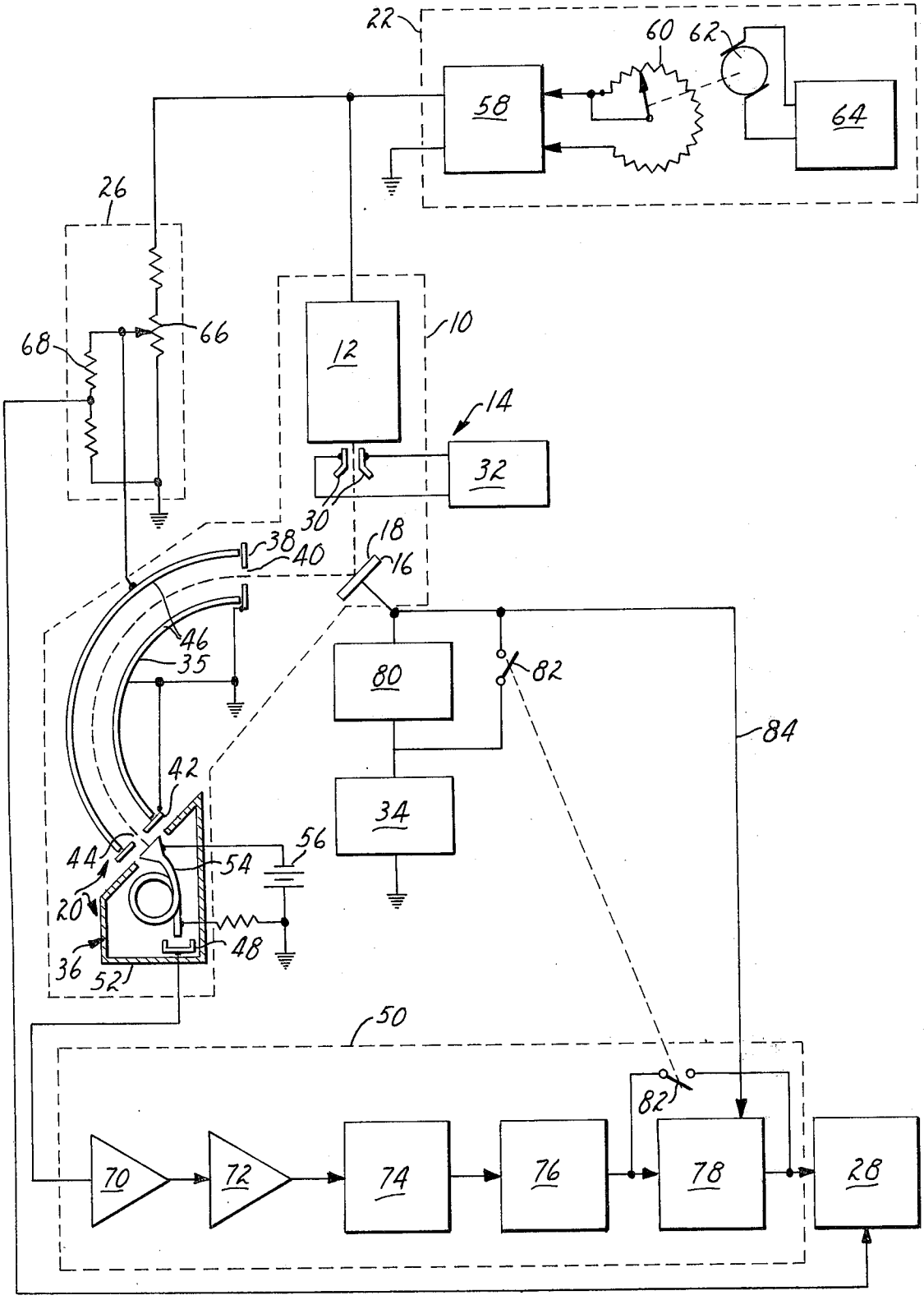

10
12
ION SOURCE
DIRECTING MEANS
14
16
18
20
28
VARIABLE VOLTAGE POWER SUPPLY
SCATTERED ION ANALYZER AND DETECTOR
DISPLAY
22
SYNCHRONOUS MASS SELECTOR
26

FIG. 1


22
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68
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28

