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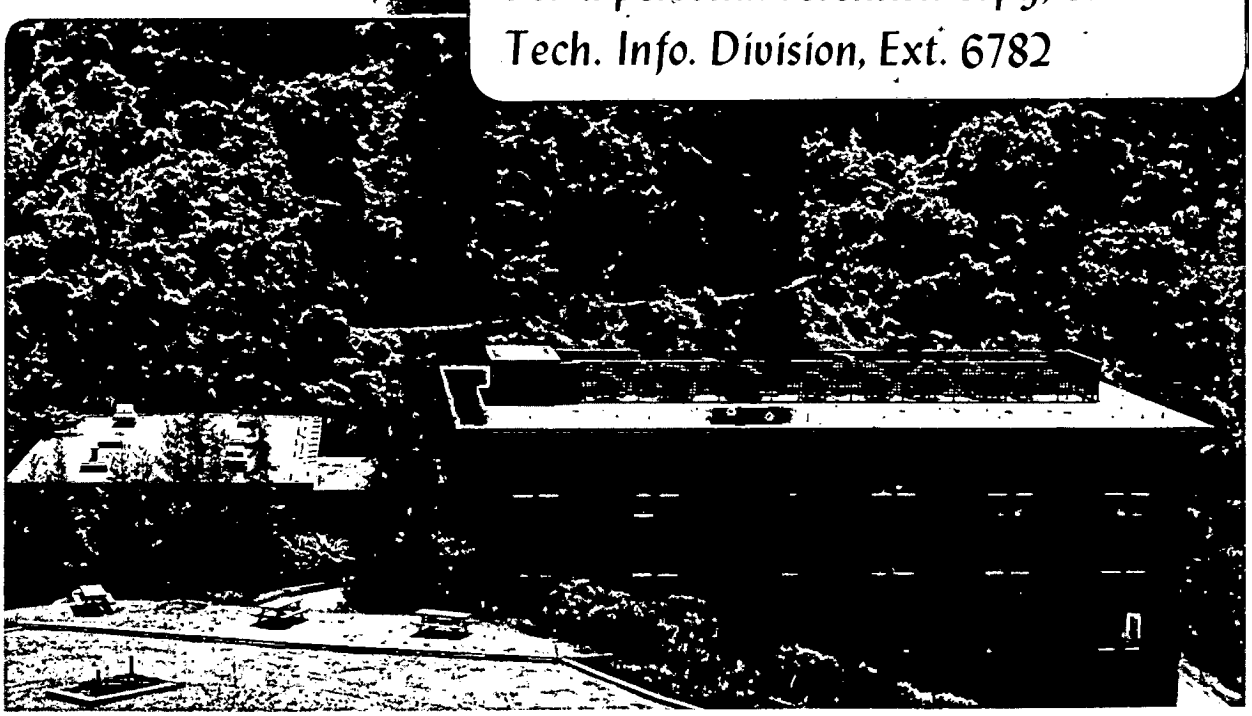

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Presence and Absence of Magnetism in Thin Ni Films

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We calculate the magnetization of Ni films, with thicknesses from one to four atomic layers, on Cu(100) and Cu(111) substrates. The substrate acts to suppress the Ni magnetization; on Cu(111) only, results are consistent with a magnetically "dead" monolayer Ni film. The effect of substrate composition and orientation on film magnetization is discussed. We thus explain disparate experimental results.

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The magnetic behavior of thin nickel films has been a subject of great interest since Liebermann et al[1] reported the observation of magnetically "dead" layers in such films. Despite extensive experiments on Ni films[1-5] and surfaces[6-8], as well as numerous theoretical calculations[9-13], a coherent picture of the important effects has not yet emerged.

It has been established, both experimentally[6-8] and theoretically[9,10,12], that there are not magnetically "dead" layers at the surface of a Ni crystal, as had been suggested[1] by Liebermann et al. For thin Ni films, however, a degree of confusion remains. Some experiments find[1-3] that Ni films of less than three atomic layers are paramagnetic, and these reports have sparked great interest. However, other experiments[4,5] indicate that even a film of 1-2 atomic layers of Ni is ferromagnetic.

