



PERGAMON

Solid State Communications 116 (2000) 137–141

solid
state
communications

www.elsevier.com/locate/ssc

Depletion of the density of states near the Fermi energy induced by disorder and electron correlation in alloys

H.-J. Noh^a, T.-U. Nahm^{b,*}, J.-Y. Kim^a, W.-G. Park^{a,†}, S.-J. Oh^a,
J.-P. Hong^b, C.-O. Kim^b

^aDepartment of Physics, Seoul National University, Seoul 151-742, South Korea

^bDepartment of Physics, Hanyang University, Seoul 133-791, South Korea

Received 2 May 2000; received in revised form 16 June 2000; accepted 10 July 2000 by H. Kamimura

Abstract

We have performed high-resolution photoemission study of substitutionally disordered alloys Cu–Pt, Cu–Ni, and Pd–Pt. The ratios between alloy spectra and pure metal spectra are found to have dips at the Fermi level when the residual resistivity is high and when strong repulsive electron–electron interaction is expected. This is in accordance with Altshuler and Aronov’s model which predicts a depletion of the density of states at the Fermi level when both disorder and electron correlation are present. © 2000 Published by Elsevier Science Ltd.

Keywords: A. Metals; B. Electron–; electron interactions; D. Photoelectron spectroscopies

PACS: 79.60.-i; 71.20.Be; 71.55.Ak

1. Introduction

Two decades ago Altshuler and Aronov interpreted tunneling data of some disordered systems as showing the electron–electron interaction effect which induces change in the density of states (DOS) around Fermi level [1,2]. Their model predicted the reduction of DOS in the case of three-dimensional (3D) solids given by the relation

$$\delta\nu = \frac{\lambda}{4\sqrt{2\pi^2}} \frac{\sqrt{|\epsilon|}}{(\hbar D)^{3/2}}, \quad (1)$$

where $\delta\nu$ is the change of the density of states, ϵ the energy measured from Fermi level, D the diffusion coefficient which is inversely proportional to the disorder driven resistivity ρ , λ the electron–electron interaction strength. Recently, it was applied to the interpretation of the photoemission spectra of La(NiMn)O₃ and La(NiFe)O₃ which undergo metal–insulator transition (MIT) [3]. The reduction

of DOS at the Fermi energy (E_F) was observed as Mn or Fe ions were substituted, and it was interpreted as due to the disorder and electron correlation effect following Altshuler and Aronov’s theory. However, the reduction of DOS has not been observed before for typical disorder metallic alloy system, and this is the subject of the present investigation.

Among metallic alloys, the most probable candidates showing both disorder and electron correlation effects are the late transition metal alloys. In fact, it is well known that the residual resistivity of many disordered alloy systems such as Cu–Au and Pd–Pt show simple Nordheim behavior, but one component of most of binary alloys which is a noble-metal and the other transition metal with approximately 9d valence electrons Ni, Pd, and Pt (henceforth designated as *d-9* transition metals) show great deviation from the Nordheim behavior [4]. For example, Pt-rich Cu–Pt and Pd-rich Ag–Pd alloys have ill-defined Fermi surface especially around X point due to the broadening of the Bloch spectral function at and near the Fermi wavevector \mathbf{k}_F [5,6] and as a result, both theoretically and experimentally an asymmetric residual resistivity curve with values of as high as 85 $\mu\Omega$ cm has been observed. It is thus expected that due to strong disorder at E_F in noble-*d-9* transition metal alloys and due to the strong electron–electron interaction between

* Corresponding author. Tel.: +82-2-2290-0912; fax: +82-2-2290-6868.

E-mail address: tschnahm@email.hanyang.ac.kr (T.-U. Nahm).

† Present address: Center for Science in Nanometer Scale, Seoul National University, Seoul 151-742, South Korea.