FIG. 2

PRIOR ART

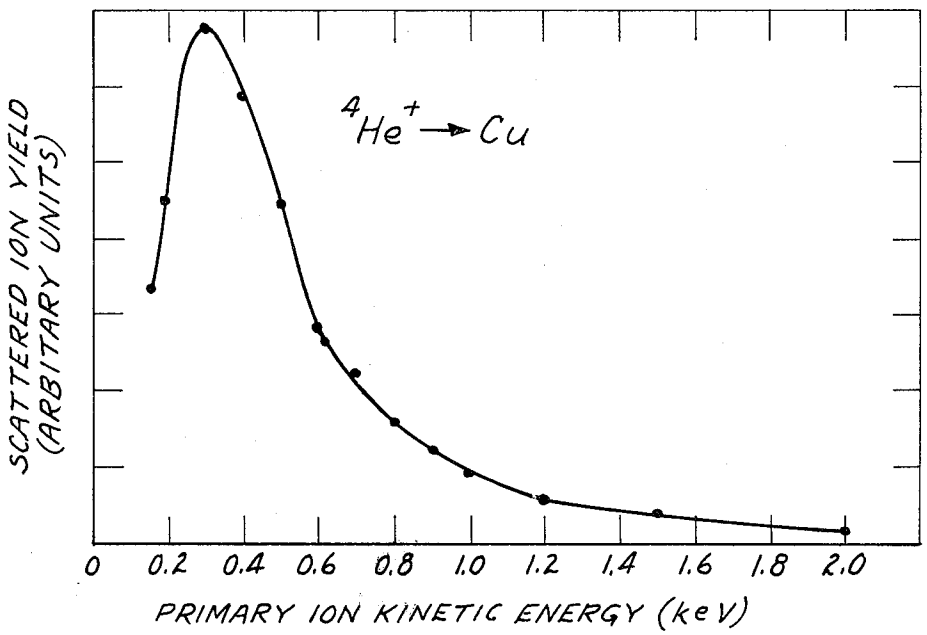

FIG. 3

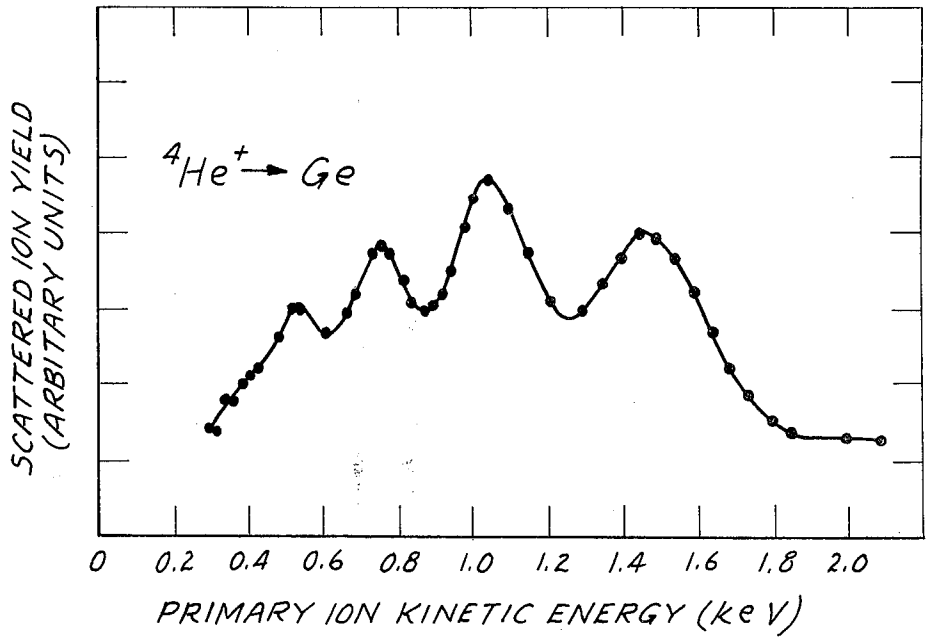

FIG. 4

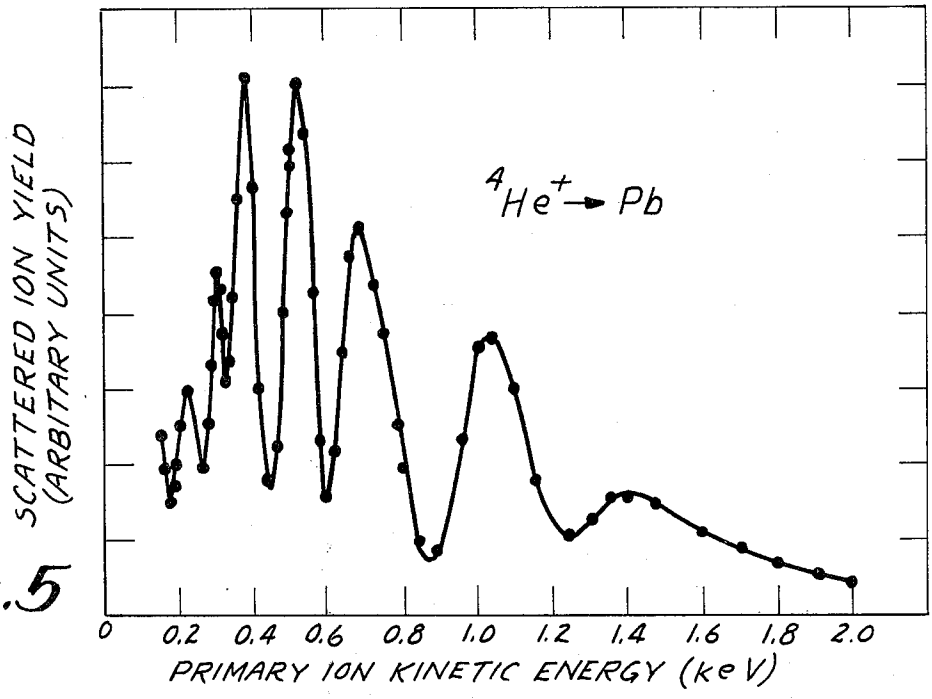
$^4He^+ \rightarrow Pb$
SCATTERED ION YIELD (ARBITARY UNITS)
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0
PRIMARY ION KINETIC ENERGY (keV)

FIG. 5

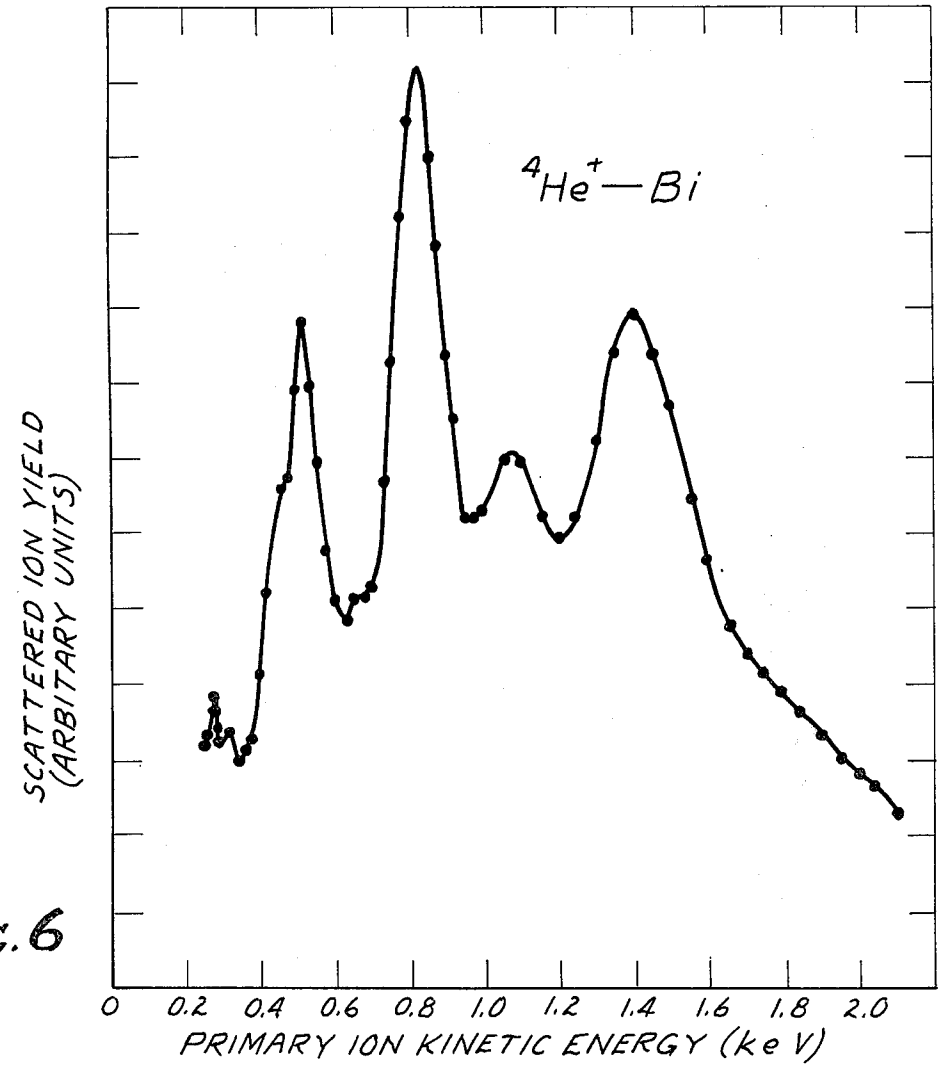
$^4He^+ - Bi$
SCATTERED ION YIELD (ARBITARY UNITS)
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0
PRIMARY ION KINETIC ENERGY (keV)