Only one theoretical calculation for a supported Ni film has been reported. Wang et al[13] find that a single atomic layer of Ni on Cu(100) is ferromagnetic, though with a magnetic moment reduced from the bulk Ni value. Here we report results of an extensive theoretical investigation of the magnetization of Ni films on the (100) and (111) surfaces of Cu, and of the respective ideal Ni surfaces. We find that a single atomic layer of Ni on Cu(100) is ferromagnetic, in quantitative agreement with Wang et al[13]. However, for a monolayer of

Ni on Cu(111), we find only a minute magnetic moment ($\lesssim 0.1\mu_B$), consistent with the possible observation of a magnetically "dead" layer. In addition, we find that the magnetization of a thin Ni film is very sensitive to the degree of coupling of the Ni d band to the substrate conduction band. Thus for substrates other than Cu, one might expect very different behavior. This explains the fact that experiments[2,3] which use normal-metal substrates generally find 2 or 3 "dead" layers, while experiments performed with noble-metal substrates set an upper bound of one dead layer[4,5], except for the original report by Liebermann et al[1] of two dead layers, based on an extrapolation from relatively thick films (≥ 5 atomic layers). Our results are thus consistent with all experiments reported to date except perhaps that of Liebermann et al[1]. Moreover, by demonstrating the crucial importance of substrate composition and orientation, we resolve most of the apparent discrepancies among experimental results.

Our calculations were based on the Slater-Koster parameterized scheme[14]. The electron-electron interaction was treated in the generalized single-site model, which has been extensively discussed[15]. In this way

$$H = H_0 + H_{ee} \quad , \tag{1}$$

$$H_{ee} = \sum_{i\sigma\sigma'} \sum_{\mu\nu\lambda\kappa} U_{\mu\nu\lambda\kappa}\, c^{\dagger}_{i\mu\sigma}\, c^{\dagger}_{i\nu\sigma'} c_{i\lambda\sigma'} c_{i\kappa\sigma} \quad , \tag{2}$$

where $c^{\dagger}_{i\mu\sigma}$ creates, at site i, an electron in an orbital of symmetry μ and spin σ. The one-electron term H_0 is parametrized in terms of one and two-center integrals, chosen so as to give the correct paramagnetic band structure. The interaction term H_{ee} was treated in the Hartree-Fock approximation. The ratios of the screened interaction parameters $U_{\mu\nu\lambda\kappa}$ were chosen from atomic data[16,17], solid state Auger measurements[18], etc.; and the overall magnitude was adjusted to give the correct[19] bulk spin polarization, $n_{\uparrow}-n_{\downarrow}=0.56$.

To treat charge transfer and potential shifts at the surface in a simple way, we impose upon our potential the constraint

$$\Delta n_{sp} = \Delta n_d = 0 \quad . \tag{3}$$

That is, the average on-site potential of the d orbitals, and of the s and p orbitals, are fixed by the requirement that the total occupancies of the sp and d complexes at any site not differ from the bulk values. More fully self-consistent calculations[11,20] suggest a transfer of about 0.1 electrons per atom from the sp band to the d band at the surface. By neglecting this, we may expect to exaggerate the surface magnetization by roughly $0.1\mu_B$ per atom, an acceptable level of error.

Within the approximations described above, we solve the problem selfconsistently to very high accuracy; details will be presented elsewhere. While it is impossible to estimate a priori the errors introduced by the approximations made here, we do find quantitative agreement with available results of fully selfconsistent calculations. In any case there is no calculational method whose quantitative accuracy has been clearly established for this sort of problem.

In Figure 1 we display our results for the magnetic moment of the surface and interface layers of Ni films on Cu(100). The results of refs. 12 and 13 are also shown. The agreement is excellent. The films exhibit reduced magnetization at the interface and enhanced magnetization at the surface [perhaps somewhat exaggerated by approximation (3)].

