elsewhere.

In conclusion, we have used self-consistent-field calculations to study the effect of both symmetry-lowering and symmetry-preserving lattice distortions on the electronic structure of an isolated neutral vacancy in Si. We find that distortions of reasonable magnitude are very important and bring the bound-state energy to within the range of experimental measurements.

We would like to express our appreciation to G. D. Watkins for his interest in this work and many valuable discussions. This work has been supported in part by the U. S. Air Force Office of Scientific Research under Contract No. F49620-77-C-0005.

[1]J. Bernholc, N. O. Lipari, and S. T. Pantelides, Phys. Rev. Lett. 41, 895 (1978).

[2]G. A. Baraff and M. Schlüter, Phys. Rev. Lett. 41, 892 (1978).

[3]G. D. Watkins, in *Lattice Defects in Semiconductors—1974*, The Institute of Physics Conference Proceedings No. 23, edited by F. A. Huntley (The Institute of Physics, Bristol and London, 1975), p. 1.

[4]The calculations were carried out using the ten-orbitals–per-atom basis of Ref. 1 and repeated with additional orbitals at sites 0.5 Å from the ideal nearest-neighbor positions in order to ensure convergence.

[5]Similar results have been obtained by the authors of Ref. 2 (private communication). Baraff, Kane, and Schlüter further adopted a phenomenological model for elastic forces and estimated the atomic displacements for various charge states of the vacancy.

[6]Experimentally, G. D. Watkins, J. R. Troxell, and A. P. Chatterjee [In, *Defects and Radiation Effects in Semiconductors—1978*, The Institute of Physics Conference Proceedings No. 46, edited by J. H. Albany, The Institute of Physics, Bristol and London, 1979), p. 16] identify a level at $E_v + 0.13$ eV, which they assign to either the $V^- \rightarrow V^0$ or the $V^0 \rightarrow V^+$ transition (see their Fig. 5). The energy level of the neutral vacancy is thus deduced to lie between $E_v + 0.04$ and $E_v + 0.04$ eV.

[7]The main argument is based on Pauling's bond-order/bond-length relation. For a summary of all arguments, see J. A. Van Vechten, Phys. Rev. 10, 1482 (1974). Semiempirical cluster calculations [e.g., R. P. Messmer and G. D. Watkins, Phys. Rev. B 7, 2568 (1973); K. L. Yip, Phys. Status Solidi (b) 66, 619 (1974)] have arrived at the same conclusion. Our calculations show that the backbond charge decreases when the nearest neighbors are moved toward the vacant site and increases in the opposite case. This result is consistent with a similar finding for surfaces [see, e.g., J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 31, 106 (1973), and Phys. Rev. B 8, 1777 (1973)]. See also the discussion by S. G. Louie, M. Schlüter, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 13, 1654 (1976).

[8]J. Bernholc and S. T. Pantelides, Phys. Rev. B 18, 1780 (1978). See also J. Bernholc, N. O. Lipari, and S. T. Pantelides, to be published, and compare with the defect-molecule model, first introduced by C. A. Coulson and M. J. Kearsley, Proc. Roy. Soc. London, Ser. A 241, 433 (1957).

[9]See, e.g., W. A. Harrison, Surf. Sci. 55, 1 (1976).

[10]A more detailed discussion of these arguments will be given elsewhere.

[11]See Messmer and Watkins, Ref. 7.

Field-Induced Resistance Minimum in Palladium with Lattice Defects

G. Bergmann
Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, West Germany
(Received 14 June 1979)

Pd quench condensed onto a quartz plate in ultrahigh vacuum exhibits a pronounced resistance minimum in an external field. This anomaly has a two-dimensional origin but is not caused by the free surface atoms. A superposition with a small fraction of a Ni or Fe layer causes a similar anomaly as the magnetic field. The two effects are not additive. I suggest that a thin Pd sheet below the surface shows two-dimensional band ferromagnetism.

Low-temperature anomalies in the resistivity of metallic systems can indicate interesting physical phenomena such as ordering processes, phase transitions, formation of bound states, etc. A particularly interesting example is the occurrence of resistance minima in different metals, such as Kondo systems and metallic glasses. These systems respond differently to a magnetic field. An external magnetic field reduces the Kondo minimum but leaves the metallic-glass minimum unchanged.[1]

I will describe an experiment where an applied magnetic field builds up a pronounced resistance minimum. The subject of this investigation is quench-condensed Pd. Pd is a fascinating metal. It is nearly magnetic and has a Stoner enhancement factor of about 10. The magnetic properties of its surface have been subjected to many theoretical investigations, predictions, and suggestions. Slight changes in its structure alter its magnetic properties drastically as the superconductivity of irradiated Pd demonstrates.[2]

