

Energetics of Co adatoms on the Cu(001) surface

N. A. Levanov, V. S. Stepanyuk,* and W. Hergert

Fachbereich Physik, Martin-Luther-Universität, Fr.-Bach-Platz 6, D-06099 Halle, Germany

D. I. Bazhanov

*Max-Planck-Institute für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany
and Solid State Physics Department, Moscow State University, 119899 Moscow, Russia*

P. H. Dederichs

Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

A. Katsnelson

Solid State Physics Department, Moscow State University, 119899 Moscow, Russia

C. Massobrio

Institut de Physique et de Chimie des Matériaux de Strasbourg, 23 rue du Loess F-67037 Strasbourg, France

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By using an N -body potential scheme constructed by fitting the interaction parameters to accurate first-principles calculations, we investigate the structural stability of Co atoms and clusters deposited on Cu(100). We found that Co atoms and clusters prefer to be embedded inside the substrate, in a way compatible with the formation of a surface alloy observed experimentally. Enhanced stability is achieved when Co atoms are deposited on a preformed Co cluster embedded on the uppermost layer of the substrate. Co atoms deposited on Co islands are best stabilized when they concur to complete the islands, by promoting layer-by-layer growth.

Ultrathin films of ferromagnetic metals have found considerable interest in recent years due to their technological applications in the area of magneto-optical and transport properties.¹⁻³ In particular the growth of Fe and Co films on Cu(001), which takes place pseudomorphically on the fcc substrate, has been investigated extensively.⁴⁻¹⁰ The quality of the grown layers and of the interfaces has a strong influence on properties like giant magnetoresistance,⁵ magnetic anisotropy,^{6,7} and oscillatory interlayer exchange coupling.^{8,9} Kief and Egelhoff¹⁰ have reported the observation of non-ideal film growth, characterized by the formation of compact Co clusters and the segregation of substituted Cu on the surface. Recently, the interfacial intermixing of ultrathin Co films on a Cu(001) was observed,¹¹ despite the fact that Co and Cu are immiscible in the bulk.¹² The intermixing in the upper layers might not only be favored kinetically, but also energetically.¹³

In this paper we resort to a newly developed n -body interatomic potential scheme to ascertain the energetics of atoms and clusters of Co on the Cu(001). A strong tendency for a direct exchange mechanism into the Cu layer is found. Our results demonstrate that at the initial stage of monolayer growth small Co clusters are formed in the Cu surface. We investigate the mechanism of adatom-cluster interactions and show how heteroepitaxial thin film growth takes place.

Our approach is based on accurate first-principles calculations of selected cluster-substrate properties, which have been employed in the fitting of the potential parameters. This results in a manageable and inexpensive scheme able to account for structural relaxation and including implicitly mag-

netic effects, crucial for a realistic determination of interatomic interactions in systems having a magnetic nature.

The potentials are formulated in the second moment tight-binding approximation (TB-SMA).^{14,15} The attractive term (band energy) E_B^i contains the many-body interaction. The repulsive term E_R^i is described by pair interactions (Born-Mayer form). The cohesive energy E_{coh} is the sum of the band energy and repulsive part:

$$E_{coh} = \sum_i (E_R^i + E_B^i), \quad (1)$$

$$E_R^i = \sum_j A_{\alpha\beta} \exp \left[-p_{\alpha\beta} \left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1 \right) \right], \quad (2)$$

$$E_B^i = - \left\{ \sum_j \xi_{\alpha\beta}^2 \exp \left[-2q_{\alpha\beta} \left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1 \right) \right] \right\}^{1/2}. \quad (3)$$

r_{ij} is the distance between the atoms i and j . $r_0^{\alpha\beta}$ is the first neighbor distance in the crystalline structures of the pure metals for atom-like interactions and becomes an adjustable parameter in the case of the cross interaction. ξ is an effective hopping integral; $p_{\alpha\beta}$ and $q_{\alpha\beta}$ describe the decay of the interaction strength with distance of the atoms.