Results for Ni films on Cu(111) are displayed in Figure 2. The (111) films show no significant surface enhancement of the moments, and also less substrate-induced suppression of interface magnetization than (100) films, consistent with the smaller change in Ni coordination at the (111) surface and interface. However for the monolayer Ni film on Cu(111) we find a moment smaller than $0.1\mu_B$ per atom, which is consistent with a "dead" layer if approximation (3) is taken into account. Finite temperatures should kill the small magnetization, if any.

For an itinerant ferromagnet such as Ni, low coordination causes band narrowing, and may reduce sp-d hybridization; both these effects favor stronger magnetization. The isolated Ni atom is more strongly spin-polarized than an atom in the bulk. Calculations[11] for an unsupported Ni monolayer find a spin polarization intermediate between the atomic and bulk values. It is the interaction of the Ni film with the substrate conduction band which suppresses the film magnetic moment here, just as the sp-d interaction suppresses the moment of a magnetic impurity in the Anderson model[21]. We attribute the stronger magnetization of the (100) surface and monolayer film largely to the symmetry-induced "decoupling" of adjacent layers, which occurs [at certain wavevectors] for the (100) surface.

Most experimental investigations of thin Ni films have been carried out with polycrystalline fcc substrates, which form microfacets mostly of (111) orientation, so comparison with theoretical results for the (100) surface may be misleading.

Finally, to illustrate the crucial role of the coupling between the Ni d band and the substrate conduction band, we report results of a numerical "experiment" in which we vary this coupling. Specifically, we consider the monolayer Ni film on Cu(100). We multiply all matrix elements in the Hamiltonian which couple Ni d orbitals to Cu s and p orbitals, by a factor t. Thus $t = 1$ corresponds to the realistic case already discussed, while $t > 1$ corresponds to enhanced

coupling. For various values of $\underline{t}$, we calculate the Ni film magnetization selfconsistently. The results are shown in Figure 3. The magnetization of the Ni film is strikingly sensitive to the degree of coupling to the substrate conduction band. For sufficiently small coupling we find magnetization greater than that in bulk Ni, in agreement with the enhanced magnetization reported[11] for the hypothetical isolated monolayer Ni film. On the other hand, when the coupling is doubled relative to the Ni-Cu(100) value, the Ni is found to be paramagnetic. Since the $\underline{sp}$-$\underline{d}$ coupling may vary among substrates, our results suggest that generalizations about film magnetization which ignore substrate composition are risky at best.

In conclusion we find that the Ni monolayer film on Cu(100) is substantially magnetic, while on Cu(111) it may be magnetically "dead". Similarly the Ni(100) surface has a magnetization which is significantly enhanced relative to the bulk, while the Ni(111) surface does not. We attribute these differences largely to the partial uncoupling of neighboring layers due to symmetry for the (100) surface. It should be noted that the results of Figures 1 and 2 exhibit a strong non-linear behavior with layer thickness, and cast serious doubts on extrapolated conclusions from thick film measurements[1,4]. Finally, we find that the

Ni film magnetization is very sensitive to the degree of coupling between the Ni d band and substrate conduction band. Thus the magnetic behavior of Ni films depends crucially on both substrate composition and orientation. These results serve to explain the origin of the apparent discrepancies among experiments. Since the substrate plays a direct role in modifying Ni film magnetization, it is essential to consider the substrate composition and orientation in making comparisons between results of various experiments and calculations.

