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Low-Energy Ion Scattering Measurements from an Al-Pd-Mn Quasicrystal

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Abstract

Energy-angle distributions of low-energy inert-gas ions scattered from surfaces provide information about surface composition and structure. We have measured energy spectra of He^+ scattered from an $Al_{71}Pd_{20}Mn_9$quasicrystal, which was oriented perpendicular to the 5-fold axis, along various azimuthal directions. Strong scattering signals are seen from Al and Pd, but only a weak Mn signal is observed. From measurements made of He^+ at an oblique angle of incidence scattered in the forward direction, we observe a 72° periodicity in the azimuthal dependence of the scattering signal intensity from Al surface atoms. The effect arises from shadowing effects involving neighboring surface atoms and provides direct evidence that Al surface atoms exist in a local environment with 5-fold symmetry. In addition, measuring the variation of the signal intensity with incidence angle provides information about neighboring atom distances, which compare favorably with a model of the quasicrystal surface derived from the bulk structure.

Keywords

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Disciplines

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Comments

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ABSTRACT

Energy-angle distributions of low-energy inert-gas ions scattered from surfaces provide information about surface composition and structure. We have measured energy spectra of He^+ scattered from an $Al_{71}Pd_{20}Mn_9$ quasicrystal, which was oriented perpendicular to the 5-fold axis, along various azimuthal directions. Strong scattering signals are seen from Al and Pd, but only a weak Mn signal is observed. From measurements made of He^+ at an oblique angle of incidence scattered in the forward direction, we observe a 72° periodicity in the azimuthal dependence of the scattering signal intensity from Al surface atoms. The effect arises from shadowing effects involving neighboring surface atoms and provides direct evidence that Al surface atoms exist in a local environment with 5-fold symmetry. In addition, measuring the variation of the signal intensity with incidence angle provides information about neighboring atom distances, which compare favorably with a model of the quasicrystal surface derived from the bulk structure.

INTRODUCTION

Low energy ion scattering (LEIS) is a surface analysis method that can identify atoms in the topmost layer of a material. It consists of directing a beam of monoenergetic ions at a surface and measuring the kinetic energy of the scattered ions. If a beam of inert-gas ions with an incident energy below a few keV is used, nearly all ions that survive scattering result from events involving surface atoms. The energy loss of an incident ion following a binary collision is kinematically related to the mass of its collision partner, so energy analysis of scattered ions provides mass analysis of the surface [1-3]. Angle-resolved LEIS, in which the orientation of the sample surface is varied with respect to the incident ion beam, further provides real-space structural information about surface atoms. The information gathered is obviously of particular importance when multicomponent metallic systems are investigated. In such systems preferential segregation or favored surface terminations may cause the topmost layer to differ significantly in composition from underlying layers [4-6].

We present here angle-resolved LEIS studies of an icosahedral phase (*i*) sample of an Al-Pd-Mn alloy. Icosahedral quasicrystalline materials, such as this, are of particular interest because of their unique structures which, while not periodic, exhibit long range, yet aperiodic order [7,8]. Our interest in studying this system using LEIS arises from the basic question "Is the surface of a quasicrystal itself quasicrystalline?". Most surface structure techniques probe several layers and there remains a question about the nature of the *topmost* layer of a quasicrystal. Thus, our goal in this study was to examine the composition and structure of the topmost layer. Based upon data obtained with low energy electron diffraction (LEED) [9-14], scanning tunneling microscopy [10,15-18], secondary electron imaging [19,20], surface X-ray diffraction [21,22] and X-ray photoelectron diffraction [23-25], the surface structure of *i*-Al-Pd-Mn appears quasicrystalline within the experimental resolution of these techniques. Dynamical LEED calculations for a 5-fold surface of *i*-Al-Pd-Mn by Gierer et al., suggest that the topmost layer of clean *i*-Al-Pd-Mn prepared under ultrahigh vacuum (UHV) conditions through a combination of sputtering and annealing should be predominately Al (about 90 atomic percent Al and 10% Mn) with a second layer about 0.4 Å below the first consisting of about 49% Al, 42% Pd and 9% Mn [12,13]. A similar relative contraction compared to the bulk was also obtained by surface X-ray diffraction for the same surface prepared under UHV conditions by high temperature annealing [21,22]. Results with surface X-ray diffraction suggest a composition of the top layer close to Al_3Pd [21,22]. As will be shown, our results are consistent with aperiodicity being maintained at the topmost layer of this material. In addition, our results are consistent with the LEED results in respect to both the composition of the top layer and the relative difference between the first and second layers.