After determination of the Cu-Cu parameters which are fitted to experimental data only (see Ref. 14 and Ref. 15), the Co-Co and Co-Cu parameters are optimized simultaneously by including in the fit the results of first-principles Korringa-Kohn-Rostoker (KKR) calculations.¹⁶ To this purpose, we

TABLE I. Data used for the fitting of the potential together with the values calculated with the optimized potential. (Cohesive energy E_c , bulk modulus B , elastic constants C_{ij} from Refs. 14,15, first and second neighbor interaction energies $E_{1,b}^{\text{Co-Co}}$, $E_{2,b}^{\text{Co-Co}}$ from Ref. 17, solution energy $E_S^{\text{Co in Cu}}$ from Ref. 18, binding energies of small Co clusters $E_{1,on}^{\text{Co-Co Cu(100)}}$, $E_{1,in}^{\text{Co-Co Cu(100)}}$, $E_{on}^{\text{trimer Cu(100)}}$, $E_{on}^{2 \times 2 \text{ island Cu(100)}}$ are calculated using the KKR Green's function method.)

	Quantity	Data	Fitted value
Cu (fcc)	a_{Cu}	3.615 Å	3.614 Å
	E_c	3.544 eV	3.545 eV
	B	1.42 Mbar	1.42 Mbar
	C_{11}	1.76 Mbar	1.76 Mbar
	C_{12}	1.25 Mbar	1.25 Mbar
	C_{44}	0.82 Mbar	0.82 Mbar
Co (hcp)	a_{Co}	2.507 Å	2.515 Å
	E_c (E)	4.386 eV	4.395 eV
	B	1.948 Mbar	1.989 Mbar
	C_{11}	3.195 Mbar	3.337 Mbar
	C_{12}	1.661 Mbar	1.426 Mbar
	C_{13}	1.021 Mbar	1.178 Mbar
Co-Cu	C_{33}	3.736 Mbar	3.665 Mbar
	C_{44}	0.824 Mbar	0.646 Mbar
	$E_S^{\text{Co in Cu}}$	0.4 eV	0.38 eV
	$E_{1,b}^{\text{Co-Co}}$	-0.12 eV	-0.18 eV
	$E_{2,b}^{\text{Co-Co}}$	0.03 eV	-0.05 eV
	$E_{1,on}^{\text{Co-Co Cu(100)}}$	-1.04 eV	-1.04 eV
	$E_{1,in}^{\text{Co-Co Cu(100)}}$	-0.26 eV	-0.35 eV
	$E_{on}^{\text{trimer Cu(100)}}$	-2.06 eV	-1.96 eV
	$E_{on}^{2 \times 2 \text{ island Cu(100)}}$	-3.84 eV	-3.86 eV

have taken the solution energy of a single Co impurity in bulk Cu, $E_S^{\text{Co in Cu}}$ (Ref. 17), energies of interaction of two Co impurities in Cu bulk, $E_{1,b}^{\text{Co-Co}}$, $E_{2,b}^{\text{Co-Co}}$ (Ref. 18), and binding energies of small supported Co clusters on Cu(001), $E_{1,on}^{\text{Co-Co Cu(100)}}$, $E_{1,in}^{\text{Co-Co Cu(100)}}$ (terrace position), $E_{on}^{\text{trimer Cu(100)}}$, $E_{on}^{2 \times 2 \text{ island Cu(100)}}$. Calculations for clusters on metal surfaces are based on density functional theory in the local spin density approximation and KKR Green's function method for low-dimensional systems.¹⁶ We treat the ideal surface as a two-dimensional perturbation of the bulk. The Green's function of the ideal surface and the Green's function of clusters on the surface are calculated using the multiple-scattering theory. Details of the method can be found elsewhere.¹⁶

The simultaneous determination of the Cu-Cu, Co-Co, and Cu-Co interaction potentials for the study of surface and interface properties needs more flexibility than the standard form of TB-SMA is able to provide. Therefore a modified form of the repulsive part is used:

$$E_R^i = \sum_j \left[A_{\alpha\beta}^1 \left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1 \right) + A_{\alpha\beta}^0 \right] \exp \left[-p_{\alpha\beta} \left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1 \right) \right]. \quad (4)$$

The standard form of the repulsive potential ($A_{\alpha\beta}^1=0$) is used for the Cu-Cu interaction. The modified form of Eq. (4) is used for the Co-Co and Cu-Co interactions.

The set of data used to define the potential and the corresponding values calculated by means of the optimized poten-

TABLE II. Parameters of interatomic interactions.

