

The origin of the Auger-photoelectron coincidence spectroscopy (APECS) spectral line broadening of AgPd alloy

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Abstract

Recently, Jiang et al. [Jiang et al., *J. Electron Spectrosc. Relat. Phenom.* 130 (2003) 33] concluded that when the energy fixed photoelectron analyzer is positioned below the center photoelectron kinetic energy, the extra broadening of Ag core-level photoelectron line of disordered Ag_xPd_x ($X=0.5$) alloy by the disorder broadening manifests as the Ag coincidence Auger-electron spectroscopy (AES) line broadening on the high kinetic energy side, compared to when the analyzer is positioned on the center kinetic energy. We show that the change in the coincidence AES lineshape by a different positioning of the energy fixed photoelectron analyzer is not due to the disorder broadening. When the electron analyzer is positioned below the center photoelectron kinetic energy, the lineshape change is due to the decay of the core hole left by the photoelectron which suffers from the inelastic scattering before it goes out of a solid. The inelastically scattered photoelectrons are also detected when the electron analyzer is positioned below the center photoelectron kinetic energy. The change in the relative intensity of the inelastic AES line by a different positioning of the analyzer supports the present explanation.

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1. Introduction

The core-level binding energy of an atom at site i in a solid depends on the electrostatic potential V_i at site i . In order to determine the electrostatic potential V_i at lattice point i in a random alloy relative to the surrounding elemental solid, Magri et al. [1] suggested a correlated charge model (CCM). By CCM the excess charge on each A site in an AB alloy is linearly proportional to its number of B neighbors so that even when lattice sites are randomly occupied by A and B atoms, the site charge will be correlated. Johnson and Pinski [2] developed the charge-correlated coherent potential approximation (CC-CPA) in which the charge on site i is assumed to be determined solely by the number of unlike neighbors. Cole et al. [3–5] studied the distribution of the potential $V_i(\text{Na})$ for a site with a particular number (Na) of unlike nearest neighbors about their averages. They showed that for the FCC lattice clusters the calculated distributions for each Na are Gaussian with full width at the half maximum (FWHM) smaller

than the component splitting. For the SC lattice, the component broadening and the component splitting are comparable. The overall effect of disorder is an approximately Gaussian broadening (see Fig. 2 in Refs. [3,4]).

Core-level X-ray photoelectron spectroscopy (XPS) probes the local potential at lattice site in a solid and so should be able to provide information on both conditionally averaged site potentials in a disordered alloy and fluctuation about those averages, i.e., an additional Gaussian broadening (a distribution of site potentials) [3–7]. Cole and co-workers [3–7] showed the presence of an additional Gaussian broadening in the core-level XPS spectra of random alloys (see Fig. 5 and Table 2 in Ref. [4]). The observed Gaussian broadening (the disorder broadening) is consistent with a prediction based on the CCM and point charge electrostatics, although the effect was found to be significantly smaller than predicted for perfectly random alloys. This was attributed to a tendency for short range ordering implicit in the CCM [3–7]. The nearest neighbor approximation (NNA) in which the XPS spectrum

is given by the superposition of $Z + 1$ components (Z is the number of sites in the first shell) was found to give a good description of the XPS lineshape of disordered alloys [3–7] (see Fig. 3 in Refs. [3,4]).

In an analysis of the Cu 2p-level XPS spectra of CuPd alloys, it is found that with increasing Pd concentration there is an increase in Cu 2p linewidth and intensity in the low kinetic energy photoelectron tail [4] (see Fig. 5 in Ref. [4]). The latter is due to a modest increase in the asymmetry parameter with Pd composition which reflects the local density of states at the Fermi level [8,9]. The asymmetry parameter varies with the local environment in a disordered alloy as well as with global composition [4] (see Table 2 in Ref. [4]). The use of the same asymmetry parameter for all compositions in the NNA does not introduce significant errors [4].

Recently, Jiang et al. [10] raised a question “whether it is possible to measure the photoelectrons with kinetic energy affected by the disorder broadening due to the relatively small magnitude of the effect using an energy analyzer with a limited resolution”. They studied the Ag Auger-electron spectroscopy (AES) spectrum of random substituted Ag_XPd_X ($X=0.5$) alloy by Auger-photoelectron coincidence spectroscopy (APECS) [10]. By APECS, a photoelectron and an Auger electron are detected in time coincidence. Since these electrons are generated by creation and annihilation of the same core-hole state, respectively, only features characteristic of that event contribute to the coincidence spectrum [11–22]. Thus, as compared to conventional single spectroscopies, such as XPS and AES, APECS enables the photoemission and the Auger-electron emission to be examined with unprecedented discrimination.