FIG. 6

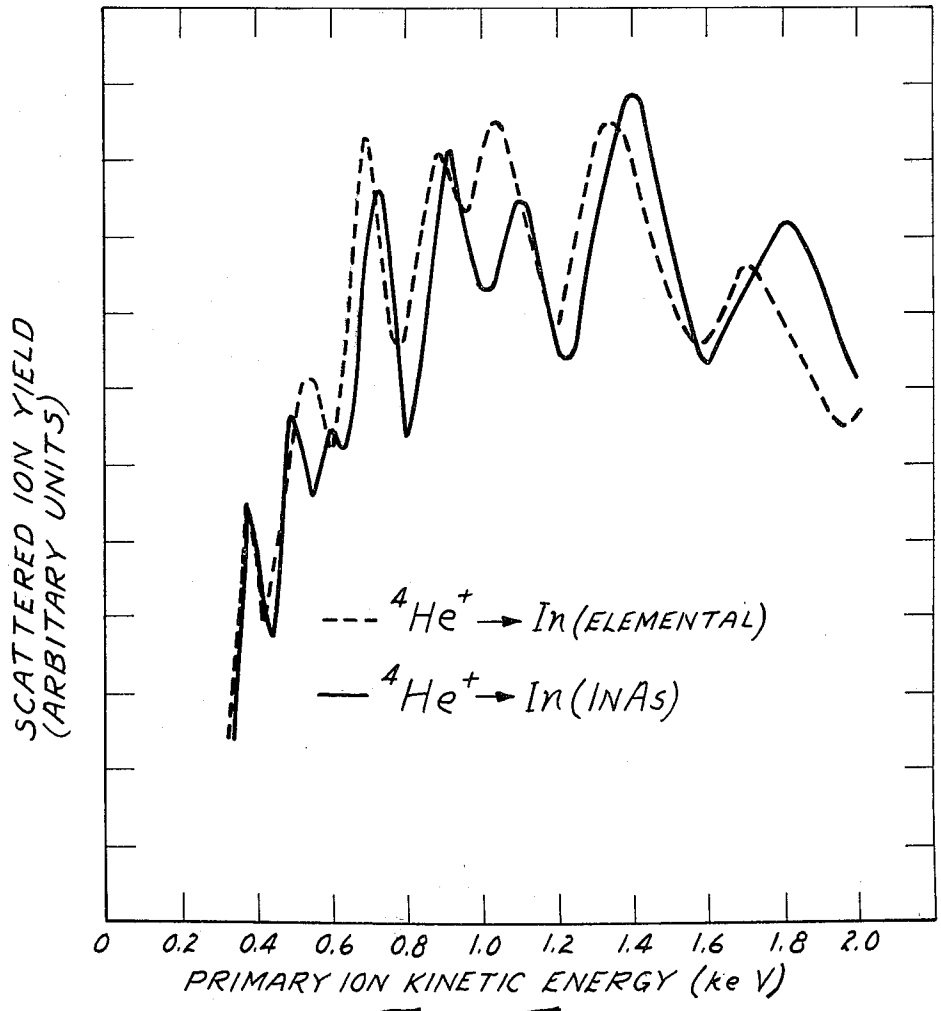
SCATTERED ION YIELD (ARBITARY UNITS)
--- $^4He^+ \rightarrow In$ (ELEMENTAL)
— $^4He^+ \rightarrow In$ (INAs)
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0
PRIMARY ION KINETIC ENERGY (ke V)

FIG. 7

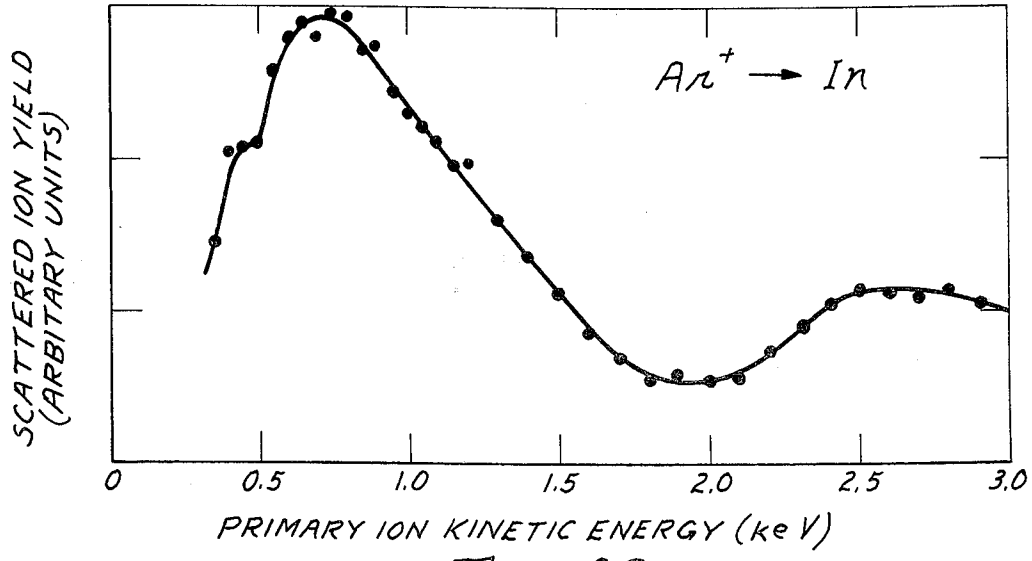
SCATTERED ION YIELD (ARBITARY UNITS)
$Ar^+ \rightarrow In$
0 0.5 1.0 1.5 2.0 2.5 3.0
PRIMARY ION KINETIC ENERGY (ke V)

FIG. 10

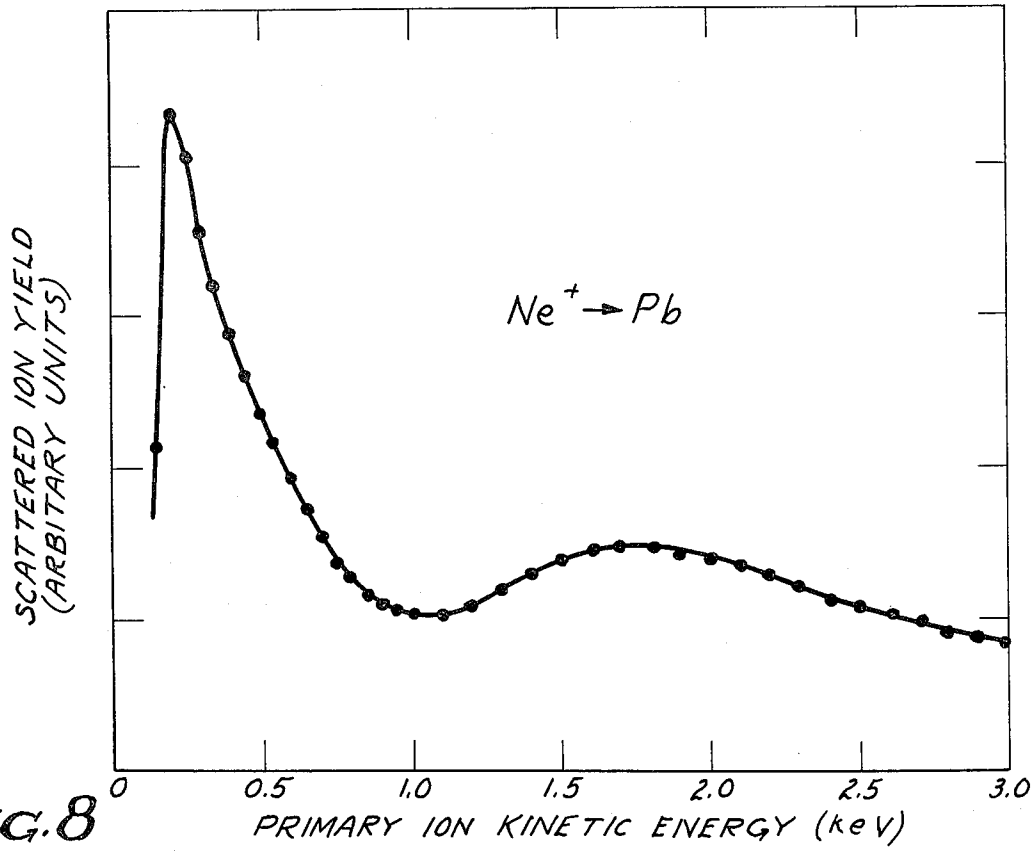
SCATTERED ION YIELD (ARBITARY UNITS)
$Ne^+ \rightarrow Pb$
0
0.5
1.0
1.5
2.0
2.5
3.0
PRIMARY ION KINETIC ENERGY (keV)

