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Fe IMPURITY IN Aℓ: MAGNETIC OR NON-MAGNETIC?

by

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ABSTRACT

First-principles electronic structure calculations were performed for a $FeA\ell_{42}$ embedded cluster, representing an Fe impurity in $A\ell$. At the equilibrium positions of the $A\ell$ first neighbors around Fe, obtained by total energy minimization, it was found that the impurity is non-magnetic. This result is consistent with experimental observations and renders unnecessary a microscopic description based on spin fluctuations.

Key-words: Magnetic moments; Fe impurity.

The problem of the existence and stability of localized magnetic moments in metals, in spite of the large amount of experimental and theoretical work, has still many questions left unanswered. Experimental properties of dilute alloys may be divided into bulk (macroscopic)[1] and local probes[2]. On the theoretical side, a transition metal impurity in a s-p host has been described by the "virtual bound state" model of Friedel[3] and Anderson[4]. On the other hand, the theory developed by Kondo[5] (and, later, Wilson[6]) to explain the behaviour of the resistivity of dilute alloys with temperature led to the concept of a Kondo temperature T_k, below which the magnetic moment of the impurity is screened by correlations with the conduction electrons and thus cannot manifest itself[7],[8]. The Kondo theory, however, did not explain the T^2 dependence of the resistivity at T→0; this behaviour was accounted for by the theory of local spin fluctuations[7],[9]. The central concept of spin-fluctuation theory is the existence of a local moment which fluctuates with a lifetime τ , that is very short for systems that display bulk properties with no evidence of magnetism.

Dilute alloys of 3d transition elements in Al may be considered as classical examples of "spin-fluctuating" systems. The low temperature impurity resistivities of AℓM have maximum values for Cr and Mn. This is opposite to the well established local moment behaviour in Cu and Au hosts, for which the resistivity is double-peaked along the series, with a minimum for Mn[7]. As a possible spin-fluctuation system, Fe in Aℓ definitely does not show the Curie-Weiss behaviour, characteristic of stable moments, in the bulk magnetic susceptibility[10]; this is true also in the liquid state, at

temperatures as high as $1090^0C^{(11)}$. The variation with temperature of the thermoelectric power does not show the typical peak of stable magnetic systems[1],[12]. On the side of local experiments, Mössbauer spectroscopy of ^{57}Fe does not show a magnetic splitting[13], although this is not conclusive evidence of zero moment since no experiments were made in the presence of an external magnetic field. The results of recent local measurements[14] with perturbed γ-ray distribution techniques following heavy-ion reactions and recoil implantation, which allows probing extremely dilute impurity systems, point to non-magnetic behaviour for Fe in $A\ell$. If spin fluctuations are considered, the characteristic temperature derived is $>10^4K$.

In spite of the overall evidence of non-magnetic behaviour, recent first-principles electronic structure calculations performed for substitutional Fe in $A\ell$, at the $A\ell$ lattice interatomic distances, found a large magnetic moment on Fe ($1.78^{(15)}$ and $1.73^{(16)}$). The question is, does this moment actually exist and is rapidly fluctuating, or does the experimental evidence result from a non-magnetic impurity?

To answer this question, we have performed first-principles Local Spin Density (LSD) calculations for embedded clusters representing an Fe substitutional impurity in $A\ell$. For the first time, the local lattice relaxation around the impurity was taken into account, by determining the Fe-$A\ell$(nearest neighbors) (NN) distance which minimizes the total energy of the system. By performing spin-polarized calculations, the effect of the local relaxation on the magnetic moment on Fe was determined.

Calculations were made for an $FeAl_{42}$ cluster embedded in the potential field of an infinite Al FCC lattice, for several values of the Fe-Al(NN) distance. The self-consistent field (SCF) Local Spin Density approximation to Density Functional theory was used[17], with the exchange and correlation potential of von Barth and Hedin. The single particle LSD equations were solved iteratively by means of the linear combination of atomic orbitals (LCAO) discrete variational method (DVM)[18], employing a basis set of numerical atomic orbitals. This approach has been shown capable of predicting magnetic moments in solids with good precision[19].

