

Co Dimers Observed by Extended X-Ray Absorption Fine Structure Spectroscopy

Giuseppe Faraci and Agata R. Pennisi

Dipartimento di Fisica—Università di Catania, Istituto Nazionale di Fisica della Materia, Corso Italia 57, 95129 Catania, Italy

Antonella Balerna

Laboratori Nazionali di Frascati, INFN, 00044 Frascati, Italy

Hugo Pattyn and Gerhard E. J. Koops

Instituut voor Kern-en Stralingsfysica, Physics Department, KU Leuven, Celestijnenlaan 200D, B-3001 Belgium

Guilin Zhang

Shanghai Institute of Nuclear Reasearch, Chinese Academy of Sciences, Shanghai 201800, People's Republic of China

(Received 24 July 2000)

Cobalt was introduced into a silver matrix by ion implantation and observed by extended x-ray absorption fine structure (EXAFS) spectroscopy. In the range 0.10–0.70 at. % evidence of Co dimers dispersed in the matrix was found. The dimers are somewhat contracted with respect to the bulk Co nearest neighbor distance and distributed in a chainlike configuration with each dimer at 90° from each other along opposite square faces of the Ag fcc lattice.

DOI: 10.1103/PhysRevLett.86.3566

PACS numbers: 36.40.Mr, 61.46.+w

Clusters of magnetic elements exhibit very exciting properties in the growing field of the nanostructures. Magnetic anisotropy, magnetic moment modification, and superparamagnetic-ferromagnetic transition are just a few examples of this frontier research [1–8]. We mention also the giant magnetoresistance effect in Co/Cu and Co/Ag films [9–11] where Co clusters play a dramatic role. The confinement of nanoclusters in a matrix and their evolution under thermal treatment are particularly important aiming at clarifying different problems such as [12–15] (i) the shape and size of the cluster; (ii) the geometrical parameters; (iii) the homo- and heteroatomic interactions; (iv) the growth mechanism in the matrix as a function of the annealing temperature, etc. As part of our present studies on Co clusters in a silver matrix [15], we report here on the very early stage of the nucleation, i.e., the dimer formation and configuration which appear particularly interesting at low cobalt concentration (0.1–0.7 at. %), in view of the possible ferromagnetic alignment and enhanced magnetic moment of the Co atoms, as expected for Co atoms embedded in silver [10]. In fact, for the first time, we find direct experimental evidence that Co atoms are grouped in dimers at 90° from each other and disposed in the fcc silver lattice along opposite and parallel square faces. Cu dimers were first observed by Montano *et al.* [16] by extended x-ray absorption fine structure (EXAFS) spectroscopy. We adopt the same technique for the geometrical characterization of the Co dimers, distinguishing Co-Co and Co-Ag first, second, and third coordination-shell distance, coordination number, and vibrational amplitude. The matrix used was silver because of its low Debye temperature ($\Theta_D^{\text{Ag}} = 225$ K at low temperature), whereas Co is a hard metal at least in its bulk form ($\Theta_D^{\text{Co}} = 440$ K

at low temperature); in addition, the nearest neighbor distance for silver is larger than for cobalt so that the silver matrix hosts cobalt atoms in a quasisubstitutional position in its fcc lattice.

In order to obtain the proper concentration of Co in the Ag matrix we adopted [17] the following method: on a thin SiO₂ substrate a layer of silver (about 50 nm thick, crystalline fcc film) was grown by molecular beam epitaxy; Co was then introduced by ion implantation at 50 keV (fluence lower than 10¹³ atoms/cm²) without breaking the ultrahigh vacuum. This procedure was repeated 15 times so as to obtain an optimal signal-to-noise ratio. With this preparation method the Co depth profile was rather homogeneous and different concentrations were obtained. Measurements were performed for several dilutions and repeated after some time in order to check for reproducibility, but here we report our data only for 0.1 and 0.7 at. % concentration.