FIG. 8

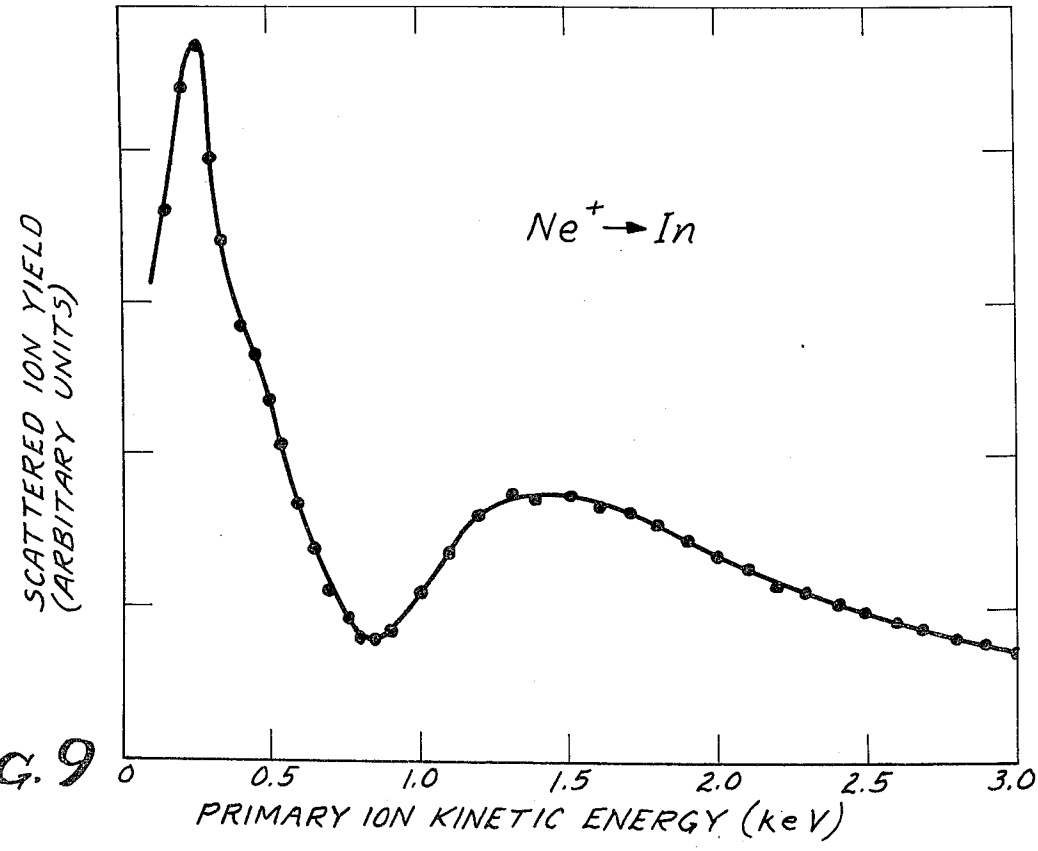
SCATTERED ION YIELD (ARBITARY UNITS)
$Ne^+ \rightarrow In$
0
0.5
1.0
1.5
2.0
2.5
3.0
PRIMARY ION KINETIC ENERGY (keV)

FIG. 9

ION SCATTERING SPECTROMETER UTILIZING CHARGE EXCHANGE PROCESSES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to ion spectroscopic methods and apparatus for analyzing the surface of a solid material wherein the loss of energy as a result of binary scattering of ions from the surface is measured to determine the composition of the surface.

2. Description of the Prior Art

Various aspects of ion scattering spectroscopy (ISS) are disclosed in U.S. Pat. Nos. **3,480,774, 3,665,182** and **3,665,185.** In conventional ISS, a primary beam of monoenergetic noble gas ions is directed toward a target (having a solid surface), and a fraction of the ions are elastically scattered from the surface in a manner similar to that of rebounding billiard balls. Assuming elastic binary interactions between the incident ions and surface atoms, and assuming that bonds between the surface atoms its immediate neighbors can be ignored, the mass of a surface atom can be calculated based on a determination of the loss of energy of a primary ion scattered at a predetermined angle. If the intensity, i.e., yield, of ions scattered at a given angle is then plotted as a function of scattered ion kinetic energy, a spectrum showing the relative concentration of surface atoms of varying masses may be prepared. Quantitiative interpretation of such a spectrum requires knowledge that the scattering cross section from all surface atoms and the ionic yield as a function of incident energy are determinable. Such spectroscopic techniques have proven to be valuable aids to the solution of numerous problems involving the identification of contamination on technologically important surfaces.

SUMMARY OF THE INVENTION

It has now been discovered that an earlier observation in conventional ISS; namely, that the ion yield as a function of incident energy has a smooth curve shape containing a single maximum value, is not always valid for every element. It has been found for certain combinations of incident ions and surface elements that the yield of ions scattered from the surface does vary in an oscillatory manner as a function of the incident ion kinetic energy, i.e., that a spectrum prepared by plotting the scattering yield as a function of incident ion kinetic energy exhibits "structure." The observation of such a variation in scattered ion yield has been found to be most pronounced when the ionization potential of the primary ions is in the same range as the electronic energy levels of the surface atoms. It has further been found that the observed structure in the spectra is indicative of electron exchange processes and is associated with the electronic, i.e., chemical, states in the surface atoms. The spectra may thus be directly interpreted to provide information concerning such exchange processes and electronic states. It has also been found that the spectra are useful in providing a unique "fingerprint" of adjacent elements in the periodic table, which because of their similar atomic mass, could not be individually resolved by conventional ISS.

In the ion scattering spectroscopic method of the present invention, a beam of ions having a known mass and known charge state is directed through a vacuum toward a predetermined area on the surface of the solid material to be analyzed such that the ions impinge thereon and are scattered therefrom. During the impingement, the kinetic energy of the incident, or primary, ions is varied over a range of predetermined primary ion kinetic energies. A fraction of the incident ions is thereby elastically scattered from atoms having a given atomic mass located thereon. As used herein, atoms having a given atomic mass are defined by a given ratio of scattered to primary ion energies. The counting rate of ions having a predetermined loss of energy and a predetermined charge state as a result of scattering at a given angle from atoms of the given atomic mass is then detected. During the detection process, the output from the ion detector is correlated with the primary ion energy to generate a signal having a magnitude which at any selected time corresponds to the yield, thus generating over a period of time a spectrum of the yield as a function of primary ion kinetic energies which may contain the useful structure discussed hereinabove.