In the present experiment the Pd is condensed onto a quartz substrate at He temperature. It is evaporated from a wire of high-purity Pd (Johnson and Matthew 99.998%) in an ultrahigh vacuum of the order of 10^{-10} Torr. After the condensation the film is annealed to 50 K. The Pd film is fine crystalline.[3] The reversible resistance is measured between 2 and 42 K in the presence of different magnetic fields. In Fig. 1 the resistance of a quench-condensed Pd film with a thickness of 40 Å and a square resistance of 212 Ω is plotted as a function of the temperature for different magnetic fields. I consider first the resistance curve for $B = 0$. At high temperature between 25 and 40 K it follows a T^2 law. The dashed curve gives the extrapolation of the T^2 law towards low temperature. The measured resistance curve exceeds the T^2 law below 25 K and shows a resistivity minimum at 6 K which has been observed previously by Schmid-Marcic and Mydosh.[4] The application of an external magnetic field up to 7.5 T (perpendicular to the film) increases the resistance and yields much more pronounced minima. In Fig. 2 the magnetoresistance $R(B, T_0) - R(0, T_0)$ is plotted for different temperatures as a function of the applied field. The magnetoresistance is always positive. The dependence of R on the external magnetic field is rather weak at high temperature and increases clearly towards low temperature. The magnetoresistance always starts with a horizontal tangent at low fields. At 2 K it changes, even at 0.1 T, into a linear dependence. The measurements are well reproducible; for about ten different experiments with equivalent Pd films the experimental results agreed within 1%.

I investigate the anomaly for different Pd thicknesses and find that the magneto*resistivity* is inversely proportional to the thickness. Obviously the low-temperature anomaly is not a bulk effect but either a surface effect or is due to two-dimensional fluctuations. Therefore I examine the sensitivity of the effect to the surface. For this purpose I superimpose a thin layer of Cu on top of the Pd film in two steps with a thickness of 0.4 and 1.8 atomic layer. The superposition with Cu leaves the magnetoresistance unchanged.

A superposition of the pure Pd film with atoms of the bulk ferromagnets Fe and Ni yields rather interesting and pronounced changes in the resistance curves. In Fig. 3 the temperature dependence of Pd ($D = 60$ Å, $R^{\square} = 80$ Ω) with different coverages of Ni is shown. The numbers at the curves give the coverage in units of atomic lay-

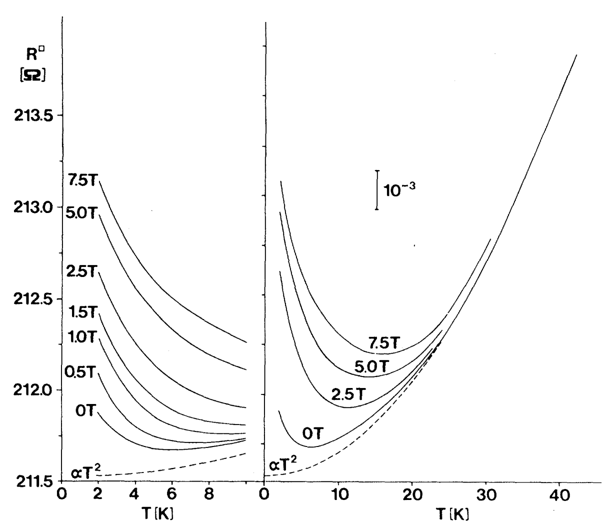

FIG. 1. The low-temperature resistance of a quench-condensed Pd film for different magnetic fields perpendicular to the film. The numbers at the curves give the applied magnetic field in teslas.

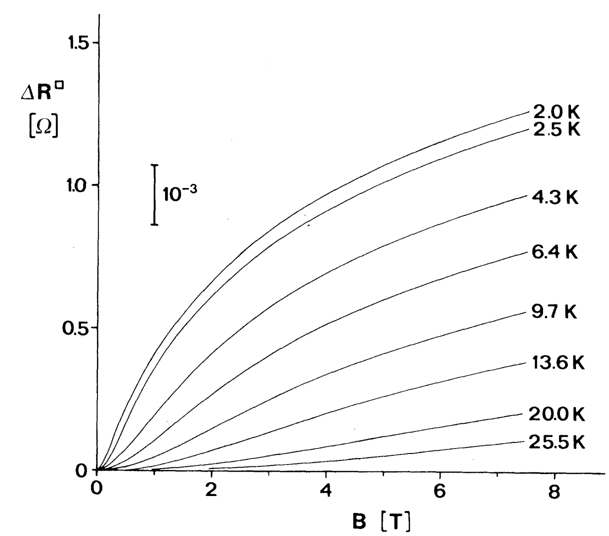

FIG. 2. The magnetoresistance $R(T,B) - R(T,0)$ as a function of the applied magnetic field. The numbers at the curves give the measuring temperature in kelvins.