EXPERIMENTAL DETAILS

Ion scattering data were obtained in a UHV apparatus with a base pressure of 7×10^{-10} Torr. The apparatus consists of an ion source connected to an analysis chamber, which contains a sample manipulator and a hemispherical electrostatic ion energy analyzer. The ion source produces monoenergetic (ΔE <1 eV), mass analyzed inert-gas ion beams in the energy range between 0.1 to 3 keV. The manipulator permits angle-of-incidence adjustment and full azimuthal rotation of the sample. The energy analyzer is mounted on a turntable that allows the observing angle (i.e., the scattering angle) to be varied from 15° to 90°. Thus, we can systematically vary the angle of incidence α, the azimuthal orientation angle ϕ, and the observed scattering angle θ. The arrangement is diagrammed in figure 1. Additional details of the apparatus can be found elsewhere [26].

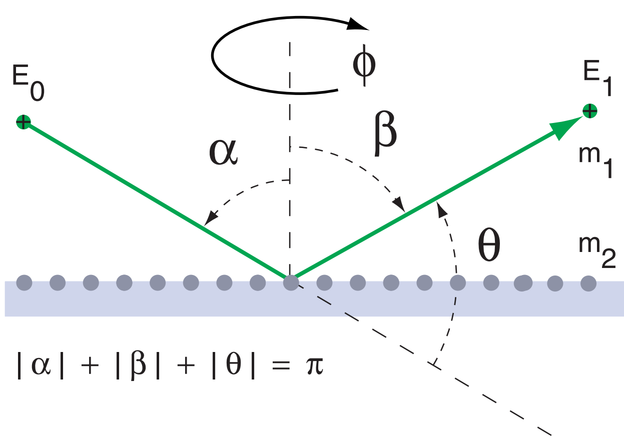

Figure 1. *Arrangement and angle definitions for angle-resolved LEIS measurements. The incident ion has kinetic energy E_0 initially and E_1 after scattering. α is the incidence angle, β is the exit angle, θ is the scattering angle, and ϕ is the azimuthal orientation angle of the surface. For an incident ion with mass m_1, the surface atom mass m_2 can be determined from the kinematic relationship $m_2 = m_1(1 + E_s - 2\sqrt{E_s}\cos\theta)$ / $(1 - E_s - Q_n)$ where $E_s = E_1/E_0$ and Q_n accounts for any inelasticity in the collision.*

The single grain sample of icosahedral *i*-Al-Pd-Mn used in this study was grown at the Ames Laboratory by the Bridgman method, as described previously [27]. The sample was oriented with the surface perpendicular to a five-fold axis and ground and polished with a final polish using 0.25 μm diamond paste. Prior to this study, the sample was checked for second phases by scanning electron microscopy and electron dispersive spectroscopy. Less than 1% second phase was observed by this method. A sample adjacent in the boule to the one used here had a bulk composition of $Al_{70.8}Pd_{20.2}Mn_{8.9}$ as determined by inductively-coupled-plasma atomic-emission spectroscopy. The sample was initially cleaned in vacuum by cycles of sputtering with helium ions followed by annealing. The helium source used for the angle-resolved LEIS experiments was also used for sputtering. An annealing temperature of 450 K was used for the first cleaning cycle. This was increased by 50 K after each cycle until a final annealing temperature of 800 K was obtained. A final annealing temperature of 800 K was chosen because this temperature yields good LEED patterns, indicative of a quasicrystalline or at least nearly-quasicrystalline surface structure [28]. Furthermore, the composition at the surface after annealing at this temperature is close to the bulk composition [29,30]. Surface cleanliness was checked by LEIS which has a detection limit for oxygen of $<1\%$ of a monolayer [31]. After the cleaning procedure and prior to each experiment, the sample was sputtered using He ions and annealed at 800 K for at least 45 minutes unless otherwise specified.