Parameter	Cu-Cu	Co-Co	Co-Cu
A^1 (eV)	0.0	-0.852	-1.905
A^0 (eV)	0.086	0.139	-0.049
ξ (eV)	1.2240	1.5247	0.7356
p	10.96	7.679	8.183
q	2.278	2.139	3.344
r_0 (Å)	2.556	2.378	2.405

tial are given in Table I. The bulk and surface properties are well reproduced. The parameters of interatomic interactions are presented in Table II.

It is important to note that the optimum length of the Co-Cu bonds are strongly influenced by the misfit strain. The data used for the fitting of the Co-Cu potentials do not include the effect of relaxation of the lattice around Co impurities. Therefore it is necessary to test our potentials performing calculations of relaxations near Co in the Cu bulk and on the Cu surface. We investigate the lattice distortion in the vicinity of the Co impurity and compare present results with a first-principles study of lattice relaxation by means of the KKR Green's function method recently performed in our group.¹⁹ Semiempirical and *ab initio* studies show that the Cu lattice is compressed due to the Co impurities. A change of the first nearest neighbor distance near the Co impurity, found in the present calculation, is $\approx 1\%$, while the first-principles calculation gives $\approx 0.5\%$. The second test of our potential is done performing calculations of interlayer distances in Co/Cu multilayers. A detailed low-energy electron diffraction study of the Co/Cu(100) films for different Co coverages was performed in Kirschner's group.²⁰ Interlayer spacing was determined for different Co coverages. We use our potentials to determine interlayer distances performing energy minimization calculations. Results presented in Table III demonstrate that the agreement with experiment is rather good. Therefore we believe that the parametrization developed in our paper gives a good description of the Co-Cu bonds.

The energetics of the elementary exchange process is considered first. In our total energy calculations the replacement of a Cu atom by the deposited Co atom [Fig. 1(b)] is preferred by 0.50 eV to its adsorption on the Cu(001) substrate [Fig. 1(a)]. Hereafter this exchange process will be referred to as "direct" exchange. The same value calculated without relaxation was found to be 0.45 eV. This value is in good agreement with our calculations by means of the KKR

TABLE III. Interlayer distances for Co/Cu(001). The experimental values are taken from Ref. 20. d_{ij} denotes the spacing (in angstroms) between deposited Co monolayers (ML) i and j , starting from the Cu surface layer with index 0.

	1ML		2ML		3ML	
	MD	Expt.	MD	Expt.	MD	Expt.
d_{01}	1.77	1.78 ± 0.03	1.76	1.73 ± 0.03	1.76	1.76 ± 0.03
d_{12}			1.71	1.77 ± 0.02	1.70	1.74 ± 0.02
d_{23}					1.72	1.76 ± 0.02

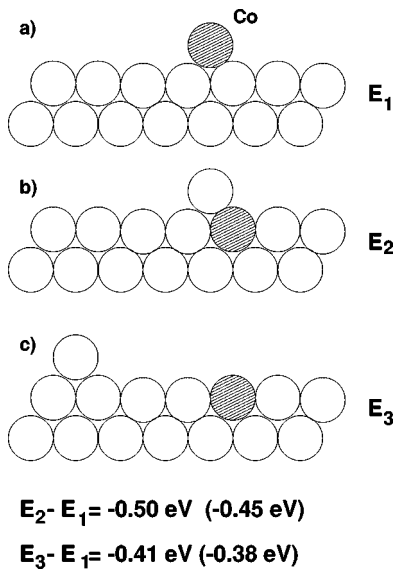


FIG. 1. Energetics of the exchange of Co and Cu at the Cu(100) surface. Energies calculated without relaxation are given in brackets.