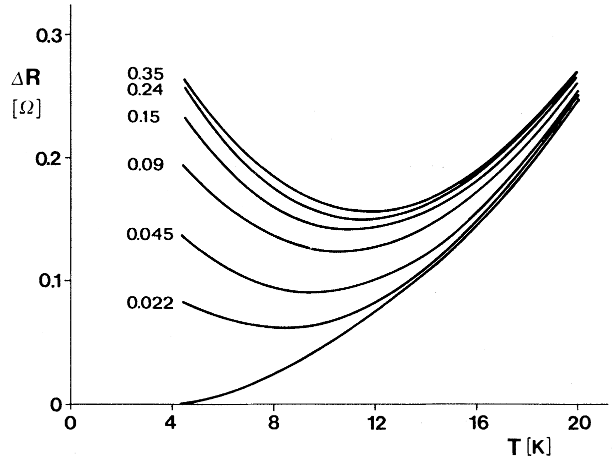

FIG. 3. The low-temperature resistance of a quench-condensed Pd film for different coverages with Ni. The numbers at the curves give the coverage with Ni in units of atomic layers. The experimental curves are shifted in such a way that the high-temperature part of their curves cover each other.

ers (atola). These experiments are performed in a cryostat with an ultrahigh vacuum of about 10^{-11} Torr. Here the lowest temperature is about 4.5 K. The superposition with Ni and Fe reduces the high-temperature resistance. In Fig. 3 the experimental curves are shifted in such a way that the high-temperature part of their resistance curves cover each other. Even rather small coverages of Ni and Fe cause a strong low-temperature anomaly. The strength of the low-temperature anomaly saturates with increasing Ni or Fe thickness. The essential contribution is obtained for 0.1 atola of Ni and 0.05 atola of Fe. The saturation curve for a coverage with Fe corresponds to the 7-T curve whereas a thick coverage with Ni corresponds to the 4-T curve. The low-temperature anomaly due to Ni or Fe is not a Kondo effect since we can increase the Ni or Fe thickness so that they are in the ferromagnetic state. This does not alter the temperature dependence of the resistance, but it excludes spin-flip processes which are necessary for the Kondo effect. If one applies a magnetic field to the Pd plus traces of Fe or Ni, its effect on the resistance is strongly reduced. The anomalies caused by the superimposed Fe or Ni and the magnetoresistance are not additive. This interference between magnetic field and Fe or Ni suggests that they act on the same Pd atoms.

The magnetoresistance cannot be caused by orbital effects of the conduction electrons, because their mean free path is much too small, nor are magnetic impurities responsible for the low-temperature anomaly. My mass spectroscopical analysis yields the following impurities for the used Pd: $c_{\mathrm{Fe}} = 1.5$ ppm, $c_{\mathrm{Co}} < 0.2$ ppm, $c_{\mathrm{Ni}} < 0.7$ ppm, $c_{\mathrm{Cr}} \approx 1$ ppm, $c_{\mathrm{Rh}} = 0.5$ ppm, and $c_{\mathrm{Ru}} < 2$ ppm. The concentration of Mn could not be determined because Mn coincides with the double-charged Pd isotope. I conclude that the observed Pd minimum is not due to magnetic impurities because (i) the concentration of the magnetic impurities is rather small and (ii) additional Fe and Ni atoms at the surface yield a different behavior in an external magnetic field.

The resistance anomaly presents an interesting puzzle. It is likely that the anomaly has a magnetic origin since it depends on the magnetic field as well as on magnetic ions. The magnetic field interacts via the magnetic energy $\vec{M} \cdot \vec{B}$ whereas the Ni or Fe atoms interact via a spin polarization of the Pd. As an important consequence of this interpretation one finds that single Fe and Ni atoms at the Pd surface with a coverage of 1/100 possess a magnetic moment.

The insensitivity of the anomaly to the superposition with Cu proves that a possible magnetism of the surface atoms of Pd is *not* responsible for the anomaly. The Cu should destroy any surface magnetism of the Pd. Measurements on the interface Ni-Cu by the author[5] showed that the Ni atoms at the interface loose their moment. Since Pd and Ni are electronically very similar a superposition of Pd with Cu should destroy a possible surface magnetism at the Pd surface.

The influence of the Ni and Fe atoms and their interference with the magnetoresistance suggest that a Pd region somewhere below the upper surface is responsible for the anomaly. This region must have a limited thickness because the magnetoresistivity is proportional to $1/D$. Therefore the source of the anomaly may be a thin Pd sheet somewhere below the upper surface.