RESULTS

Energy Spectra

Figure 2 shows a LEIS energy spectrum from a 5-fold surface of *i*-Al-Pd-Mn after sputter cleaning and and annealing at 800 K. Peaks in the energy spectrum resulting from collisions of He^+ with Al and Pd surface atoms are clearly visible, and a small feature attributed to scattering from Mn can also be discerned. The scattered ion energies are observed to be slightly below those for purely elastic scattering, presumably due to inelastic processes during the collision event. We note from this scan the near absence of scattering from oxygen, which appears below the Al peak, indicating a low oxygen atom concentration on the freshly annealed surface. An estimate of the relative concentrations of the various surface atoms can be obtained from the peak areas and the scattering cross sections. We calculated the differential scattering cross section ($d\sigma$) for 1 keV He colliding with O, Al, Mn, and Pd target atoms, using the ZBL screened Coulomb potential [32]. If we assume that the neutralization rate of scattered He^+ is a constant, which is often valid for clean metal alloy surfaces, the ratio of the peak area to $d\sigma$ gives a relative measure of the surface atom concentration. A number of LEIS spectra taken from surfaces prepared in the same manner indicates, after background subtraction, a surface composition of $Al_{85.7}Pd_{13.5}Mn_{0.8}$. This is consistent with previous LEIS results [13]. The oxygen concentration is estimated to be $<1\%$. For each element, a subtraction procedure was used to remove the broad background observed to the low-energy side of each scattering peak, which results from inelastic loss processes or subsurface scattering.

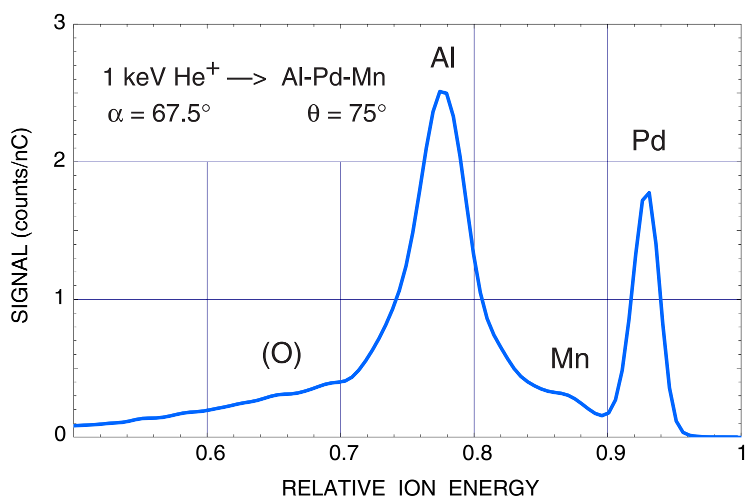

Figure 2. *LEIS energy spectrum of 1 keV He$^+$ scattered from an Al-Pd-Mn quasicrystal 5-fold surface at an angle of 75°. Under these conditions, the sensitivity to Pd is about a factor of three greater than for Al.*

Angular Measurements

Two types of angular measurements were conducted by varying either the azimuthal orientation of the sample, ϕ, or the incidence angle of the ion beam on the sample, α, while monitoring the scattering signal intensity at selected energies. Figure 3 shows a ϕ scan over a full rotation of the sample at fixed α for three scattered ion energies, corresponding to He^+ scattering from Al, Mn, and Pd surface atoms. For these measurements the ion beam struck the sample at an oblique angle of incidence. A distinct periodic intensity variation is observed in the scattering signal from Al atoms. Similar behavior can be seen in the Pd and Mn signals, although their weaker strengths make the variations more difficult to discern. The signal variations are attributed to a shadowing effect involving neighboring atoms. Shadow cones, which form behind surface atoms and are paraboloidal regions within which scattered incident ions cannot penetrate, shadow neighboring atoms in certain azimuthal directions. Peaks in the Al signal intensity appear every $72^\circ \pm 2^\circ$ and indicate that the surface atoms must exist in local environment that has 5-fold symmetry.

The variation in scattering signal intensity was also measured as a function of incidence angle at selected scattered ion energies. Figure 4 shows the dependence of the scattering signals from Al, Mn, and Pd atoms as a function of α. In this case, the sample was oriented at an azimuth corresponding to the first signal maximum seen in figure 3. Each element has a distinct angular dependence. At high values of α, the Al signal dominates. At intermediate values of α, the Pd signal becomes most intense, and the weak Mn signal peaks at slightly lower α. This indicates that Al predominates at the surface, while the Pd and Mn atoms tend to reside beneath the Al, since they are shadowed by Al atoms when the He^+ incidence angle is most oblique.