Green's function method (0.54 eV, without relaxation). When the energy difference with respect to the configuration depicted in Fig. 1(a) is taken by considering a much larger distance between the Co atom and the promoted Cu atom on the substrate [Fig. 1(c)], we obtain -0.41 eV. The corresponding value obtained without relaxation is -0.38 eV. We call this process a "complete" exchange. These calculations suggest that surface alloying is energetically favorable in the case of Co/Cu(001), a result essentially unmodified by the inclusion of structural relaxations. In addition, we calculated that the gain of energy by the transfer of a Co atom from the topmost to the next layer of the Cu(001) substrate is -0.59 eV. The energy gain by a further movement of Co into the substrate is smaller than 0.1 eV and, as expected, vanishes for a further movement of Co into the bulk.²¹ We recall that the exchange process for 3d impurities on Fe(001) has been recently investigated on the basis of total energy calculations via the KKR Green's function method.²² Unlike in the present case, it was found that for all 3d impurities the complete exchange configuration is more stable than the direct exchange. This different behavior is likely to be related to the different magnetic nature of the substrate.

The total energy difference between the dimer complex and two isolated impurities at infinite separation (see Fig. 2) can be considered as the effective interaction energy between the two impurities. Co atoms embedded in the first layer prefer to form clusters, as proved by the energy gained (-0.38 eV), when two Co atoms, originally far apart within the layer, are moved together in the nearest neighbor configuration. The interaction energy for two Co impurities on next nearest neighbor sites in the topmost layer is -0.12 eV. For the second and deeper layers the energy gain due to the aggregation of two Co impurities to the positions of nearest neighbors is equal to -0.19 eV. The corresponding value for next nearest neighbors is -0.09 eV. We have found in our calculations that the Co dimer complex gains an energy up to 1 eV in the second surface layer compared to the first surface one.

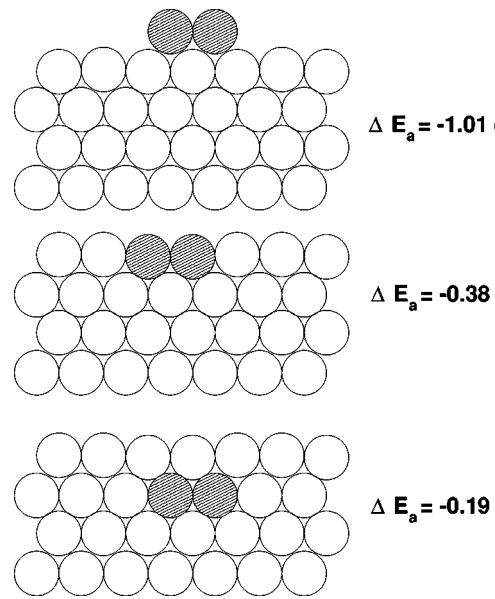


FIG. 2. Energy gain due to Co pair formation in different layers of the Cu(001) substrate.

One can conclude that two Co atoms attract each other in the topmost as well as in deeper layers of the substrate and, as a consequence, Co impurities should form clusters in top layers on the Cu(001) substrate. Indeed, formation of Co and Fe clusters in Cu(001) was observed experimentally by Fassbender *et al.*¹¹ and Johnson *et al.*² using scanning-tunneling microscopy techniques.

Let us now consider adatom-cluster interactions. It is shown in Fig. 3(a) that adsorbed Co atoms prefer to sit on top of the cluster formed by the embedded Co atoms. The adsorption energy for Co adatoms far from the cluster on the Cu(001) substrate (2.36 eV) is much lower than the one calculated for Co adatoms on top of the embedded Co cluster (3.68 eV). Accordingly, at the initial stages of thin film growth, Co islands in the topmost layer of the substrate could be considered as pinning centers for further adsorption of Co atoms. Two possible growth modes for Co clusters on the Cu(001) surface can then be envisaged. On the one hand, the

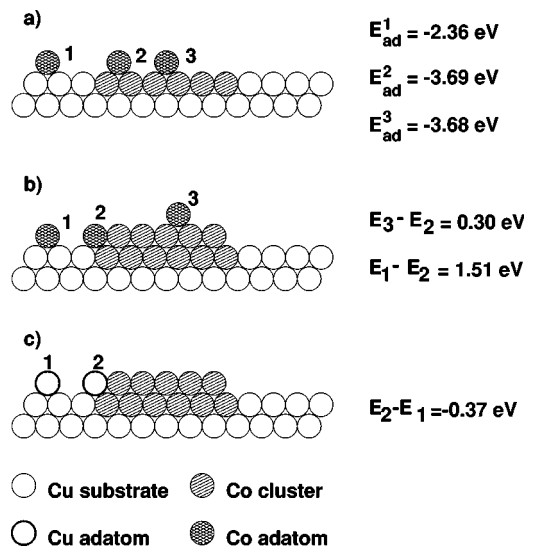


FIG. 3. Energetics of the cluster formation at the surface.

growth of three-dimensional clusters will take place provided the deposition energy of Co atoms is small. On the other hand, one can expect that if the kinetic energy of the deposited adatoms is large, the atoms can migrate from the top of the cluster down to the adsorption sites on the first layer, so as to enlarge the cluster and promote layer-by-layer growth. We focus here on the energetics of this process.