The experiment was performed at the GILDA beam line of the European Synchrotron Radiation Facility (ESRF), Grenoble, France; experimental details can be found in Ref. [15]. The as prepared samples were investigated by EXAFS spectroscopy; x-ray spectra were collected around the Co K edge (7709 eV), in the range 7500–8700 eV, in the fluorescence mode using 11 ultrapure Ge detectors cooled at 77 K. The samples were investigated at different temperatures, namely, 77, 125, 175, and 225 K.

The normalized fluorescence spectra I_{F1}/I_0 were analyzed according to a standard procedure [18–20], removing the background by means of a cubic spline, fitting the continuous component of the spectrum in the k range 2.5–14 Å⁻¹. In Fig. 1, we report the EXAFS oscillations $\chi(k)$ for the two samples at 77 K; although there is a factor of 7 in the relative concentration, the two spectra are very

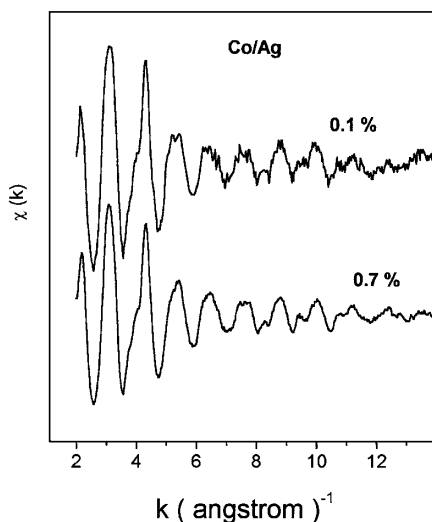


FIG. 1. EXAFS oscillations as a function of the wave vector k , extracted after the threshold by subtracting the continuous contribution in the raw spectra. The curves have been vertically shifted for the sake of clarity; the maximum amplitude of each curve is between -0.1 and 0.1 .

similar demonstrating an identical configuration of the Co inclusion in the matrix. In Fig. 2 the Fourier transforms (FT) of the $\chi(k)$ weighted by k are included. Here, the peaks correspond to the first Co-Co and/or Co-Ag coordination shell and to the successive ones as a function of the distance; reference spectra at 77 K of a Co metal foil and of Co_8 clusters in Ag are also displayed [15]. It is clear that in a Co metal foil the first four coordination shells are quite evident; in the diluted Co/Ag samples a higher number of features are present. From a qualitative comparison between the FTs, we find (i) a first small peak at the Co-Co first shell distance; (ii) a main peak at a somewhat larger distance, not present in the Co metal, which should correspond to the Co-Ag first coordination shell; (iii) a shoulder aligned at the second Co-Co distance of the metal, plus four other peaks; this implies that even at 0.1 at. % a single atom distribution of cobalt dispersed in silver is not observed and can be excluded since in this case only Co-Ag distances and coordination numbers should be visible; in contrast, a long range order and the simultaneous presence of both atoms in all the shells are evident even though some features show a very small intensity; note in fact the splitting of the first shell in the reference curve obtained for 8-atom Co clusters in Ag [15], where the Co-Co and Co-Ag first shell peaks have similar heights. For a quantitative analysis we adopted a fitting procedure on the EXAFS signal, and on its FT using a very accurate method [21], including curved wave effects, multiple scattering paths, and inelastic losses. This fit gives the best values for the unknown parameters N , R , and σ^2 [coordination number, distance, and Debye-Waller (DW) factor of each shell, respectively]. A preliminary check, by fitting the Co metal spectra, gave excellent agreement with the parameters known in the literature. However, for our samples care should be taken in the fitting procedure since two atoms (Co and Ag) could find