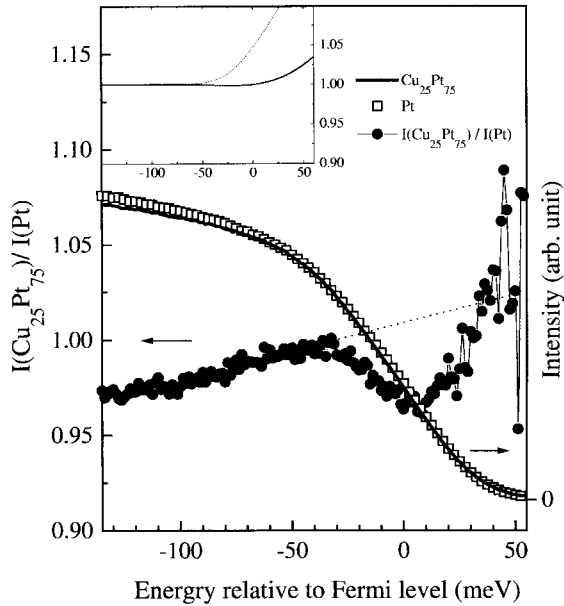


Fig. 1. Photoemission spectra of $\text{Cu}_{25}\text{Pt}_{75}$ (line) and of pure Pt (open squares) as well as the divided spectra $I(\text{Cu}_{25}\text{Pt}_{75})/I(\text{Pt})$ (filled circles) with $h\nu = 21.2$ eV at 95 K. The spectra were normalized arbitrarily after their backgrounds were removed. The dotted line is a guide to an eye for the expected behavior if the dip were absent. The inset shows the possible artifact effects; the solid line is the intensity ratio between the simulated spectra at 96 and 95 K, and the dashed line between the same simulated spectra at 95 K one of which is shifted by 1.25 meV.

Pt, Pd, or Ni d electrons at the Fermi level [7–9], one may observe the reduction of DOS at E_F , although the dip size might be smaller than in Ref. [3] due to screened Coulomb interaction between valence electrons.

In order to see such effect, we compared the angle-integrated photoemission spectra of Cu–Pt, Cu–Ni, and Pt–Pd alloys near E_F with those of pure d -9 transition metals which have almost smooth DOS near E_F . We observed some depletion of DOS at E_F in $\text{Cu}_{25}\text{Pt}_{75}$ and possibly for $\text{Cu}_{50}\text{Pt}_{50}$ and $\text{Cu}_{25}\text{Ni}_{75}$, the residual resistivity values of which are almost three times higher than those of high Cu concentration alloys due to strong disorder effect which reduces electron mean free path. This along with the absence of depletion for $\text{Pd}_{50}\text{Pt}_{50}$ whose electron mean free path is expected to be much longer due to sharp Bloch spectral function at E_F [10] show clear signature that the Altshuler and Aronov's theory is applicable to ordinary disordered transition metal alloys as well as to transition metal oxides showing MIT [3].

2. Experimental

The polycrystalline Cu–Pt, Cu–Ni, and Pd–Pt alloys were made by arc melting of 99.99% Cu, 99.9% Pt, and 99.997% Ni, and then annealed at temperature of 950°C to

ensure disorder phase which was confirmed with X-ray diffraction. The data were taken with VG Microtech CLAM 4 multi-channeltron detector electron energy analyzer with a resolution of 40 meV full width at half maximum (FWHM), and the base pressure was 1.5×10^{-10} Torr. Photon source was unmonochromatized He I line ($h\nu = 21.2$ eV). The samples were cooled down to 95 K with liquid nitrogen and the surfaces were scraped in situ at that temperature. In order to prevent contamination during the experiment, further scraping was done frequently.