By starting from a preformed small Co cluster, incoming Co atoms can take one of the following three positions [Fig. 3(b)]: (i) far away from the cluster on the surface (pos. 1), (ii) near the edge of the cluster (pos. 2), and (iii) on the top of the cluster (pos. 3). The configuration with the adsorbed Co adatom near the edge of the Co cluster was found to be the most stable one. This means that it is favorable for a Co atom to jump from the top of the island to the uppermost layer level and reside near the edge of the cluster. The energy gain corresponding to this configuration is 0.30 eV. The above process can occur provided the fraction of the atomic kinetic energy still available after transfer and dissipation into the substrate is sufficiently large to overcome the Schwoebel barrier.²³ On the basis of our calculations we also observe that Co atoms adsorbed on the surface are more stable when they reach the edge of the cluster, as indicated by the large energy gained (-1.51 eV) for such a process.

Finally, let us consider the situation in which additional Cu atoms have been promoted by the exchange on the top of the substrate [Fig. 3(c)]. When a Cu atom approaches the cluster to stick to its edge, the energy of the system is lowered by 0.37 eV. Therefore islands will continue to grow by incorporating either Cu or Co.

In summary we have investigated the energetics of an heterogeneous system consisting of Co atoms either adsorbed on the top of a Cu(100) substrate or embedded within it. On the experimental side, it appears that a surface alloy might be formed upon deposition of Co on Cu(001). We have addressed this issue by relying on a sound theoretical model able to conjugate (a) a careful determination of the interatomic forces which involves magnetic contributions and (b)

a flexible account of relaxation effects. This goal has been achieved by constructing an n -body interatomic potential partially fitted to accurate *ab initio* data. This tool has allowed us to draw the following conclusions. First, Co atoms lower the energy of the total system when they lie inside the Cu(100) substrate, more than when they are adsorbed on the top of it. The Co/Cu(100) system is further stabilized when the Co atoms form clusters, and when these clusters reside in deeper layer of the substrate. The most recent experiments performed by Zimmermann *et al.*,²⁴ have found a burrowing of Co nanoparticles in Cu substrate. This finding is in line with our main results.

We have found that the adsorption energy of a single Co atom is much higher when the deposition takes place above a preformed Co cluster, embedded on the first layer of the substrate. This gives rise to special sites on the surface terraces acting as preferential centers for growth. We have also proved that layer-by-layer growth is preferred from the energetic point of view, since Co atoms prefer to join an existing adsorbed Co cluster. We would like to emphasize that the main results of our calculations show that atoms try to maximize their total number of neighbors in both Co-Co and Co-Cu arrangements.

The considerations developed in this paper do not account for kinetic effects, which are crucial to understand how the surface morphology of the heterogeneous system develops. In particular, the competition between the energetic effects, driving the system toward layer-by-layer growth, and the kinetic barriers, preventing diffusion and step-down motion from the terraces, is necessary to establish under which condition one specific growth mode can prevail. Calculations along these lines are currently in progress within the theoretical framework used for this investigation.

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*Electronic address: stepan@valinux.physik.uni-halle.de

¹B. Heinrich and J. F. Cochran, *Adv. Phys.* **42**, 523 (1993).

²K. E. Johnson, D. D. Chambliss, R. J. Wilson, and S. Chiang, *Surf. Sci.* **313**, L811 (1994).

³L. M. Falicov, D. T. Pierce, S. D. Bader, R. Gronsky, K. B. Hathaway, H. J. Hopster, D. N. Lambeth, S. P. Parkin, G. Prinz, M. Salamon, I. K. Schuller, and R. H. Victoria, *J. Mater. Res.* **5**, 1299 (1990).