A measure of the atom distances on the topmost Al layer and of the interlayer spacing can be obtained through shadow cone analysis. We used the universal shadow cone expressions developed by Oen to calculate the cone radius as a function of the distance behind the scattering atom [33]. Taking the inflection point in the Al signal (α=80°) as the point at which shadow cone edges frequently pass through nearby surface atoms, the distance to these atoms is found from geometry to be 7.5±1 Å. At α=80°, only 10° from glancing incidence, shadow cones project a substantial distance over the surface, so this value is not the distance between nearest neighbors, but between atoms with a spacing that is frequently encountered on the 5-fold surface. The peak in the Al signal at 68°, which can result from a flux focusing effect from many weakly-deflected

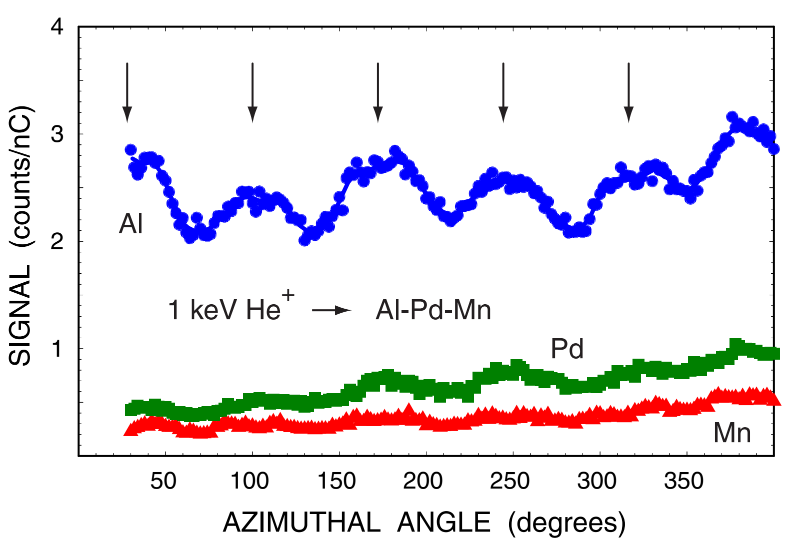

Figure 3. *Azimuthal (ϕ) dependence of He^+ signal intensity scattered from an Al-Pd-Mn quasicrystal surface at energies corresponding to collisions with Al, Mn, and Pd surface atoms. A 72° periodic variation (marked by arrows) in the signal strength is clearly seen for He^+ scattered by Al surface atoms.*

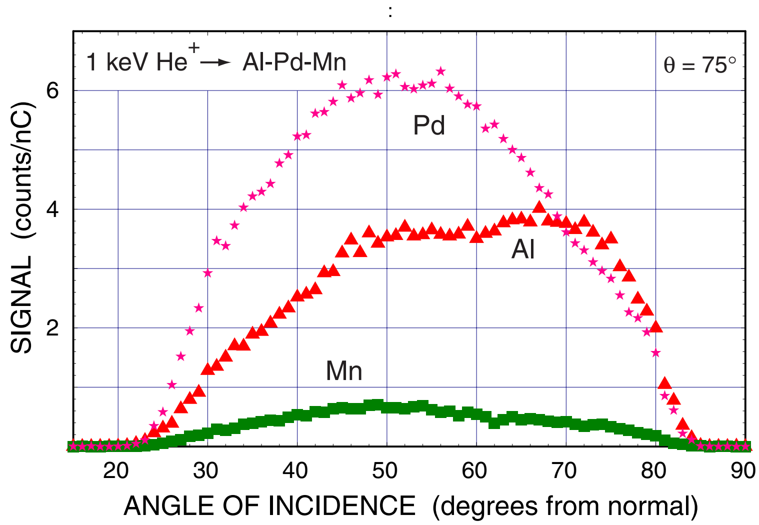

Figure 4. *Angle-of-incidence (α) dependence of He$^+$ signal intensity scattered from an Al-Pd-Mn quasicrystal surface at three energies, corresponding to collisions with Al, Mn, and Pd surface atoms. The Al signal peaks at a higher α than does the Pd signal, indicating that Pd atoms are beneath Al atoms. The Mn signal peaks at the lowest α value.*

He$^+$ ions passing near the shadow cone boundary, indicates a nearest-neighbor distance of 2.2±1 Å. From the peak in the Pd signal at α=52°, a distance of 0.4±0.5 Å is found for the depth between Al atoms in the topmost layer and the majority of exposed Pd atoms. At this time, we are unable to reduce the error estimates for these measurements due to uncertainties in the α angle values. However, it should be possible in the future to increase the accuracy by using more exact calibration procedures.