3. Results and discussion

Fig. 1 shows the photoemission spectra of disordered $\text{Cu}_{25}\text{Pt}_{75}$ along with that of Pt near E_F . We can see that the lineshape of $\text{Cu}_{25}\text{Pt}_{75}$ and that of Pt around E_F are not quite the same, which indicates the detailed difference in DOS. Since the difference of spectral lineshape between $\text{Cu}_{25}\text{Pt}_{75}$ and Pt is quite small, we tested several possibilities which may induce such change besides the difference of DOS. Apparently, this kind of experimental lineshape difference cannot be attributed to a result of Fermi–Dirac distribution functions at slightly different temperatures. If it really were, the spectrum of a specimen at the lower temperature should have smaller spectral intensity at energy $E > E_F$ and more at $E < E_F$ and this difference should be symmetric about E_F , which is not the case in the figure. We even tried to fit the alloy spectrum with broadened Pt spectra to take account of possible temperature difference, but the lineshape was not the same at all. Repeating the measurements with new batch of samples also confirmed this behavior. Also, one might think that the Fermi level alignment can cause much uncertainty on the comparison of the two spectra, but when we shifted one of the spectra being compared by more than 2 meV, which was beyond the experimental error, the alignment was completely out of sense (see below and the inset of Fig. 1).

In order to see whether there really is some difference in the DOS near the Fermi level, we divided the spectrum of the alloy by that of pure Pt, assuming that the Pt DOS near E_F does not have any sharp structure. The absence of sharp structures in pure Pt DOS is confirmed by fitting the Pt spectrum with a linearly changing DOS, which is reasonably a good approximation within the energy region of interest [11]. This approximated DOS was multiplied by the Fermi–Dirac distribution and convoluted with a Gaussian curve corresponding to the instrumental resolution. The fitting was found to be perfect as expected, and the same was true for pure Cu spectrum.

The divided spectrum clearly reveals the presence of a dip at E_F which extends to almost 50 meV above and below the Fermi level. The dip size is very small with its relative value of only 6% of the divided spectral weight near the ends of the dip. The slope in the divided spectra seems to be caused by the detailed band structures of alloys and of pure Pt.

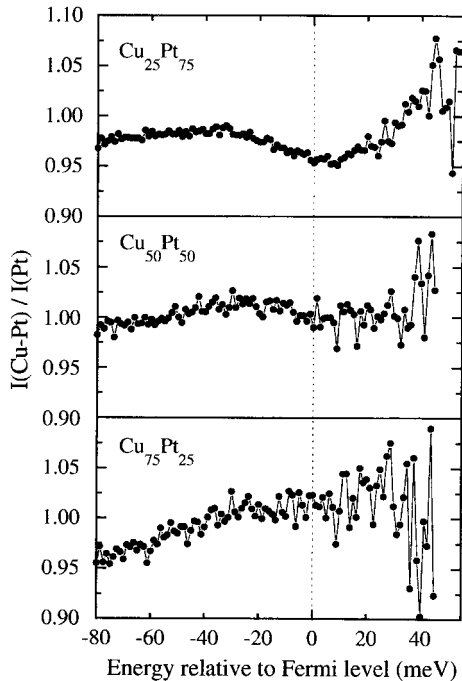


Fig. 2. Divided spectra $I(\text{Cu}_x\text{Pt}_{1-x})/I(\text{Pt})$ for $x = 0.25, 0.50$, and 0.75 . Note the absence of a dip for $x = 0.75$.

This dip structure could not be removed by any of the assumptions such as the misalignment of the Fermi level, temperature difference, inclusion of the satellites of He I line and the background treatment. These factors have their own effects when we simulate a curve, but none of them could be an explanation of the dip. For instance, the smooth decrease or increase of the divided spectral weight above the Fermi level was observed when there is slight difference in the temperature. If the temperatures at which spectra are taken are different from each other by only 1 K, great increase of the divided spectra above E_F can be observed for the same specimen. The solid line in the inset of Fig. 1 shows the simulated spectral intensity ratio between 96 and 95 K, assuming a constant DOS. However, the presence of a dip near E_F was not disputable since the shape of the simulated divided spectrum did not change much below E_F with the temperature difference of even 5 K. We also checked the possibility of misalignment of the Fermi level as a probable explanation for the dip, but it was found to give only smooth change in the divided spectrum, not affecting the presence of a dip. The dotted line in the inset of Fig. 1 shows the simulated spectral intensity ratio between the same spectra at 95 K, one of which is shifted by 1.25 meV. Neither can small difference in temperature along with small shift in energy explain the observed dip.