The variational cluster consists of three coordination shells (12+6+24) of Al atoms surrounding a central Fe atom, in FCC geometry. The spin-dependent effective Hamiltonian for the cluster is determined from the total spin densities $\rho_\sigma^{total} = \rho_\sigma^{cluster} + \rho_\sigma^{ext.at.}$. In the present work the spin densities of the external atoms $\rho_\sigma^{ext.at.}$ are modelled by superposition of free Al atom densities at the crystal sites of many shells exterior to the cluster.

The cluster density is determined as

$$\rho_\sigma^{cluster} = \sum_i n_{i\sigma} \, |\psi_{i\sigma}(\vec{r})|^2 \tag{1}$$

where $n_{i\sigma}$ are Fermi-Dirac occupation numbers and $\psi_{i\sigma}$ are the single particle eigenfunctions. In order to efficiently solve the Poisson equation for the

-4-

Coulomb potential, densities are projected onto a superposition of overlapping spherical densities[20]

$$\rho_\sigma^{model} = \sum_{\nu n \ell} f_{n \ell \sigma}^\nu |R_{n\ell}(r_\nu)|^2 \tag{2}$$

Here the amplitudes $f_{n\ell\sigma}^\nu$ for atom ν, radial shell $(n\ell)$ and spin σ are found by least squares error minimization, and $R_{n\ell}$ are the numerical LCAO radial wavefunctions. Magnetic moments associated with a particular site are defined as the difference between spin $\uparrow$ and spin $\downarrow$ Mulliken populations of the basis functions at the site.

The total energy associated with a given volume Ω with nuclei at positions $\{\vec{R}_\nu\}$ is defined as the expectation value (sum over integration mesh) of the energy density $e(\vec{r}, \{\vec{R}_\nu\})$ over the volume:

$$E_\Omega(\{\vec{R}_\nu\}) = \langle e(\vec{r}, \{\vec{R}_\nu\}) \rangle_\Omega \tag{3}$$

We define the _relaxation energy_ as the difference in total energy between the system with nuclear positions $\{\vec{R}_\nu\}$ and a reference system $\{\vec{R}_\nu^0\}$. We take $\{\vec{R}_\nu^0\}$ to be the experimentally determined Aℓ FCC lattice (a=4.05Å) and Ω the cluster volume. In order to control numerical errors, the actual computation of E_Ω is made via point-by-point subtraction of a system of _noninteracting_ atoms (NI) located at cluster and host sites[21]:

$$E_\Omega = \langle e(\vec{r}, \{\vec{R}_\nu\}) - e^{NI}(\vec{r}, \{\vec{R}_\nu\}) \rangle_\Omega + E_\Omega^{NI} \qquad (4)$$

A convenient form for $e(\vec{r}, \{\vec{R}_\nu\})$ is[22]

$$e(\vec{r}, \{\vec{R}_\nu\}) = \sum_\sigma \left[\rho_{\varepsilon,\sigma}(\vec{r}) - 1/2 \left\{ \rho_\sigma(\vec{r}) + \sum_\nu' z_\nu \delta(\vec{r} - \vec{R}_\nu) \right\} V^c(\vec{r}) \right.$$

$$\left. + \rho_\sigma(\vec{r}) \left\{ \varepsilon_{xc}(\vec{r}) - \mu_{xc,\sigma}(\vec{r}) \right\} \right] \qquad (5)$$

where the single particle energy is written as

$$\rho_{\varepsilon,\sigma}(\vec{r}) = \sum_i n_{i\sigma} \, \varepsilon_{i\sigma} \, |\psi_{i\sigma}(\vec{r})|^2 \qquad (6)$$

and is partitioned into atom-localized contributions in a manner similar to that of Eq. (2). This step introduces no errors, since the partitioning is constructed so as to leave the total (integral) single particle energy invariant. The second term in Eq. (5) are corrections to the Coulomb energy due to electron-electron and nuclear-nuclear repulsion; in the third term, ε_{xc} and $\mu_{xc,\sigma}$ are the exchange-correlation energy density and chemical potential, respectively[17]. The sum and delta function in Eq. (5) restricts the nuclear contributions to sites within the integration volume; the prime (') denotes the omission of interaction of a given nucleus with

itself. In numerical evaluation of Eq. (5), least-squares determined model densities (Eq. (2)) were used, consistent with the variational SCF procedure. It was found that 19,500 numerical integration points in both the SCF and energy procedures (with different sampling), with the use of Eq. (4), were sufficient to produce an average relative precision of the order of ± 0.1 eV in the relaxation energies. With this degree of precision it is possible to clearly evaluate the competition between magnetic and non-magnetic configurations, even though the absolute errors in the total energies are of the order of eV. Errors due to basis set truncation and the use of model densities, which are the primary sources of discrepancies, largely cancel when comparing magnetic and non-magnetic configuration energies.