BRIEF DESCRIPTION OF THE DRAWING

FIG. **1** is a block diagram of the apparatus of the present invention;

FIG. **2** is a combined block and schematic diagram showing details of the apparatus of the present invention;

FIG. **3** is a spectrum of scattered ion yield as a function of primary ion kinetic energy according to prior art concepts;

FIG. **4** is a typical spectrum of scattered ion yield as a function of primary ion kinetic energy showing the newly discovered structure;

FIGS. **5** and **6** are spectra of the scattered ion yield as a function of primary ion kinetic energy for two elements, Pb and Bi;

FIG. **7** shows spectra of scattered ion yield as a function of primary ion kinetic energy for He^+ ions scattered from In (elemental) and from InAs (In in compound form). The InAs spectrum has been doubled in amplitude for comparative purposes;

FIG. **8** is a spectrum of scattered ion yield as a function of primary ion kinetic energy showing the structure in the yield of Ne^+ ions scattered a Pb surface;

FIG. **9** is a spectrum of scattered ion yield as a function of primary ion kinetic energy showing the yield of Ne^+ ions scattered from an In surface; and

FIG. **10** is a spectrum of scattered ion yield as a function of primary ion kinetic energy showing scattering of Ar^+ ions from an In surface.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As shown in the block diagram of FIG. **1** the apparatus of the present invention comprises a number of components which directly interact with ions and which are therefore adapted to be operated within an evacuated chamber **10.** Certain other components are also provided to control the electrical potentials and signals relating to the ionic interactions. The components located within the chamber **10** thus comprise an ion source **12,** a means **14** for directing the ions from the source **12,** a target **16** having a surface **18** toward which the ions are directed, a supporting structure for the target (not shown) and an energy analyzer and detector **20** positioned to receive ions scattered from the target at a predetermined scattering angle. The ion

source **12** is energized by a variable voltage power supply **22,** to produce a beam of primary ions having a range of predetermined primary ion kinetic energies. A signal proportional to the time varying kinetic energy is coupled from the power supply **22** to a synchronous mass selector **26** which provides a similarly varying signal to the energy analyzer and detector **20** to cause the analyzer portion thereof to pass only such scattered ions as have a fixed fraction of the predetermined primary ion kinetic energies, i.e., those ions which have scattered at a given angle from atoms of a given atomic mass, regardless of their primary kinetic energy prior to impingement. The thus passed ions are subsequently detected by the detector portion of the analyzer-detector **20** to generate a signal the magnitude of which is proportional to the yield of scattered ions at any given time, i.e., at any given energy. The signal is coupled to a display unit **28** together with a signal from the mass selector **26** in order to graphically portray the scattering yield as a function of primary ion kinetic energy.

A more detailed description of the apparatus shown in block form in FIG. **1** is set forth in FIG. **2** and the following remarks. As in FIG. **1,** those portions of the apparatus directly interacting with the ions are adapted to be operated within an evacuatable chamber **10.** A preferred ion source **12** for use in the apparatus is disclosed in detail in U.S. Pat. No. **3,665,182,** the specification of which is incorporated herein by reference. Such an ion source operates by electron bombardment of residual gas atoms present within an ionization region within the source. To control the composition of the resultant ion beam during operation of the apparatus, the chamber **10** is evacuated to a pressure of les than about 10^{-8} Torr by a vacuum pump (not shown). A getter (not shown) is positioned within the chamber to further remove the active gases remaining in the chamber. The inert gas pumping is discontinued by shutting off the vacuum pump or closing the valve therebetween. A partial pressure of the desired gas such as a noble gas is released into the chamber by suitable valves (not shown) until the static pressure is increased to approximately 5×10^{-5} Torr, such as may be measured on Bayare-Alpert type pressure gauges, and all openings to the chamber are then closed. The noble gas used herein may be any noble gas, however, Helium (He), Argon (Ar) and a Neon (Ne) are commonly used. Insulated electrical feedthroughs or connectors (not shown) project through the chamber to provide the necessary electrical connections between the components within the chamber and those components located outside the chamber.

A support frame (not shown) is positioned within the chamber to support the target **16** such that a surface **18** thereof is in path of the beam of ions produced by the ion source **12.** A multi-positionable support such as that disclosed in the above incorporated specification, may be preferred to thus support the target. Similarly, to facilitate positioning the target surface **18** precisely at the focal point of the ion beam, thereby enhancing the capability of impinging the ion beam on only a particularly desired portion of the target surface, a modified target disc, having multiple target positions, may be provided. In such an embodiment, each position is provided with a temporary fastening means such as a screw or spring fastener to enable temporary fastening of a sample on any of the target positions. A conventional mechanically driven mechanism is then provided to enable the positioning of a given target in the path of the ion beam.

The preferred ion source **12** comprises several elements not shown. These include a heated filament for producing electrons, a semi-transparent grid which together with an extractor plate defines an ionization region, and several anode plates, each of which are provided with a circular opening and which are positioned along a path to accelerate the ions therealong. The power supply **22** powers the filament to produce electrons and biases the grid with respect to the filament.

The produced electrons from the filament are accelerated by the grid to a potential sufficient to ionize the noble gas atoms. For example, if He gas is used, the electrons would have at least **100** electron volts (eV) of energy, which is sufficient to ionize He which has an ionization potential of about **25**eV. The repeller repels or deflects any approaching electrons to result in a long electron path which increases the probability of the electrons striking an atom in the ionization region.

If the static pressure of the noble gas within the evacuatable chamber is increased, then the ion beam current is increased. Therefore, by regulating the electron ionization current at a constant gas pressure the ion beam current is regulated. In other plasma sources of the prior art, many adjustments could be made to regulate ion beam current but none of the adjustments could be easily related to the ion beam current. With such other plasma sources it is extremely difficult to build a beam current regulating feedback circuit. A feedback stabilization loop between the filament supply and the grid supply is therefore preferably also provided as a part of the power supply **22.** This stabilization loop maintains a stable electron grid current which controls the ion beam current throughout pressure changes within the evacuatable chamber.

The power supply **22** further includes an ion gun voltage divider network which biases the extractor plate to a potential to extract positive ions from the ionization region. The extracted ions are directed into a beam by the anode plates. Each anode plate has a potential applied thereto from the power supply **22.** A first anode plate is primarily used to control, modulate and initially focus the extracted ions into a collimated beam, while the remaining plates further collimate and focus the ion beam. The beam passing out of the ion source **12** is directed through the noble gas atmosphere a distance of less than **10** cm toward a surface **18** of the target **16** composed of a solid material to be analyzed. At least two pairs of deflector plates **30,** positioned near the end of the source **12** and on opposite sides of the beam, serve to deflect the beam to scan the sample and thereby obtain an image of the sample. The plates **30** are charged by an ion deflector power supply **32** controlled either manually or programmed.