One might be tempted to interpret the depletion of DOS at the Fermi level as a real structure in calculated DOS within

one electron picture. However, the coherent-potential-approximation (CPA) calculation which gives good description of one-electron DOS of alloys does not show any hint of a sharp dip at the Fermi level [12]. It is also well known that when d -9 transition metals form alloys with other metals, the DOS near E_F is lowered in some cases, but this happens only for low concentration of d -9 transition metals, not for high concentration, extending over almost 1 eV around E_F [13]. Furthermore, any sharp structure near E_F , if existed, should manifest itself more prominently in pure metals or ordered phase rather than in disordered phase because of strong broadening of Bloch spectral function due to disorder for the latter. To the best of our knowledge, there has not been any report about the presence of sharp structure in high-resolution photoemission spectra of pure metals. Therefore, this kind of reduction of DOS at the Fermi level, we believe, can only be interpreted as a result of the electron–electron interaction in disordered system.

In Fig. 2, we show divided spectra of Cu–Pt alloys with Pt concentration of 25, 50, and 75 at.% to see the possible sharp change of DOS near E_F as a function of composition. From the figure, it is apparent that any such structure at E_F does not exist in the case of Cu-rich alloy, and it can be safely argued that dips at E_F for $\text{Cu}_{25}\text{Pt}_{75}$ and $\text{Cu}_{50}\text{Pt}_{50}$ cannot be understood within one-electron picture. For Cu–Pt alloys, the residual resistivity has its maximum value at 60 at.% Pt, and the reduction of DOS near E_F should be the greatest around that concentration if we assume constant electron–electron interaction strength λ throughout the whole concentration. However, due to the filling of Pt d holes [14], λ will be decreased with the increase of Cu concentration, and as a result, smaller dip is expected for $\text{Cu}_{50}\text{Pt}_{50}$. This indeed is in agreement with the experiment where the depletion of DOS is observed only for $\text{Cu}_{25}\text{Pt}_{75}$ and $\text{Cu}_{50}\text{Pt}_{50}$, the latter having a dip with only 3% reduction.

To observe similar effect, we have also studied Cu–Ni alloys. From the spectra of $\text{Cu}_{25}\text{Ni}_{75}$ and of Ni and the divided spectrum shown in the upper panel of Fig. 3, the reduction of DOS is clearly visible. On the other hand, the divided spectrum of $\text{Cu}_{50}\text{Ni}_{50}$ in the lower panel did not show such behavior. Although the values of ρ_0 are almost the same for these two compositions as in Cu–Pt alloys, the electron correlation effect of Ni $3d$ must be small for $\text{Cu}_{50}\text{Ni}_{50}$ than for $\text{Cu}_{25}\text{Ni}_{75}$, because it is also known that the partial DOS of Ni $3d$ at E_F diminishes as Ni is diluted [15]. Therefore, the absence of a dip for $\text{Cu}_{50}\text{Ni}_{50}$ alloy can be explained within the context of Altshuler and Aronov's model.

The ill-defined Fermi surface itself does not mean explicitly that the electrons at E_F have relatively small mean free path, because the electron states with short lifetime slightly below or above the Fermi level can cause the smearing of Fermi surface. Pd–Pt alloys show such behavior. In this case, although the Fermi surface could not be defined clearly because of short lifetime of the electrons just below and above the Fermi level, the spectral function becomes very