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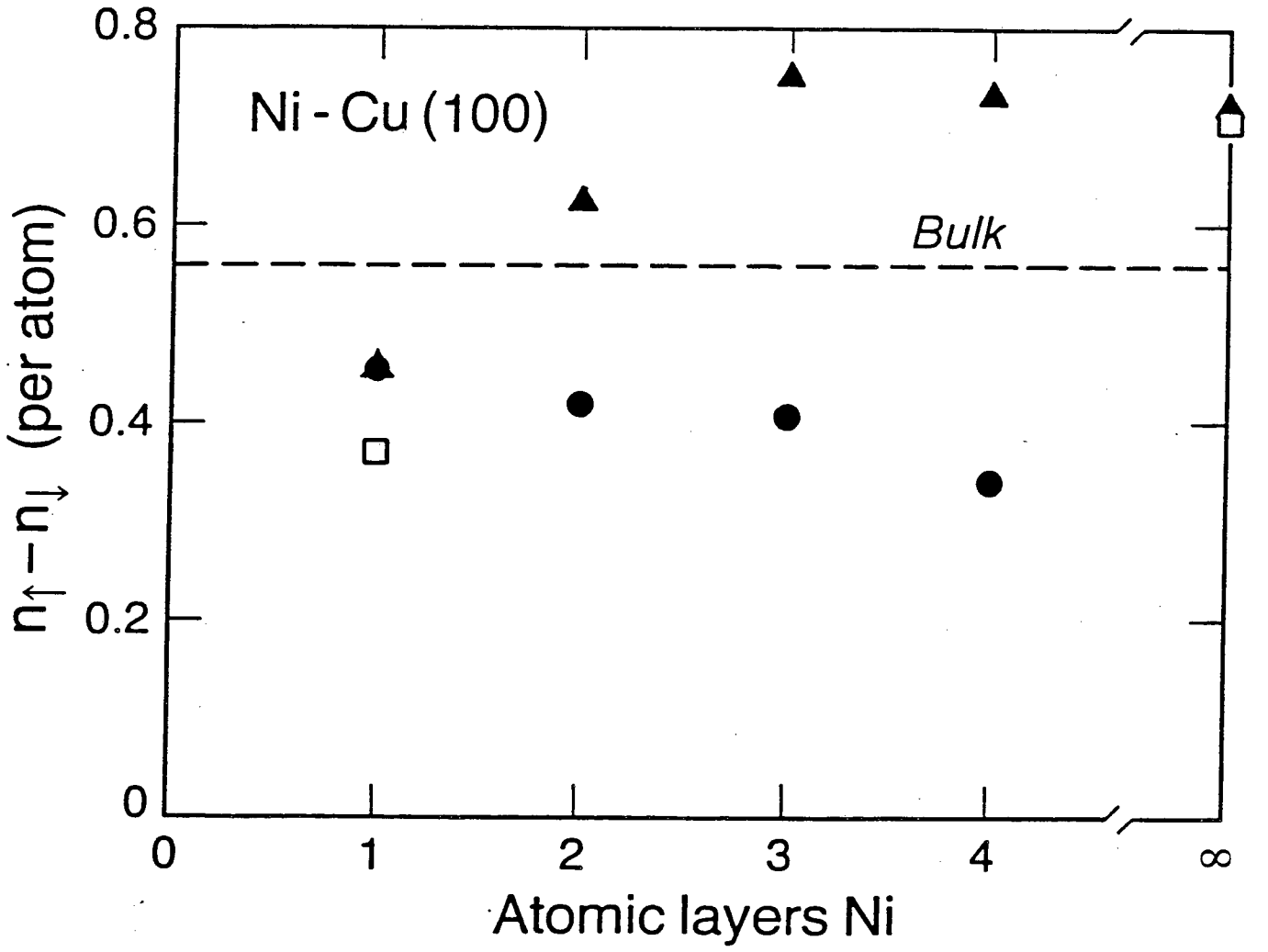
FIGURE CAPTIONS

Figure 1 Spin polarization of surface (triangles) and interface (circles) layers of Ni films on Cu(100), for films of from one to four atomic layers. The point for "infinite" film thickness refers to the ideal Ni surface. The bulk value (dashed line) is shown for comparison, as are results of refs. 12 and 13 (squares) for the monolayer (100) film and the Ni(100) surface.

Figure 2 Spin polarization of Ni films on Cu(111); symbols as in Figure 1.