In Fig. 1 are shown the relaxation energies of the $FeA\ell_{42}$ embedded cluster. Only the $Fe-A\ell(NN)$ distances were varied, the positions of the atoms in the 2nd and 3rd shells being kept fixed, as in the $A\ell$ host lattice. From this figure it is seen that the minimum in the energy is achieved at a $Fe-A\ell(NN)$ distance ("d") around 2.7Å, ~6% smaller than the NN distance experimentally measured for the $A\ell$ host lattice (2.86Å). It is interesting that the energy minimum is reached at a value of d very similar to the sum of the Fe and $A\ell$ atomic radii (1.26 and 1.43Å, respectively). Deviations of the points from a smooth curve may be observed in Fig. (1); in addition to the effects of numerical noise in the sampling scheme, there may be real features due to the constraints imposed by single shell (NN) relaxation.

Observing in Fig. (2) the Fe magnetic moments self-consistently

obtained for the same Fe-Aℓ(NN) displacements, one immediately perceives that the Fe magnetic moment, which has a total (3d+4s+4p) value of $0.96\mu_B$ for the calculation at the Aℓ lattice constant, collapses to zero well before reaching the Fe-Aℓ(NN) distance d$\simeq$2.7$\AA$, which roughly corresponds to the energy minimum. Therefore, our calculations indicate that, as the Aℓ nearest neighbors relax towards the Fe atom, the increased interaction between host and impurity destroys the local moment. The abrupt vanishing of moment is consistent with qualitative features of the Friedel-Anderson model.

For values of d larger than 2.70$\AA$, we have performed both spin-polarized and spin-restricted calculations. The energy difference between magnetic and non-magnetic configurations is surprisingly small, even for values of d larger than in the Aℓ lattice. The main cause of this result may be seen in Fig. (3), in which the Fe $3d_\uparrow$ and $3d_\downarrow$ populations are plotted. It is observed that for larger values of the distance d, increase of the Fe 3d moment is achieved by depletion of the $3d_\downarrow$ orbitals and simultaneous increase in $3d_\uparrow$ occupation, in such a way as to leave the total 3d population almost unchanged. We find that differences in the Coulomb energies between spin-polarized and non-polarized calculations outweigh by far the differences in the exchange-correlation term; i.e., a rigid band model is inappropriate. The conservation of the total 3d population largely explains the small net differences observed. In order to obtain a smooth convergence of the SCF procedure, we have applied a "thermal broadening" $\Delta\varepsilon\simeq0.13$ eV to the Fermi-Dirac occupations of the discrete levels, around the Fermi energy. This has the effect of averaging over configurations within

~$\Delta\varepsilon$ of the ground state, and also smooths the magnetic-nonmagnetic transition as shown in Fig. (2).

It may be observed that the equilibrium Aℓ lattice constant that would be found in a similar calculation for a Aℓ_{43} cluster may differ somewhat from the experimental value used here as reference; however, this is irrelevant in the context of the present work, since relaxation can be measured relative to any convenient configuration. What we have shown here is that, if the local lattice relaxation is taken into account, the equilibrium distances obtained result in an Fe impurity in Aℓ which is non-magnetic. This result is consistent with the prediction made applying the Friedel-Anderson model[3],[7].

For the unrelaxed lattice, the magnetic moments of the Aℓ atoms of the cluster align antiferromagnetically with the Fe moment, so that the total cluster moment is smaller than that of the impurity. For example, for d=2.86$\overset{\circ}{A}$ (Aℓ lattice NN distance) the Fe moment is 0.96μ_B and the total cluster moment is 0.55 μ_B. The antiferromagnetic response of the Aℓ atoms in the cluster is oscillatory, such that in the first (NN) shell each Aℓ has μ=-0.011μ_B, in the second shell +0.002μ_B and in the third shell μ=-0.012μ_B.