Jiang et al. [10] argued as follows. When the energy fixed electron analyzer is positioned below the center photoelectron kinetic energy, the difference in the overlap of the APECS apparatus analyzer’s response function (line IV in Fig. 6 in Ref. [10]) with the photoelectron line of pure Ag metal (line I) and that of random substituted alloy (line II), namely the photoelectrons in the dark shaded region are “those from atoms where the charge transfer has resulted in a significant shift in their kinetic energies” and “affected by the disorder broadening”. “A bias in the distribution of the disorder broadening affected core-level electron binding energies” can then be introduced by positioning the energy fixed electron analyzer below (or above) the center photoelectron kinetic energy so that the relative proportion of the dark shaded photoelectrons of a lower kinetic energy is greater (or smaller) than those of a higher kinetic energy. A different distribution of atomic sites is sampled so that the AES spectrum measured in coincidence with the selected photoelectron energy is expected to reflect a different disorder broadening.

They concluded that compared to the singles Ag M45–N45N45 AES spectrum, when the electron analyzer is positioned on the center photoelectron kinetic energy, the peak in the coincidence AES spectrum is narrowed on both sides of the peak and the peak position is almost unshifted

from the singles one (Fig. 5 in Ref. [10]). In the present paper, we denote the atomic shells M_x and N_y by MX and NY , respectively. When the energy fixed electron analyzer is positioned at 0.8 eV above the center photoelectron kinetic energy (III in Fig. 6 in Ref. [10]), the coincidence AES peak is shifted from the singles one to the low kinetic energy by -0.39 eV (Fig. 7 in Ref. [10]). When the energy fixed electron analyzer is positioned at -0.8 eV below the center photoelectron kinetic energy (IV in Fig. 6 in Ref. [10]), the coincidence AES peak is shifted from the singles one to the high kinetic energy by 0.47 eV. The coincidence line is broadened on the high kinetic energy side (Fig. 8 in Ref. [10]). They interpreted that the broadening is due to “the disorder broadening affected photoelectrons”.

The core-level XPS spectrum of a disordered alloy is essentially a Gaussian distribution of site potentials broadened by the core-hole lifetime [3,4]. When the core-hole lifetime is predominantly governed by the Auger transitions, the core-hole lifetime of a random alloy is equal to that of a pure metal. Thus, when the XPS width of a random alloy is compared with that of a pure metal, the disorder broadening becomes an additional Gaussian broadening. The singles M5 photoelectron line width of Ag metal and that of AgPd alloy are 0.51 eV and 0.59 eV, respectively (the data by Weightman et al. cited in Ref. [10]). According to Ref. [10], they are 0.59 eV and 0.68 eV, respectively. The disorder Gaussian broadening (addition in quadrature) is then 0.3 eV (or 0.34 eV). It is 0.26 eV for CuPd alloy [3]. They are similar. The lifetime width of Ag metal is 0.31 eV [8]. The FWHM of Gaussian distribution of potential for a site i with a particular number of unlike nearest neighbors about their averages is smaller than the component separation [3,4]. The latter is $0.30/4.2 = 0.07$ eV (or $0.34/4.2 = 0.08$ eV) because the FWHM of the overall Gaussian distribution (disorder broadening) is 4.2 times the peak (component) separation [3]. The broadening and splitting of the component are fairly independent of the number of unlike neighbors [3,4]. Thus, by comparing Fig. 2 in Refs. [3,4] with Fig. 6 in Ref. [10] we can see that a difference in the energy fixed electron analyzer’s positioning shown in Fig. 6 in Ref. [10] does not result in a different AES line disorder broadening. It is not only the “dark shaded” photoelectrons which are affected by the disorder broadening.

If a bias in the distribution of the disorder broadening affected core-level photoelectrons can be introduced by positioning the energy fixed electron analyzer above (or below) the center photoelectron kinetic energy, we expect that when the energy fixed electron analyzer is positioned above (or below) the center photoelectron kinetic energy, the coincidence AES spectrum becomes narrowed on the high (or low) kinetic energy side compared to that when the energy fixed electron analyzer is positioned on the center photoelectron kinetic energy. Because compared to when the energy fixed electron analyzer is positioned on the center photoelectron kinetic energy, when the energy fixed electron analyzer is positioned above (or below) the center photoelectron kinetic

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