The ion beam strikes or bombards the target on the pre selected target surface **18** and the impinging primary ions are scattered therefrom. The current flowing through the target is measured by the current measuring device **34** such as a Model **610C** electrometer, manufactured by Keithley, Inc. Cleveland, Ohio. The measured current is used in conjunction with auxiliary beam measurements to determine the current density striking the surface **18** of the target **16.**

The energy analyzer and detector **20** preferably comprises a conventional **127°** electrostatic energy analy-

zer, shown generally as **35** and an ion detector shown generally as **36.** The electrostatic analyzer **35** comprises an entrance diaphragm **38,** having a rectangular entrance slit **40** (long and narrow), an exit diaphragm **42,** having a rectangular exit slit **44** (also long and narrow), and two curved electrostatic analyzer plates **46.** The entrance and exit diaphragms **38** and **42** respectively, are preferably grounded, although in some situations it may be desirable to bias each diaphragm to the same or different potentials with respect to ground. The slits **40** and **44** in the diaphragms **38** and **42** have a preferred width ranging from approximately **0.005** inch (**0.125** mm) to approximately **0.040** inch (**1.0** mm). The entrance diaphragm is spaced approximately one cm from the surface **18** being investigated.

As disclosed in detail in U.S. Pat. No. **3,480,774** (Smith), surface analysis via measurement of the loss of energy of scattered ions having a known mass requires that only such ions as have scattered at a given angle be thus measured. Accordingly, the sample holder and analyzer **35** are designed to maintain as closely constant a scattering angle as is practical, regardless of the portion of the target surface **18** on which the incident primary beam is directed.

The analyzer plates **46** are charged by the output from the synchronous mass selector **26,** which permits a suitable potential to be applied to the plates **46** to direct ions having a predetermined mass and energy entering through the slit **40** in the entrance diaphragm **38,** to pass between the analyzer plates **46** and to pass out the exit slit **44** in the exit diaphragm **42.** The analyzer plates **46** have a mean radius of **2** inches (**51** mm). While the analyzer **35** is preferably a standard **127°** electrostatic energy analyzer, such an analyzer is by no means the only such analyzer having particular utility herein. A variety of known analyzers are similarly useful, including cylindrical mirror analyzers.

Scattered ions having a requisite energy determined by the instantaneous potential applied to the plates **46** are thus passed through the analyzer **35.** Such ions as are passed, detected, and converted into electrons by the ion detector **36** are then received by the electron collector **48.** The electron collector **48** converts the collected electrons into an electronic signal received by a signal processing circuit **50.** The signal from the circuit **50** may then be permanently recorded as a graph on a suitable display unit **28,** such as an X-Y recorder, and/or visually observed on an oscilloscope.

The ion detector **36** comprises an enclosure **52** and a continuous channel electron multiplier **54,** having an **8 millimeter diameter entrance cone which encom**passes the entire exit slit in the exit diaphragm of the energy analyzer **35** and which is powered by a high voltage power supply **56.** The electron multiplier **54** may be a commercially available device such as Model No. CEM-**4028** manufactured by Galileo Electro-Optics Corp.

The variable voltage power supply **22** preferably includes a programmable high voltage power supply **58** such as a O-**2500** V voltage supply manufactured by KEPCO, Inc. The output of such a supply can be controlled by varying the resistance across appropriate input terminals thereof. A ten turn variable resistor **60** such as a Beckman Helipot is thus so connected, the rotatable shaft of which is coupled to a D.C. motor **62,** which in turn is controlled by a power source **64** such as that manufactured by Power Designs, Model TW-**4005** voltage supply to control the rate at which the resistance of the variable resistor **60,** and hence the voltage applied to the ion source **12,** is varied. It is readily apparent that the rate can be mechanically or electrically varied to generate a variety of wave shapes, such as to provide a single or multiple sweep over a range of predetermined energies.

The voltage from the power source **58** is also applied to the synchronous mass selector **26,** which comprises a voltage divider network including a variable potentiometer **66** which may be positioned such that a given and constant fraction of the voltage applied to the ion source **12** is developed. This developed voltage is applied across the plates **46** of the analyzer **35.** Accordingly, at any given time, regardless what voltage is applied to the ion source **12,** when the primary ions are scattered from atoms having a given atomic mass and so lose a given fraction of their original kinetic energy, the voltage across the plates **46** will be such as to allow only those scattered ions to be transmitted through the exit slit **44** to the detector **54.** If desired, the mass selector **26** may provide equal and opposite potentials to each of the plates **46,** such that a substantially constant potential is maintained along the center line through the analyzer.

The mass selector **26** further comprises another voltage divider **68** to provide a voltage proportional to the voltage applied to the plates **46** of the analyzer **35,** which proportional voltage is coupled to the display unit **28.**

The electronic signal produced as a result of electrons collected by the electron collector **48** is coupled to the signal processing circuit **50.** The circuit **50** comprises a conventional preamplifier **70,** such as Model **113** manufactured by Ortec, Inc., a main pulse amplifier **72** such as Model **435** A manufactured by Ortec, Inc., an integral discriminator **74** such as Model **421** manufactured by Ortec, Inc., a rate meter **76,** such as Model **441** manufactrued by Ortec, Inc., and a phase sensitive lock-in amplifier **78** such as Model HR-**8** manufactured by Princeton Applied Research Corporation.

The signal from the electron detector **48** is proportional to the counting rate of scattered ions, and is amplified by the preamplifier **70.** The thus amplified signal is further amplified and shaped by the main pulse amplifier **72.** The integral discriminator **74** rejects spurious noise in the signal, thereby improving the correspondence of the detected signal with the counting rate of scattered ions. The output of the integral discriminator unit **74** is then coupled to and counted in the rate meter **76** to produce an analog output voltage which accurately corresponds to the counting rate of the scattered ions.

In order to further enhance the analog output voltage by taking its derivative, a low frequency oscillator **80** is provided in series with the target **16** and the current measuring device **34,** to thereby modulate the potential on the target **16** and thus controllably vary the kinetic energy of the primary ions. It is understood that such a potential modulation can be achieved by a variety of other methods such as by modulating the voltage applied to the ion beam source. A preferred oscillator is Model **202**-CR, manufactured by Hewlett-Packard Instruments, Inc. This modulation induced change in the kinetic energy of the primary ions is consequently observable in the ultimately detected electronic signal using conventional small signal analysis techniques. A

signal from the oscillator **80** is coupled by a lead **84** to the lock-in amplifier **78** to provide a reference signal corresponding to the modulation. The modulation of the analog output voltage is detected by the lock-in amplifier **78** in accordance with the reference signal, and thus provides a signal representative of the derivative of the original electronic signal. In certain cases, such signal processing can further improve the signal-to-noise ratio of the signal corresponding to the counting rate of scattered ions. Where such an embodiment is not desired, a double pole switch **82** is provided to disconnect or otherwise disable the oscillator **80** and lock-in amplifier **78.** The thus processed signal is coupled to the display device **28** such as an X-Y recorder. The signal is preferably used to drive the Y-axis of the recorder, while a signal from the synchronous mass selector **26** is coupled to the X-axis of the recorder. Accordingly, a graph of the counting rate of the scattered ions as a function of the primary ion kinetic energy may be provided.