Figure 3 Spin polarization of a monolayer Ni film on Cu(100), for various values of the (artificially altered) coupling t between Ni d and Cu s and p orbitals. The value t=1 corresponds to the realistic case.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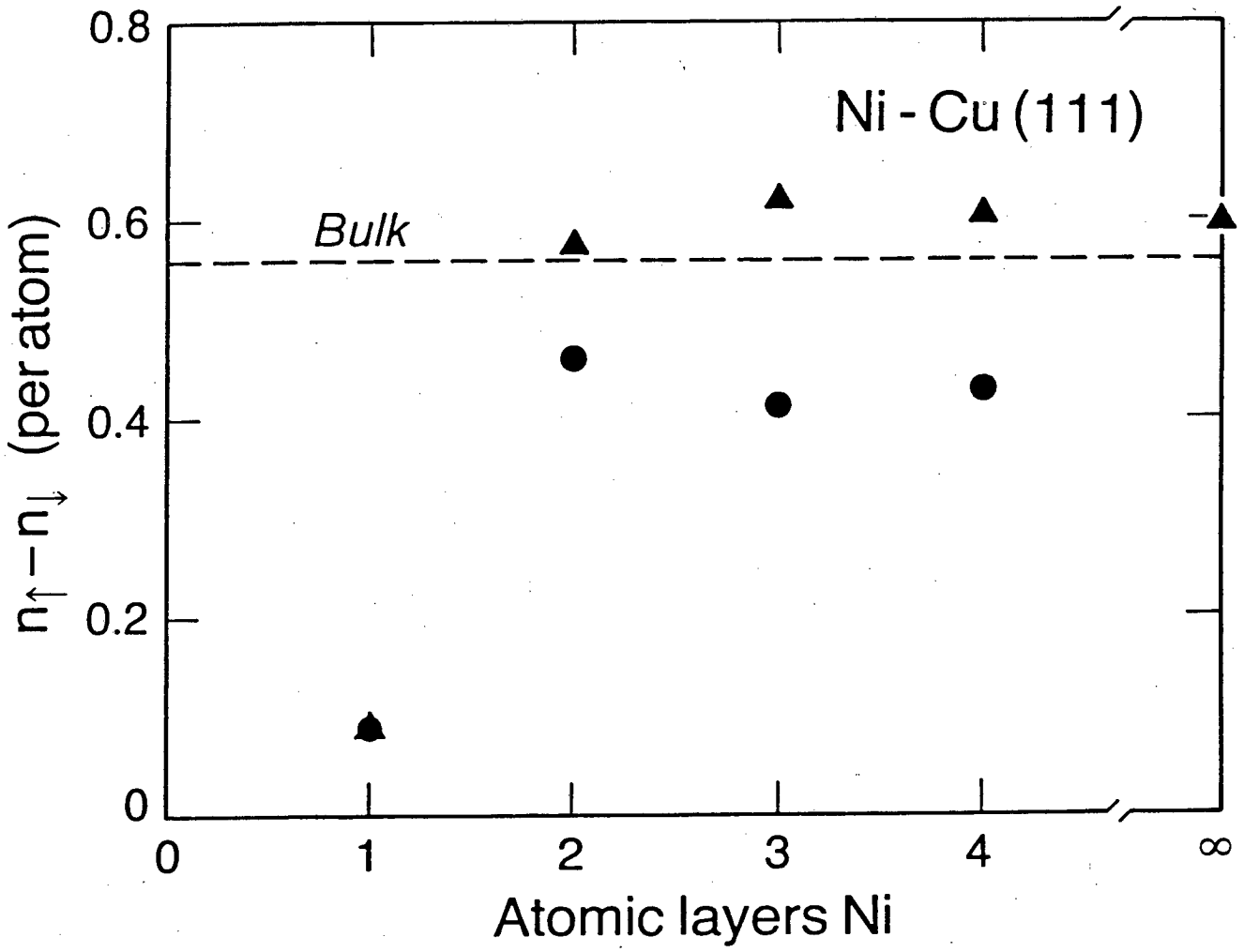
0.2
0
$n_{\uparrow} - n_{\downarrow}$ (per atom)
0
1
2
3
4
∞
Atomic layers Ni