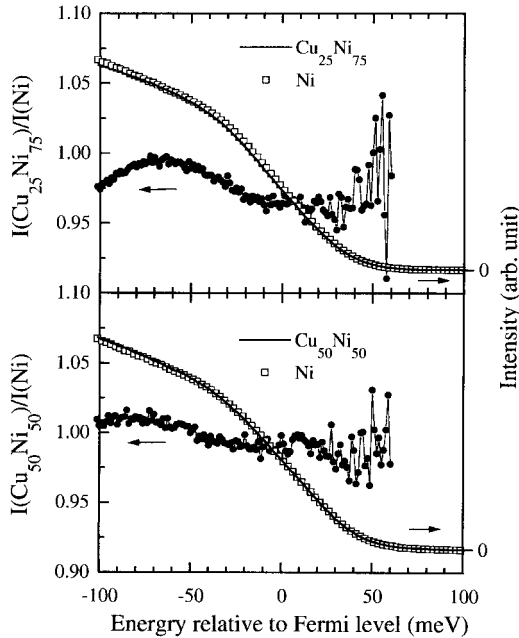


Fig. 3. Photoemission spectra of alloys, pure elements, and the divided spectra for Cu₂₅Ni₇₅ (upper panel) and Cu₅₀Ni₅₀ (lower panel). Note the presence of a dip at the Fermi level for Cu₂₅Ni₇₅.

sharp as the wavevector \mathbf{k} crosses \mathbf{k}_F [10]. This results in an ordinary Nordheim behavior of ρ_0 . If such non-uniform lifetime broadening would cause some change in DOS, we may expect some increase of DOS at E_F and small decrease just above and below E_F in the experimental spectra. However, as in Fig. 4, we could not see such structure for Pd₅₀Pt₅₀ with small ρ_0 value. This shows that both disorder and electron correlation effect are necessary to observe a dip at E_F in agreement with Altshuler and Aronov's model. For Cu–Pt alloys, the spectral function does have finite lifetime even at \mathbf{k}_F which accounts for the relatively high ρ_0 values and this is the reason

we could observe disorder and electron interaction induced depletion of DOS.

The existence of the electron–electron interaction for Cu–Pt and Cu–Ni alloys observed here suggests important implication for the understanding of the electronic structures of d -9 transition metals. The transition metals with 9 d electrons in their outermost shell have strong correlation effect and it is now well known that the so-called 6 eV satellite in photoemission spectrum of Ni [7] can only be understood with the inclusion of many-body interaction. For Pd, it was suggested that the satellites of core levels and even of the valence band must be due to the same origin [8,9]. From our results, it is quite likely that even pure Pt metal can have some electron correlation effect.

In fact, the presence of satellite structure in Pt $4f$ core level spectra suggests rather strong electron–electron interaction. A study by present authors [16] shows that the relative satellite intensities of Ni $2p$, Pd $3d$, and Pt $4f$ levels to the total core level intensities are 32, 19, and 10%, respectively. Also the relative satellite intensities of the valence d bands are found to be 25, 17, and 9%. Since the relative satellite intensity is mainly determined by U/W , the ratio between the electron–electron interaction strength U and the bandwidth W , it can be concluded that $U_{\text{Pt}5d}$ is not much smaller than $U_{\text{Ni}3d}$, but they are of the same order of magnitude.

Since the residual resistivity of Cu–Ni alloys are around 2/3 that of Cu–Pt alloys [4], we can also estimate the relative electron–electron interaction strength. From Eq. (1), the dip size will be comparable for Cu–Pt and Cu–Ni if the λ value of Pt $5d$ is around half that of Ni $3d$, which is in agreement with the above estimation.

4. Conclusion

We have studied the photoemission spectra of transition metal alloys and pure elements. We found dips at E_F for some alloys with high ρ_0 values when one of the two

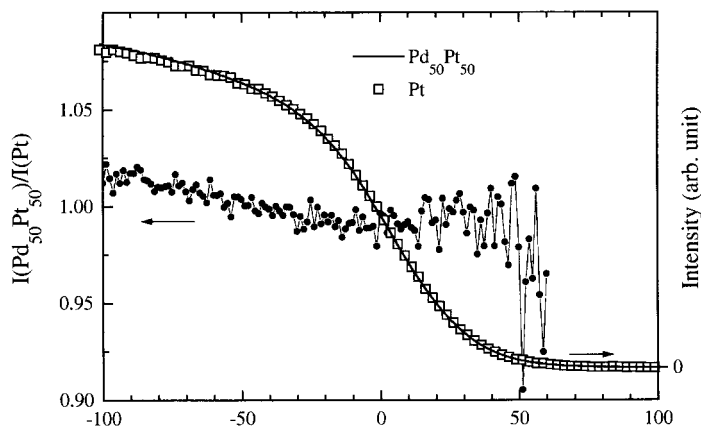


Fig. 4. Photoemission spectra of Pd₅₀Pt₅₀ and Pt, and the divided spectra $I(\text{Pd}_{50}\text{Pt}_{50})/I(\text{Pt})$.