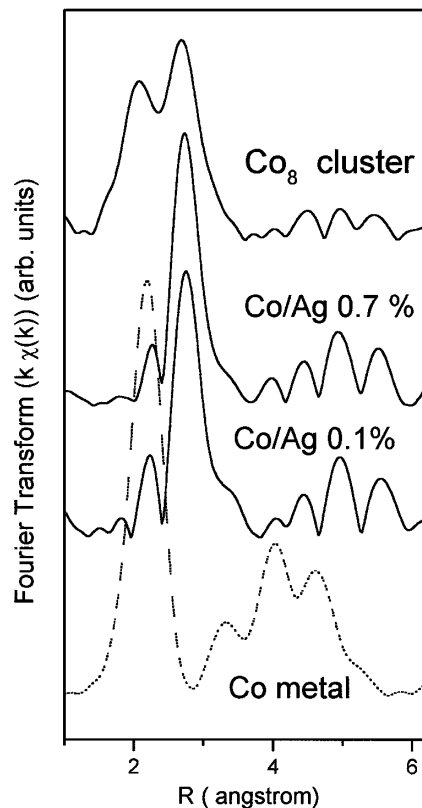


FIG. 2. Fourier transforms of the EXAFS spectra $\chi(k)$ weighted by k . The lowest curve is the FT of the Co bulk crystal; the upper curve is the FT of a Co_8 cluster. Very clearly visible is the Co-Co I shell coordination in the diluted samples corresponding to the analogous main peak of the Co foil and to the first feature of the cluster, where the distance is somewhat contracted; the highest peak in the diluted samples corresponds to the Co-Ag I shell distance. For the sake of clarity the curves have been shifted and amplified.

a place in each coordination shell with slightly different distances and therefore with some overlap which should be disentangled. Taking into account possible constraints, we performed many analyses whose typical parameters for the first shell are reported in Table I; a standard analysis was obtained fixing the same amplitude factor s_0^2 as that obtained for fitting bulk Co, i.e., $s_0^2 = 0.8$; this procedure gives the smallest χ^2 fit for a reduced number of atoms around the Co absorber. In fact, we get 1 Co + 9 Ag in the shell, corresponding to some vacancies in the Ag fcc lattice. This can be a consequence of the high energy exchanged during the 50 KeV, room temperature ion implantation, which produces a local damage [22] along the path of the ion. In Fig. 3 the FT for sample B (0.7 at. %) is reported together with a typical fit obtained by the FEFFIT code. The agreement between experiment and simulation is very good. A detailed discussion of the significance of each parameter will be presented elsewhere, but we stress that the amplitude reduction factor s_0^2 should not significantly depend on the chemical environment around the absorber [23] so that it is justified to use the value deduced from the fit of bulk Co. At present we pay attention

TABLE I. Fit parameters of the first shell around a Co absorber obtained by the FEFFIT code, fixing the $s_0^2 = 0.8$ as in bulk Co. We distinguish the Co-Co and the Co-Ag contributions.

Sample	N	Co-Co		N	Co-Ag	
		R (Å)	σ^2 ($\times 10^{-4}$ Å ²)		R (Å)	σ^2 ($\times 10^{-4}$ Å ²)
0.1%	0.9 ± 0.1	2.47 ± 0.02	25.0 ± 4.0	9.0 ± 0.1	2.815 ± 0.005	65.0 ± 4.0
0.7%	1.0 ± 0.1	2.49 ± 0.02	23.0 ± 4.0	9.0 ± 0.1	2.814 ± 0.005	60.0 ± 4.0

mainly to the cobalt-cobalt coordination in the first shell: we have shown with high reliability that in any case only 1 ± 0.1 cobalt atom is present around the absorber; this implies the presence of Co dimers; furthermore, we observe that the Co-Co first shell coordination number does not change at all for an increase of Co concentration up to a factor of 7; this means that the Co-Co dimer configuration should be a low energy preferential state in which the cobalt ensemble is driven by a strong Co-Co interaction. The previous result disproves also the possible presence of cobalt diffused in the matrix and forming small clusters with a wide size dispersion; in fact, if a mixing of monomers and small clusters (dimers, trimers, and so on), would be present, the average should give a first shell coordination number rapidly increasing with the atomic percentage. This is not observed at all. We are therefore dealing at both concentrations with an ensemble of dimers with a larger dimer density when the total amount of Co goes up to 0.7 at.%. The jump of the raw spectra at the threshold confirms this point as it increases as the Co concentration.