Figure 1


Ni - Cu (111)
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$n_{\uparrow} - n_{\downarrow}$ (per atom)
0
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Atomic layers Ni

Figure 2

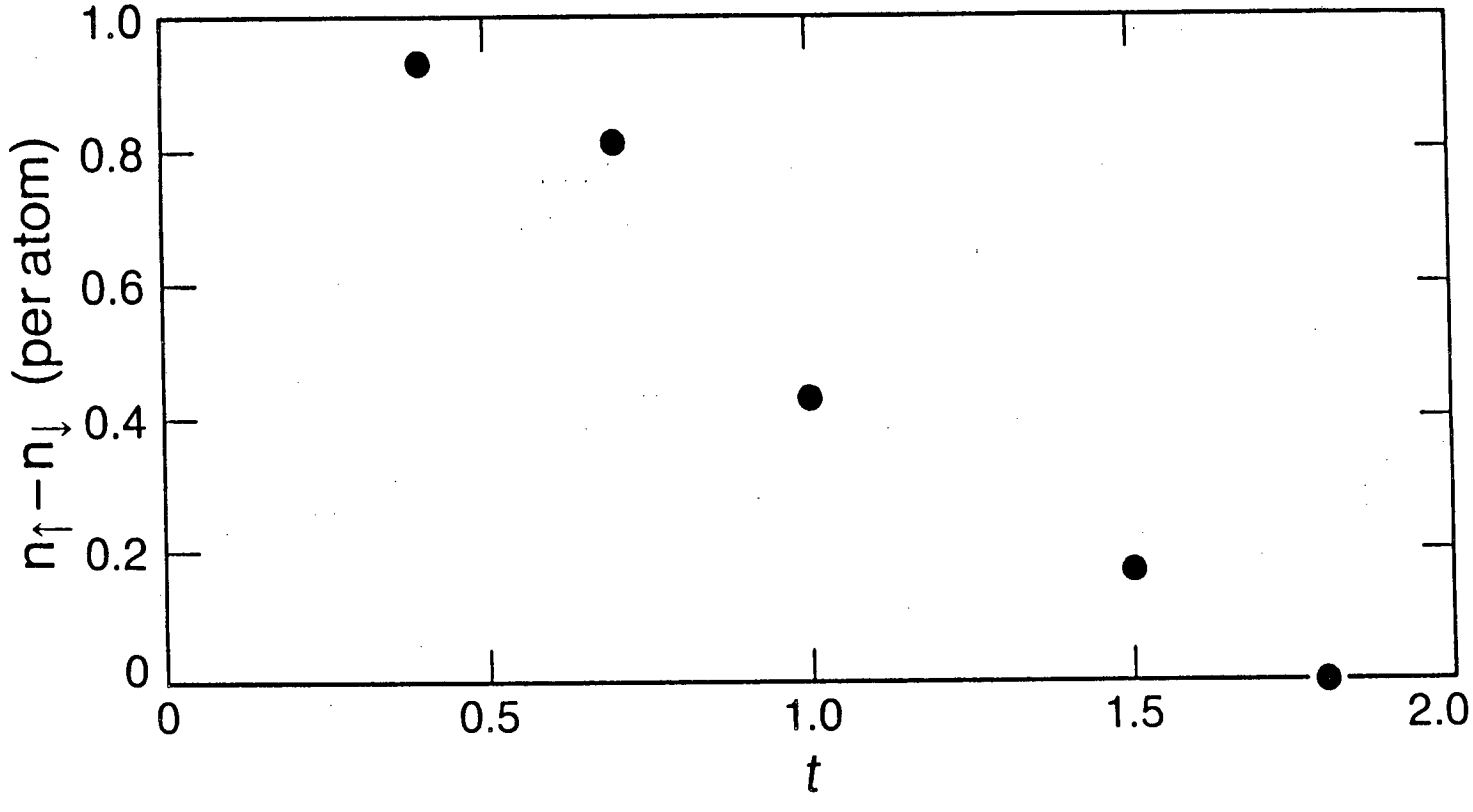

Figure 3

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