elements has non-negligible electron correlation effects at E_F . The dip size at E_F and its width were smaller than those observed for a material with pseudo-gaps [17] and those observed near the MIT of transition metal compounds [3], but their existence was clearly established. We argue that substitutional disorder in alloys causes depletion of the DOS at E_F when electron–electron interaction is present. This conclusion can be qualitatively interpreted within the context of Altshuler and Aronov’s model [1,2].

Acknowledgements

T.-U.N. wishes to acknowledge the financial support of Hanyang University, Korea, made in the program year of 1998. This work was also supported in part by the Korean Science and Engineering Foundation through Center for Strongly Correlated Materials Research (CSCMR) at Seoul National University.

References

- [1] B.L. Altshuler, A.G. Aronov, *Solid State Commun.* 30 (1979) 115.
- [2] B.L. Altshuler, A.G. Aronov, in: M. Efros, A.L. Pollak (Eds.), *Electron–electron interactions in disordered systems*, North-Holland, Amsterdam, 1979–1985, p. 1.
- [3] D.D. Sarma, A. Chainani, S.R. Krishnakumar, E. Vescovo, C. Carbone, W. Eberhardt, O. Rader, Ch. Jung, Ch. Hellwig, W. Gudat, H. Srikanth, A.K. Raychaudhuri, *Phys. Rev. Lett.* 80 (1998) 4004.
- [4] N.F. Mott, H. Jones, *The Theory of the Properties of Metals and Alloys*, Oxford University Press, London, 1936 (p. 296 and references therein).
- [5] A.J. Pindor, W.M. Temmerman, B.L. Gyorffy, G.M. Stocks, *J. Phys. F* 10 (1980) 2617.
- [6] J. Banhart, P. Weinberger, J. Voitländer, *J. Phys. Cond. Matt.* 1 (1989) 7013.
- [7] N. Mårtensson, B. Johansson, *Phys. Rev. Lett.* 45 (1980) 482.
- [8] N. Mårtensson, R. Nyholm, B. Johansson, *Phys. Rev. Lett.* 45 (1980) 754.
- [9] D. Chandessris, G. Krill, G. Maire, J. Lecante, Y. Petroff, *Solid State Commun.* 37 (1981) 187.
- [10] G.M. Florio, B. Ginatempo, E.S. Giuliano, J.B. Staunton, *J. Phys. Cond. Matt.* 1 (1989) 8385.
- [11] L.F. Mattheiss, R.E. Dietz, *Phys. Rev. B* 22 (1980) 1663.
- [12] J. Banhart, P. Weinberger, J. Voitländer, *Phys. Rev. B* 40 (1989) 12079.
- [13] J.C. Fuggle, F.U. Hillebrecht, R. Zeller, Z. Zolnierok, P.A. Bennet, Ch. Freiburg, *Phys. Rev. B* 27 (1983) 2145.
- [14] E.-J. Cho, S.-J. Oh, *J. Kor. Phys. Soc.* 31 (1997) 323.
- [15] G.M. Stocks, R.W. Willams, J.S. Faulkner, *Phys. Rev. B* 4 (1971) 4390.
- [16] T.-U. Nahm, J.-Y. Kim, H.-J. Noh, S.-J. Oh, unpublished.
- [17] T. Susaki, Y. Takeda, M. Arita, K. Mamiya, A. Fujimori, K. Shimada, H. Namatame, M. Taniguchi, N. Shimizu, F. Iga, T. Takabatake, *Phys. Rev. Lett.* 82 (1999) 992.