As set forth hereinabove, the variable voltage power supply **22** may be desirably designed to include a sweep generator to provide multiple time varying sweeps of voltage over a predetermined range, thereby repetitively sweeping the energy of the ions in the ion beam through a range of energies. In such an embodiment, it is desirable to provide the signal processing unit **50** with signal averaging means for comparing the signals produced on successive repetitive sweeps to thus produce an average signal having improved signal-to-noise ratios. In a preferred such embodiment, such a signal averaging means comprises a digital multichannel scaling circuit, such as Model **1062** instrument computer manufactured by Nicolet Instrument Corp., synchronized to the mass selector **26** and coupled to the output from the integral discriminator **74.**

Graphs of the counting rate as a function of the primary ion kinetic energy may be used to construct scattered ion yield curves that are independent of variations in primary ion current and analyzer resolution resulting from changes in the primary ion energy. At each of a number of chosen values of primary energy, the counting rate value is obtained from the aforementioned graph and divided by the primary ion current corresponding to the associated primary ion kinetic energy. The value obtained by this division is then further divided by the primary ion kinetic energy value to give the ion yield value for that primary ion kinetic energy. This last division process is carried out because the number of ions passing through the energy analyzer is proportional to the energy at which they pass through because of the resolution characteristics of this particular analyzer. FIGS. **3 – 10** show such corrected yield curves. The points shown are those calculated by the above method using the experimentally obtained counting rate data. Such signal normalization procedures are readily effected using conventional electronic techniques.

FIG. **3** shows a typical prior art spectrum of the scattered ion yield as a function of primary ion kinetic energy, (i.e., for Cu), wherein the spectrum is seen to exhibit a smooth curve shape containing only a single maximum value. Such a spectrum is shown as FIG. **9** in an earlier publication by one of the inventors of the present invention, D.P. Smith, "Analysis of Surface Composition with Low-Energy Backscattered Ions," Surface Science, Vol. No. **25** No. **1,** March, **1971,** pp **171–191.** See also references there cited.

In contrast to such spectra showing only a single maximum value, FIG. **4** shows the oscillatory structure in the yield curve for the case of Ge, which is believed to be the result of resonant charge exchange during the ion-atom collisions. During such collisions an electron from a **3***d* electron orbital state associated with the Ge surface atom may be transferred to the vacant **1s** electron orbital state associated with the incident He^+ ion carried away with it after the scattering event. When this happens, the yield of scattered He^+ ions is reduced because of the neutralization resulting from electron exchange. This reduction in yield appears in the yield spectrum as one of the minima of the oscillatory structure.

The binding energy of the **3***d* electron orbital state of the Ge surface atom is approximately **29** electron volts, while that of the **1s** electron orbital state of the incident He^+ ion is approximately **25** volts. As used herein the binding energies of the electron orbital states of the surfaces atoms are measured relative to the Fermi level of the target **16.** To allow proper comparison of the binding energy of the incident ion with that of the target atom, the work function of the target must be considered. Typical values for the binding energies cited herein are given in Appendix I of the publication of K. Siegbahn et al, "ESCA: Atomic, Molecular and Solid State Structure Studied By Means Of Electron Spectroscopy," Nova Acta Regiae Societatis Scientiarum Upsaliensis, Ser. IV, Vol. **20,** Uppsala **1967,** pp **224–229.** It has been found that oscillatory structure in the yield spectra occurs when the interacting energy states (i.e., that of the incident ion and surface atoms) are not more than approximately **10**eV different. Accordingly, as discussed herein, resonant charge exchange is meant to include both pure resonance wherein the interacting energy states are exactly equal and quasi-resonance wherein the interacting energy states are approximately, but not exactly, equal.

In order for resonant charge exchange to occur, the initial and final energy states of the system, i.e., the total electronic energy of the target atom plus that of the primary ion and the total electronic energy of the ionized target atom plus that of the neutralized ion, respectively, must be nearly degenerate at infinite separation distances, i.e., that the initial and final states of each system are nearly equal in energy. Such a requirement is similar to that existing in coupled harmonic oscillators wherein the oscillators must have approximately the same frequency (i.e., energy) of oscillation for resonant interactions to occur. See L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, (**1935**), pp **314–331.**

During the collision event when the incident ion and target surface atom are in close proximity, the two can be considered as being in a quasi-molecular ionic state, where the electrons which initially were in atomic orbitals about their respective nuclei now orbit about both the parent surface atom and the colliding He nuclei in molecular orbitals. With an electron orbiting back and forth between the two nuclei, there will be an ion velocity at which the collision occurs so fast that the electron has only time to transfer to the ion and neutralize it. At a slightly lower ion velocity, the electron may transfer to the ion and transfer back to its parent surface atom,

leaving the ion unneutralized. Similarly, for progressively lower ion energies, the electron exchanges back and forth may lead to a succession of neutralizations of the ion, which in the ion yield measurement lead to a corresponding series of minima in the yield as a function of primary ion velocity and energy. In general, for any given primary ion kinetic energy, if the number of such exchanges is an odd number, a minima will occur in the yield curve, and conversely, if there is an even number of such exchanges, no decrease in the yield curve is observed.

The frequency of oscillation for such a molecular orbiting electron can then be given by $f = E_i/h$ where E_i is an interaction energy between the two near degenerate states (i.e., the initial and final states) of the system and h is Planck's constant. For some of the lighter elements, calculations of E_i have been possible, and the oscillatory features have been described with reasonable success. See "Resonant Charge Exchange in Atomic Collisions. II. Further Applications and Extension to the Quasi-Resonant Case," William Lichten, Phys. Rev. **139** No. **1A**, pp **A27-A34**, Jul. **5**, **1965**, and articles there cited.

The premary ion kinetic energy difference between successive minima in the yield can be related to differences in the interaction times associated with the energy at each minima. A given primary ion kinetic energy associated with a first minima having an energy E_1, has a velocity V_1 and thus has a time t_1 proportional to $1/v_1$ during which the ion and atom are sufficiently close for the charge exchange to occur. Similary, the primary ion kinetic energy associated with a second minima adjacent the first minima has an energy E_2, velocity v_2 and a time t_2 governing the exchange period. The corresponding difference between the times t_1 and t_2 at which minima in yield and hence resonant charge exchange occur can then be given by $t_2 - t_1 = a/v_2 - a/v_1 \sim 1/f$, where a is some "distance" over which the collision occurs. Since a is not a well defined quantity, it is usual to define an effective quantity $\langle E_i a \rangle$ so that $\langle E_i a \rangle_n = h/(v_{n+1}^{-1} - v_n^{-1})$

By making an approximation of the value of a, the interaction energy can be obtained from the data, and in principle related back to the electronic energy states of the surface atom.