Actually, we have established the presence of Co dimers in the matrix and to our knowledge this is the first experimental observation by the EXAFS technique. However, the spectra and their fits give still more information. We find indeed a Co-Co nearest neighbor distance somewhat contracted with respect to the bulk crystal (2.507 Å),

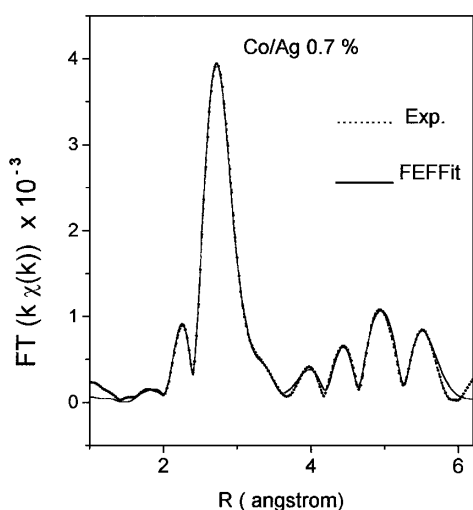


FIG. 3. Typical FT of the experimental spectrum with the simulated curve using the fitting procedure and the FEFFIT code of Ref. [21]. In this fit $s_0^2 = 0.8$; we fit all the shells although the parameters of the third and the fourth shells are less reliable because of the multiscattering contributions.

whereas the Co-Ag I shell distance is at 2.815 Å. Furthermore, the fits give also the second coordination values: we obtain a Co-Co II shell coordination number of 1.1 ± 0.2 at a distance $R_2 = 3.6 \pm 0.05$ Å, whereas the corresponding Co-Ag coordination is 4.5 ± 0.2 at 4.05 ± 0.05 Å. Also the third and fourth coordinations are quite well resolved even though the multiscattering contribution gives a larger uncertainty on the actual value; since the presence of cobalt in the third shell is well defined, in any case we can affirm that the third coordination number Co-Co is 2.0 ± 0.5 . Taking into account the previous results, we point out that a small amount of cobalt is contained not only in the second coordination shell but also in the third coordination shell. This means that the dimers are not very distant from each other since in this case we should have found only silver in the higher coordination shells; on the contrary the dimers seem to interact mutually so as to bring the dimers in a particular configuration not allowing for the Co coalescence (otherwise we would see small clusters) but still with a clear cobalt contribution in the second and third coordination shells.

Possible dimer configurations in a quasisubstitutional position in the silver lattice should be hypothesized, calculating the average coordination numbers. A model was developed calculating for many possible configurations the average coordination values to be compared with the experimental ones: the most probable configuration was obtained disposing the dimers along the fcc square faces of the lattice in the orthogonal direction from each other and somewhat closer with respect to the ideal substitutional positions; if we put, e.g., four dimers in this way, on the average, the first, second, and third coordination seen from the Co absorber is 1.0, 0.75, and 1.5, respectively; with six dimers in the previous configuration these figures become 1.0, 0.83, and 1.67. Therefore, we believe that in our diluted Co samples the EXAFS results give evidence of such preferential dimer confinement, looking like orthogonal sticks separated somewhat less than the silver lattice distance (4.09 Å).