Let us describe the Pd film with a Landau equation[6]

$$\alpha(\vec{r})M(\vec{r}) + \beta M^3(\vec{r}) - \gamma\nabla^2 M(\vec{r}) = B,$$

where $M(\vec{r})$ is the position-dependent magnetization, B is the applied magnetic field, α, β, and γ are Landau parameters. In a ferromagnetic metal below the Curie temperature, one has $\alpha < 0$.

The Landau parameter, $\alpha(\vec{r})$, of the Pd shall be $\alpha_0 > O$ as in bulk Pd. However, in the thin magnetic Pd sheet of thickness $2a$ the Landau parameter α may be negative at zero temperature and take the value α_1.

If α_1 is less than a threshold value {given by the implicit relation $\tan[(\alpha_1/\gamma)^{1/2}a] = (\alpha_0/\alpha_1)^{1/2}$}, then the thin sheet is at $T = 0$ K in the ferromagnetic state with a finite $M(\vec{r})$. The application of an external magnetic field increases $M(\vec{r})$ [in the homogeneous case one obtains $dM = (1/2|\alpha|)B$].

The calculation of the resistivity in a ferromagnetic metal is a difficult task. One has to consider the different number of final states for scattered conduction electrons (Mott picture) as well as the additional exchange potential due to the polarization of the d electrons. Finite temperatures increase the difficulties dramatically. Therefore the author offers only a suggestion for the anomalous behavior of the resistance in Pd film. Consider the model as discussed above. The magnetic polarization $M(\vec{r})$ in the thin sheet of the thickness $2a$ at $T = 0$ K leaves, in first approximation, the charge distribution of the d electrons unchanged. However, the conduction electrons feel a different exchange potential depending on their spin orientation. For one spin orientation the thin ferromagnetic sheet presents a potential barrier and for the opposite spin direction the sheet is a potential valley. The magnetic sheet introduces inner surfaces in the Pd film. Conduction electrons with a small velocity component perpendicular to the sheet are partially reflected by the sheet. I expect that the reflection is not purely specular because of the lattice disorder of the Pd. Then the splitting of the film into different parts increases the resistivity (normal size effect). An external magnetic field increases the magnetization of the sheet and therefore the height of the potential barrier. This enlarges the amount of repelled electrons by the magnetic sheet and increases the resistance.

At finite temperatures the fluctuations destroy the long-range order of this two-dimensional system.[7] One obtains with increasing temperature a reduction of $|M(\vec{r})|$ in the sheet which reduces the reflection of the conduction electrons by the sheet boundaries and therefore the resistance.[8] The application of a magnetic field restores the long-range order and increases $M(\vec{r})$ with increasing field which raises the resistance.

One may speculate about the origin of this proposed two-dimensional ferromagnetic Pd sheet. In the literature[9] there is an interesting suggestion about the properties of Pd below its surface. These authors calculate that a thin Pd sheet—a few atomic layers below the surface—may become ferromagnetic in a mean-field theory. The origin of the magnetic instability are Friedel oscillations of the density of states—due to the surface potential—which increase the Stoner enhancement factor and cause its divergence. This (mean-field) magnetic Pd sheet possesses essentially the properties which we derived from our experimental results. We would like to stimulate a detailed calculation of its thermodynamic properties at finite temperature and its influence on scattering of conduction electrons.

[1]R. W. Cochrane, R. Harris, J. O. Ström-Olson, and M. J. Zuckermann, Phys. Rev. Lett. 35, 676 (1975).

[2]B. Stritzker, Phys. Rev. Lett. 42, 1769 (1979).

[3]G. Bergmann, Phys. Rev. B 19, 3933 (1979).

[4]S. Schmid-Marcic and J. A. Mydosh, Solid State Commun. 17, 795 (1975).

[5]G. Bergmann, Phys. Rev. Lett. 41, 264 (1978).

[6]J. Mathon, Proc. Roy. Soc. London, Ser. A 306, 355 (1968).

[7]See, e.g., *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1974), Vol. 3.

[8]There is little disorder scattering as long as the coherence length is larger than the mean free path.

[9]M. T. Béal-Monod, P. Kumar, and H. Suhl, Solid State Commun. 11, 855 (1972); M. T. Béal-Monod, P. Kumar, D. L. Mills, H. Suhl, and R. A. Weiner, in *Low Temperature Physics—LT13*, edited by W. J. O'Sullivan, K. D. Timmerhaus, and E. F. Hammel (Plenum, New York, 1974), Vol. 4, p. 29; E. Zaremba and A. Griffin, Solid State Commun. 13, 169 (1973); J. P. Muscat, M. T. Béal-Monod, D. M. Newns, and D. Spanjaard, Phys. Rev. B 11, 1437 (1975).