DISCUSSION

The results show a composition at the annealed *i*-Al-Pd-Mn quasicrystal surface that is significantly different than in the bulk. Al is enriched, while Pd is slightly depleted and Mn is substantially depleted. Evidence also exists from other studies of Al-based icosahedral quasicrystals that the composition of the topmost layer differs from the bulk composition, including studies using LEED [12,13], LEIS [12-14], and X-ray diffraction [21,22]. It is difficult to assess whether the altered surface composition is an intrinsic property of the material or has resulted from the cleaning procedure. Preferential sputtering can alter the near-surface composition, but the use of relatively low energy He$^+$ reduces this effect [34]. However, we find that under the conditions of this study, preferential sputtering leads to a depletion of Al in the topmost surface layer. This has been confirmed by LEIS measurements during long-term sputtering of the Al-Pd-Mn surface at 350 K [35]. The Al signal intensity was observed to decrease, while the Mn and Pd signal intensities increased. Another explanation for the increase in Al in the topmost layer relative to the bulk is evaporation of one or more components during annealing. This may be occurring for Mn, which has a higher vapor pressure than either Al or Pd. But either process does not explain the enrichment of Al at the surface, which could be a characteristic property of the *i*-Al-Pd-Mn surface. Gierer, et al., found from dynamical LEED calculations based on the bulk structural model by Boudard, et al., that there appear to be favored surface terminations and that these favored terminations are all Al-rich [12,13,36].

The azimuthal scan clearly shows the 5-fold symmetry of the surface. This is in sharp contrast to the crystalline Al(111) surface, which displays hexagonal symmetry when similar angle-resolved LEIS measurements are made [37]. It is somewhat surprising to us that the Al signal intensity exhibits 5-fold and not 10-fold periodicity in the ϕ scan data, since 10-fold rotational symmetry, resulting from two 5-fold domains, is usually encountered in LEED measurements of this *i*-Al-Pd-Mn surface. At the incidence angle used for these measurements (α=67.5°), each shadow cone passes through atoms in the vicinity of the scattering center, so the observed 5-fold symmetry arises from the local atomic environment. However, the irradiation area is large (>1 mm²), so a similar ordering must extend across much of the surface. Evidently there is a preferred orientation of pentagonal motifs in the topmost layer.

One real-space model of the *i*-Al-Pd-Mn 5-fold surface, which has been shown to be consistent with fine structure in STM data [17], is based on surface terminations of bulk pseudo Mackay icosahedral clusters that are adjusted to agree with dynamical LEED calculations of Gierer, et al. [12,13]. The distances between Al surface atoms in this model have been tabulated and a number of preferred distances are found in their distribution. The three shortest preferred distances are 4.8, 7.7, and 12.5 Å. We find that the 7.5±1 Å distance indicated by our LEIS measurements is close to one of the preferred Al-Al distances. Visual inspection of the Al surface plane in the model shows that this distance (7.7 Å) corresponds to the 1,4 atom spacing in the 10-atom rings that are prevalent on the surface. The 2.2±1 Å distance seen for more closely spaced Al atoms probably relates to the atom spacing either between adjacent surface atoms or between surface atoms and the next exposed plane of atoms. This distance is smaller than that between nearest neighbors on the Al(111) surface (2.9 Å), suggesting either a densely packed or rumpled surface. However, the relatively large error in this measurement does not allow us to make a definitive statement about surface atom density at present. It is also interesting to note that the 0.4±0.5 Å spacing between the surface plane and the Pd-rich second plane indicated by the angle-resolved LEIS data is in good agreement with the aforementioned surface model. We anticipate making a better assessment of nearest neighbor distances and interplaner spacings following more precise measurement of the shadowing angles.

CONCLUSIONS

Angle-resolved LEIS measurements provide composition and structural information about the *i*-Al-Pd-Mn 5-fold surface. The surface of an annealed quasicrystal sample is composed primarily of Al atoms and its composition is approximately $Al_{86}Pd_{13}Mn_{\leq 1}$. A Pd-rich layer appears to exist just below the topmost Al layer. Exposed surface layers appear deficient in Mn. The Al atoms at the surface exhibit local 5-fold symmetry. An observed near-neighbor distance on the Al surface layer is 7.5±1 Å, which is close to a preferred Al-Al distance in a surface model based on the bulk structure.

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