This geometrical arrangement and its inferred stability find support in recent Mössbauer studies [8]. The previous conclusions are corroborated by the analysis performed for the spectra collected at different temperatures (77, 125, 175, and 225 K). At all temperatures we checked the self-consistency of the significant physical parameters, looking also for the variation of the DW factors as a function of the temperature. The σ^2 values found for the first shell (Co-Co and Co-Ag) were quite reliable and are plotted in Fig. 4. For comparison, the σ^2 value of the Co

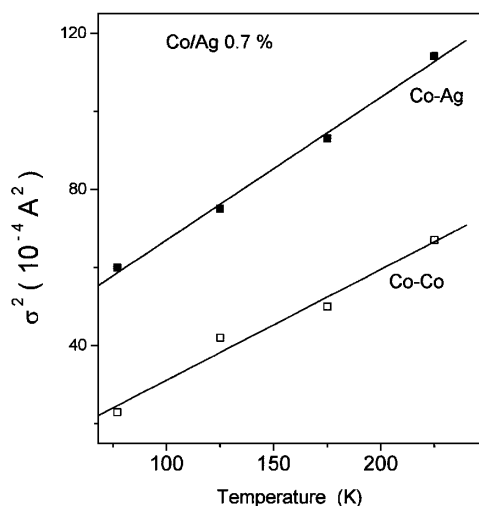


FIG. 4. Debye-Waller factor for the first shell Co-Co and Co-Ag as a function of the temperature, for sample Co/Ag 0.7 at.%. In the range of the measurements the trend is linear; the mean square relative displacement shows the higher hardness of the Co-Co dimer bond with respect to Co-Ag. The continuous lines are only a guide for the eye.

metal foil was measured ($\sigma^2 = 27 \times 10^{-4} \text{ \AA}^2$) and the correspondent Debye temperature was deduced within the Debye model; we obtained $\Theta_D = 418 \text{ K}$ at 77 K in good agreement with the literature [24]. We comment on the increase of the relative vibrational amplitude of the cobalt dimers as reported in Fig. 4; it appears that the dimers are mutually bound by a harder bond than with Ag as it is expected because of the expanded (with respect to the bulk Co) host lattice of silver which is therefore only weakly connected with cobalt. This can also explain the nearest neighbor Co-Co distance which is found almost at the same value as in the bulk Co, and not so close as in the Co_2 molecule (2.385 \AA) [25] because of the pulling forces of the silver atoms.

In conclusion, we have been able to produce by weak implantation Co dimer confinement in a quasisubstitutional position in the fcc Ag lattice. The determination of the Co-Co and Co-Ag distances has clearly shown the presence of the dimers interconnected to each other in configurations which very likely appear as short chains. This can be indicated as the first stage before the growth of small clusters.

The authors gratefully acknowledge the excellent collaboration of the ESRF staff during the experiments.

-
- [1] J. B. Kortright *et al.*, *J. Magn. Magn. Mater.* **207**, 7 (1999).
 [2] S. N. Khanna and S. Linderoth, *Phys. Rev. Lett.* **67**, 742 (1991).
 [3] B. Piveteau *et al.*, *Phys. Rev. B* **53**, 9251 (1996).
 [4] H. A. Dürr *et al.*, *Phys. Rev. B* **59**, R701 (1999).