As was stated earlier, for near resonant exchange to occur, the initial and final states of the system of two interacting particles must be nearly degenerate. For the specific cases shown in FIGS. **3** and **4**, i.e., He^+ scattering ions, it is necessary that the target atom have an electronic energy level near the ionization potential of He (**24.6** eV) in order for resonant charge exchange to occur. In the case of Cu, there is a **3***d* electron level at about **2** eV and a **3***p* electron level at about **74** eV. Neither of these levels is sufficiently close to the **1s** ionization potential of He^+ (**24.6** eV) to satisfy the near resonant condition. In the case of Ge, there is a **3***d* level at **29** eV which is near enough to provide for a near resonant condition and oscillatory structure shown in FIG. **4**.

The utility of the present invention is further illustrated in FIGS. **5** and **6**, which show the yield of $^4He^+$ ions scattered from a Pb and a Bi surface respectively. Because these elements have atomic masses **207** and **209** amu (avg.) respectively, being adjacent in the periodic table, they are generally indistinguishable due to the insufficient mass resolution of conventional ion scattering spectrometers. As is clearly seen in the FIGS. **5** and **6**, using the resonance charge exchange technique of the present invention, demonstratively different spectra results from the two elements, which spectra may then be compared against known reference spectra to unequivocably identify the two elements. It is believed that the structure shown in the Pb spectrum of FIG. **5** is attributable to electronic exchanges from either the $5d_{3/2}$ level or the $5d_{5/2}$ level, which levels have a binding energy of **22** and **20** eV respectively, which values are sufficiently closely associated with the ionization potential of He (**24.6** eV) to account for the structure. Similarly, the structure in the yield of He ions scattered from Bi shown in FIG. **6** is believed attributable to electronic states in the $5d_{3/2}$ and $5d_{5/2}$ electron orbitals of Bi atoms, having binding energies of **27** and **25** eV respectively.

The utility of the resonance charge exchange technique of the present invention is further shown in FIG. **7** where spectra showing structure produced upon scattering of He ions from elemental In and one of its compounds, InAs, are portrayed. As is readily seen, the structure for elemental In is significantly different than In in the compound form. Conventional ion scattering spectroscopy would reveal the same spectra for scattered ions from In whether elemental or in compound form. The different structure here presented results from resonant charge exchange, and is believed demonstrative of electronic exchange phenomena on an atomic level, which phenomena are influenced by the atomic bonding to the nearest neighbor atom.

FIGS. **8**, **9** and **10** further demonstrate additional utility of the present invention. FIG. **8** is, in some respects, comparable to the spectrum shown in FIG. **5**, however, is prepared by scattering Ne ions rather than He ions from the Pb surface. As is seen, while structure is observed, the structure is significantly different from that produced by He ions (FIG. **5**). Such a difference is believed attributable to the difference in the electronic energy levels associated with Ne ions. The binding energy of the **2***p* electron orbital of Ne is approximately **18** eV, which is sufficiently close to the **22** and **20** eV binding energy value of the $5d_{3/2}$ or the $5d_{5/2}$ electron orbitals of Pb such that resonant charge exchange is still observed. FIG. **9** is likewise similar to the elemental In spectrum shown in FIG. **7**, except that it was prepared by scattering Ne ions from an elemental In surface. The binding energy of the **4***d* orbitals in In is **16** eV, as compared with the **18** eV of the **2***p* orbital of the incident Ne ions. The similar energies thus are believed to account for the observed structure. The difference in the structure of FIGS. **7**, **9** and **10** is further indicative that different resonant charge exchange processes occur with different probe ions. FIGS. **8** and **9** are further indicative of the utility of the present invention when gases other than He are used. FIG. **10** is indicative of still further utility of the present invention, showing structure produced in spectra when ions of yet another gas (Ar) are scattered from a material (In) having orbital energy levels of the same approximate energy as the ionization potential of the bombarding ions. In this case, the ionization potential of the $3p_{1/2}$ orbital of Ar is **15.7** eV. This value is sufficiently close to the binding energy of the **4***d* orbital of In (**16** eV) to account for the observed structure.

Having thus described the present invention, what we claim is:

1. An ion scattering spectroscopic method for investigating atoms having a given atomic mass on the surface of a material comprising

a. directing a beam of primary ions having a known mass and known charge state toward a predetermined area on said surface and varying the kinetic energy thereof over a range of predetermined primary ion kinetic energies;

b. detecting scattered ions having a predetermined loss of energy as a result of scattering at a given angle;

c. correlating said detecting and varying of kinetic energies to generate a signal the magnitude of which at any given time corresponds to the yield of scattered ions, affording over a period of time a spectrum of said yield as a function of the primary ion kinetic energies, which spectrum is indicative of electron exchange processes associated with the identity of and electronic states in said atoms.

2. An ion scattering spectroscopic apparatus for investigating atoms having a given mass on the surface of a material, a portion of which apparatus is adapted to fit within an evacuatable chamber comprising:

a. means for supporting a material the surface of which is to be investigated;

b. means for providing a beam of primary ions having a known mass, known charge state, and a range of time varying predetermined primary ion kinetic energies to be directed toward a predetermined area on said surface such that a fraction of said ions are scattered at a given angle therefrom;

c. analyzer means for passing and detecting ions having a predetermined loss of energy as a result of said scattering;

d. control means operatively coupled to said providing means and said analyzer means for allowing only such scattered ions as have a fixed fraction of said predetermined kinetic energies to pass through and be detected by said analyzer means to thereby generate a signal the magnitude of which at any given time corresponds to the yield of such scattered ions as had a given predetermined kinetic energy at that same instant and as were scattered from said atoms of said given atomic mass; and

e. display means operatively coupled to said control means and to said analyzer means for providing a spectrum corresponding to said yield as a function of predetermined primary ion kinetic energies, which spectrum is indicative of electron exchange processes associated with the identity of and electronic states in said atoms.

3. An apparatus according to claim 2 wherein said ion beam providing means further comprises an ion gun, an adjustable high voltage power supply the output of which is coupled to the ion gun, and a sweep generator coupled to the power supply for controllably changing the voltage applied to the gun over the said range of time varying predetermined primary ion kinetic energies.

4. An apparatus according to claim 2 wherein said control means further comprises means coupled to said analyzer means of sensing the voltages at which a maximum signal corresponds to ions scattered from atoms of a given atomic mass and for feeding back a bias signal to said analyzer means to cause said analyzer means to lock on the said scattered ion signal corresponding to the said given atomic mass.

5. An apparatus according to claim 2 wherein said ion beam providing means comprises means for repetitively sweeping the energy of said ions through a range of energies.

6. An apparatus according to claim 5 further comprising signal averaging means for enhancing said signal produced on successive repetitive sweeps to improve the signal-to-noise ratio thereof.

7. An apparatus according to claim 6 wherein said signal averaging means comprises a digital multichannel scaling circuit synchronized to said sweeping means and coupled to said analyzer means.

8. An apparatus according to claim 2, said ion detecting means further comprising an electrostatic energy analyzer having at least a pair of electrodes having interior surfaces defining a channel therebetween along which ions having a given kinetic energy pass without appreciable loss when a known potential is applied to said surfaces.

9. An apparatus according to claim 2 further comprising means for taking the derivative of said signal.

10. An apparatus according to claim 9, said derivative taking means comprising means for repetitively modulating the potential of said surface to thereby controllably vary the kinetic energy of the primary ions and frequency and phase sensitive means for sensing a similar repetitive variation in said signal.

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