⁴J. Giergiel, J. Shen, J. Woltersdorf, A. Kirilyuk, and J. Kirschner, *Phys. Rev. B* **52**, 8528 (1995).

⁵X. W. Zhou and H. N. G. Wadley, *J. Appl. Phys.* **84**, 2301 (1998).

⁶B. Heinrich, J. F. Cochran, M. Kowalewski, J. Kirschner, Z. Celinski, A. S. Arrott, and K. Myrtle, *Phys. Rev. B* **44**, 9348 (1991).

⁷P. Krams, F. Lauks, B. Hillebrands, and G. Güntherodt, *Phys. Rev. Lett.* **69**, 3674 (1992).

⁸A. Cebollada, J. L. Martinez, J. M. Gallego, J. J. Miguel, R. Miranda, S. Ferrer, F. Batallan, G. Fillion, and J. P. Rebouillat, *Phys. Rev. B* **39**, 9726 (1989).

⁹M. T. Johnson, S. T. Purcell, N. W. E. McGee, R. Coehoorn, Jaan de Stegge, and W. Hoving, *Phys. Rev. Lett.* **68**, 2688 (1992).

¹⁰M. T. Kief and W. F. Egelhoff, *Phys. Rev. B* **47**, 10 785 (1993).

¹¹J. Fassbender, R. Allenspach, and U. Dürig, *Surf. Sci.* **383**, L742 (1997).

¹²F. R. de Boer, R. Boom, W. C. Mattens, A. Miedema, and A. K. Niessen, in *Cohesion in Metals*, edited by F. R. de Boer and G. Pettifor (North-Holland, Amsterdam, 1985), Vol. 1.

¹³H. Jenniches, M. Klaua, H. Hoche, and J. Kirschner, *Appl. Phys. Lett.* **69**, 3339 (1996).

¹⁴F. Cleri and V. Rosato, *Phys. Rev. B* **48**, 22 (1993).

¹⁵V. Rosato, B. Guillope, and B. Legrand, *Philos. Mag. A* **59**, 321 (1989).

¹⁶K. Wildberger, V. S. Stepanyuk, P. Lang, R. Zeller, and P. H. Dederichs, *Phys. Rev. Lett.* **75**, 509 (1995); V. S. Stepanyuk, W. Hergert, K. Wildberger, R. Zeller, and P. H. Dederichs, *Phys. Rev. B* **53**, 2121 (1996); V. S. Stepanyuk, W. Hergert, P. Rennert, K. Wildberger, R. Zeller, and P. H. Dederichs, *ibid.* **54**, 14 121 (1996).

¹⁷B. Drittler, M. Weinert, R. Zeller, and P. H. Dederichs, *Phys. Rev. B* **39**, 930 (1989).

¹⁸T. Hoshino, W. Schweika, R. Zeller, and P. H. Dederichs, *Phys. Rev. B* **47**, 5106 (1993).

- ¹⁹N. Papanikolaou, R. Zeller, P. H. Dederichs, and N. Stefanou, *Phys. Rev. B* **55**, 4157 (1997).
- ²⁰J. R. Cerda, P. L. de Andres, A. Cebollada, R. Miranda, E. Navas, P. Schuster, C. M. Schneider, and J. Kirschner, *J. Phys.: Condens. Matter* **5**, 2055 (1993).
- ²¹Very close values are obtained by comparing adsorption and embedding energy according to the definition adopted by J. Neugebauer and M. Scheffler [*Phys. Rev. B* **46**, 16 067 (1992)], which accounts for the formation energy of a vacancy in the substrate, the adsorption of an adatom on a vacancy site, and the displacement of the extracted surface atom at a surface step.
- ²²P. H. B. Nonas, K. Wildberger, R. Zeller, and P. H. Dederichs, *Phys. Rev. Lett.* **80**, 4574 (1998).
- ²³G. Ehrlich and F. Hudda, *J. Chem. Phys.* **44**, 1039 (1966); R. L. Schwoebel, *J. Appl. Phys.* **40**, 614 (1969).
- ²⁴C. G. Zimmermann, M. Yeadon, K. Nordlund, J. M. Gibson, R. S. Averback, U. Herr, and K. Samwer, *Phys. Rev. Lett.* **83**, 1163 (1999).