- [5] J. Dorantes-Davila and G. M. Pastor, *Phys. Rev. Lett.* **81**, 208 (1998); S. Padovani, I. Chado, F. Scheurer, and J. P. Bucher, *Phys. Rev. B* **59**, 11887 (1999).
 [6] X. Chuanyun, Y. Jinlong, D. Kaiming, and W. Kelin, *Phys. Rev. B* **55**, 3677 (1997).
 [7] J. Xu *et al.*, *Phys. Rev. B* **55**, 416 (1997).
 [8] Marc Hou, M. El Azzaoui, H. Pattyn, J. Verheyden, G. Koops, and G. Zhang, *Phys. Rev. B* **62**, 5117 (2000); G. L. Zhang, J. Verheyden, W. Deweerd, G. E. J. Koops, and H. Pattyn, *Phys. Rev. B* **58**, 3026 (1998).
 [9] A. E. Berkowitz *et al.*, *J. Appl. Phys.* **73**, 5320 (1993).
 [10] F. Parent, J. Tuailon, L. B. Stern, V. Dupuis, B. Prevel, A. Perez, P. Melinon, G. Guiraud, R. Morel, A. Barthelemy, and A. Fert, *Phys. Rev. B* **55**, 3683 (1997); Feng Liu, M. R. Press, S. N. Khanna, and P. Jena, *Phys. Rev. B* **39**, 6914 (1989); R. N. Nogueira and H. M. Petrilli, *Phys. Rev. B* **60**, 4120 (1999).
 [11] T. Veres, M. Cai, R. W. Cochrane, and S. Roorda, *J. Appl. Phys.* **87**, 8504 (2000), and references therein.
 [12] Zhi-qiang Li and Bing-lin Gu, *Phys. Rev. B* **47**, 13611 (1993); J. R. Regnard, J. Juanhuix, C. Brizard, B. Dieny, and B. Mevel, *Solid State Commun.* **97**, 419 (1996).
 [13] B. Schleicher, S. Künzel, and H. Burtscher, *J. Appl. Phys.* **78**, 4416 (1995).
 [14] G. Langouche, M. de Potter, and D. Schroyen, *Phys. Rev. Lett.* **53**, 1364 (1984).
 [15] G. Faraci, A. R. Pennisi, A. Balerna, H. Pattyn, G. Koops, and G. Zhang, in *Proceedings of the International Conference on Physics of Low Dimensions, Oaxaca, 2000* (Plenum Press, Mexico, to be published).
 [16] P. A. Montano, G. K. Shenoy, E. E. Alp, W. Schulze, and J. Urban, *Phys. Rev. Lett.* **56**, 2076 (1986).
 [17] J. Verheyden, G. Zhang, J. Dekoster, A. Vantomme, W. Deweerd, K. Milants, T. Barancira, and H. Pattyn, *J. Phys. D* **29**, 1316 (1996).
 [18] P. A. Lee, P. H. Citrin, P. Eisenberger, and B. M. Kincad, *Rev. Mod. Phys.* **53**, 769 (1981).
 [19] E. A. Stern, B. A. Bunker, and S. M. Heald, *Phys. Rev. B* **21**, 5521 (1980).
 [20] A. Pinto, A. R. Pennisi, G. Faraci, G. D'Agostino, S. Mobilio, and F. Boscherini, *Phys. Rev. B* **51**, 5315 (1995); P. Decoster, B. Swinnen, K. Milants, M. Rots, S. La Rosa, A. R. Pennisi, and G. Faraci, *Phys. Rev. B* **50**, 9752 (1994).
 [21] J. Mustre de Leon, J. J. Rehr, S. I. Zabinsky, and R. C. Albers, *Phys. Rev. B* **44**, 4146 (1991); J. J. Rehr, R. C. Albers, and S. I. Zabinsky, *Phys. Rev. Lett.* **69**, 3397 (1992); J. J. Rehr, S. I. Zabinsky, A. Ankudinov, and R. C. Albers, *Physica (Amsterdam)* **208B/209B**, 23 (1995); E. A. Stern, M. Newville, B. Ravel, Y. Yacoby *ibid.* **208B/209B**, 117 (1995).
 [22] E. Rimini, in *Ion Implantation and Annealing*, edited by P. N. Butcher, N. H. March, and M. P. Tosi, *Crystalline Semiconducting Materials and Devices* (Plenum Press, New York, 1986), p. 591.
 [23] E. A. Stern and S. M. Heald *Handbook on Synchrotron Radiation* (North-Holland, Amsterdam, 1983), Vol. 1B, p. 955.
 [24] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976).
 [25] I. Shim and K. A. Gingerich, *J. Chem. Phys.* **78**, 5693 (1983).