To summarize, with the present Local Spin Density DVM calculations we have shown that, when local lattice relaxation is taken into account (an effect not considered in previous first-principles calculations[15],[16]), Fe impurities in Aℓ are found to be non-magnetic. This result indicates that for this system the non-existence of a Curie-Weiss behaviour and other

experimental evidence of non-magnetism is not a result of spin-fluctuations, but of moment quenching due to interaction of the impurity with the host.

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FIGURE CAPTIONS

Figure 1

Relaxation energy of the $FeA\ell_{42}$ cluster versus the Fe-Aℓ(NN) distance
d.   The arrow shows the interatomic distance for the pure Aℓ lattice.   ⊙
Non-polarized calculation.   X Spin-polarized calculation.

Figure 2

Magnetic moments μ on Fe for the $FeA\ell_{42}$ cluster versus d.   ■3d moment.
+ (4s+4p) moment.

Figure 3

3d populations of Fe versus d for the $FeA\ell_{42}$ cluster.

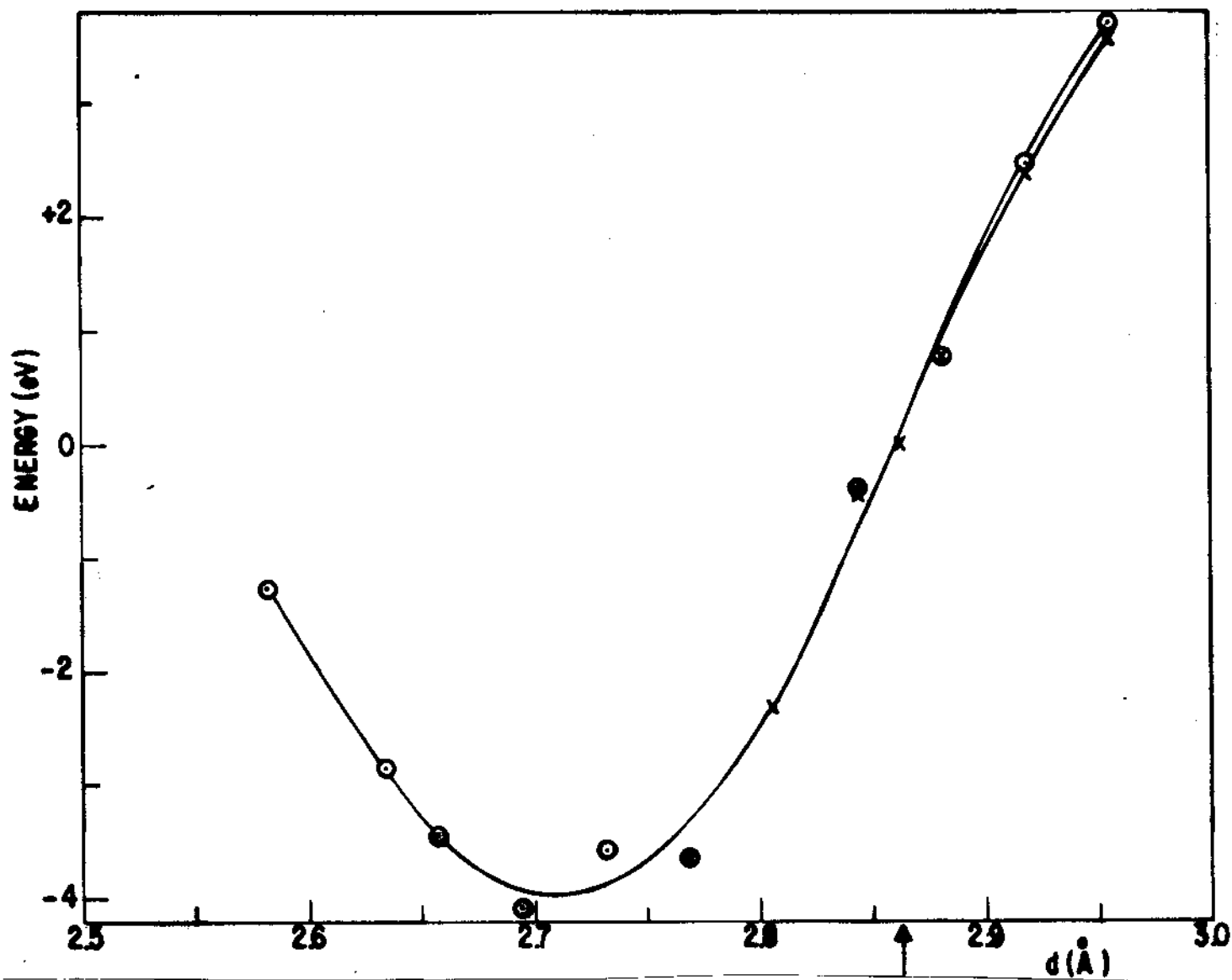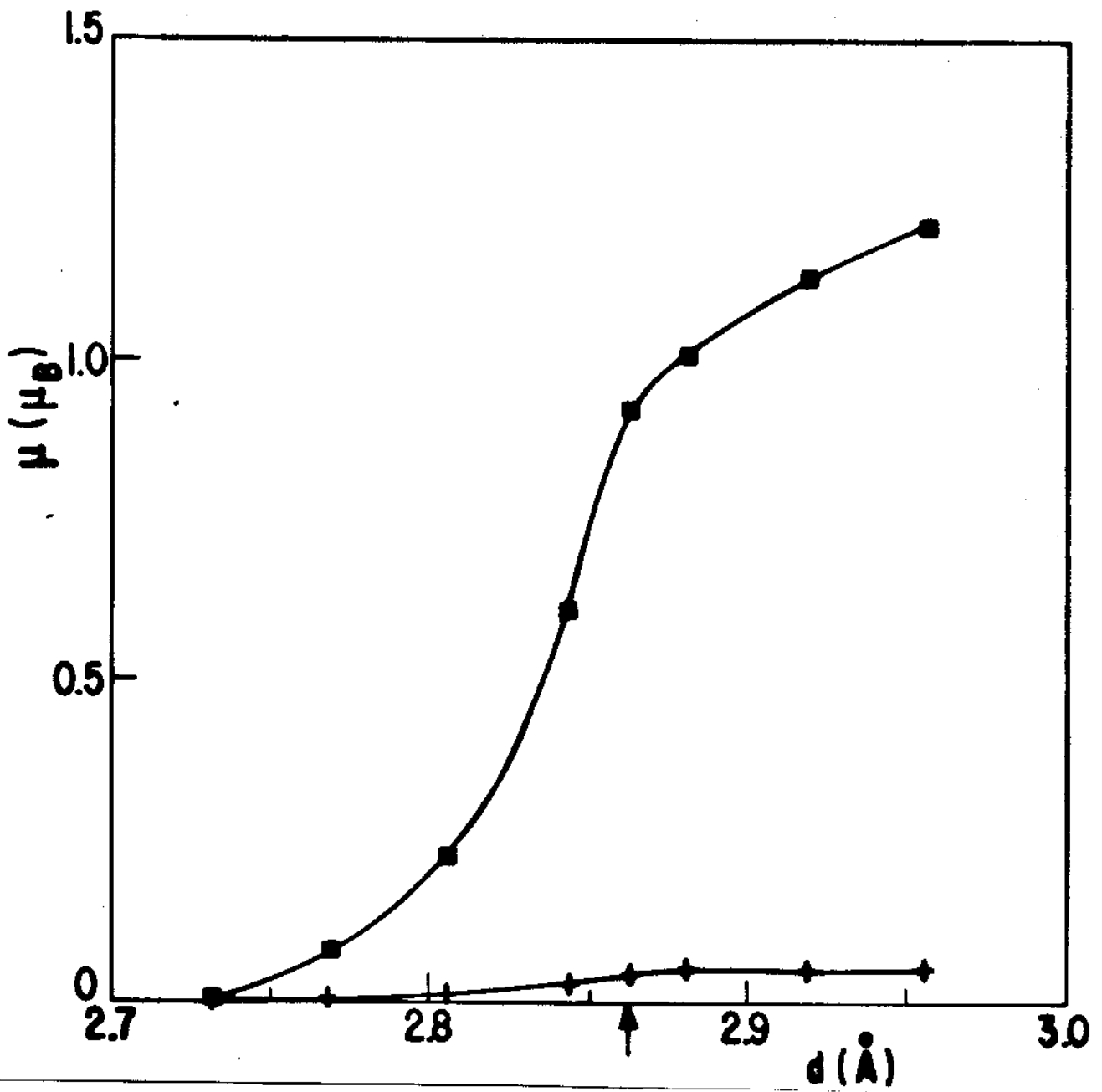FIG. 1

FIG. 2
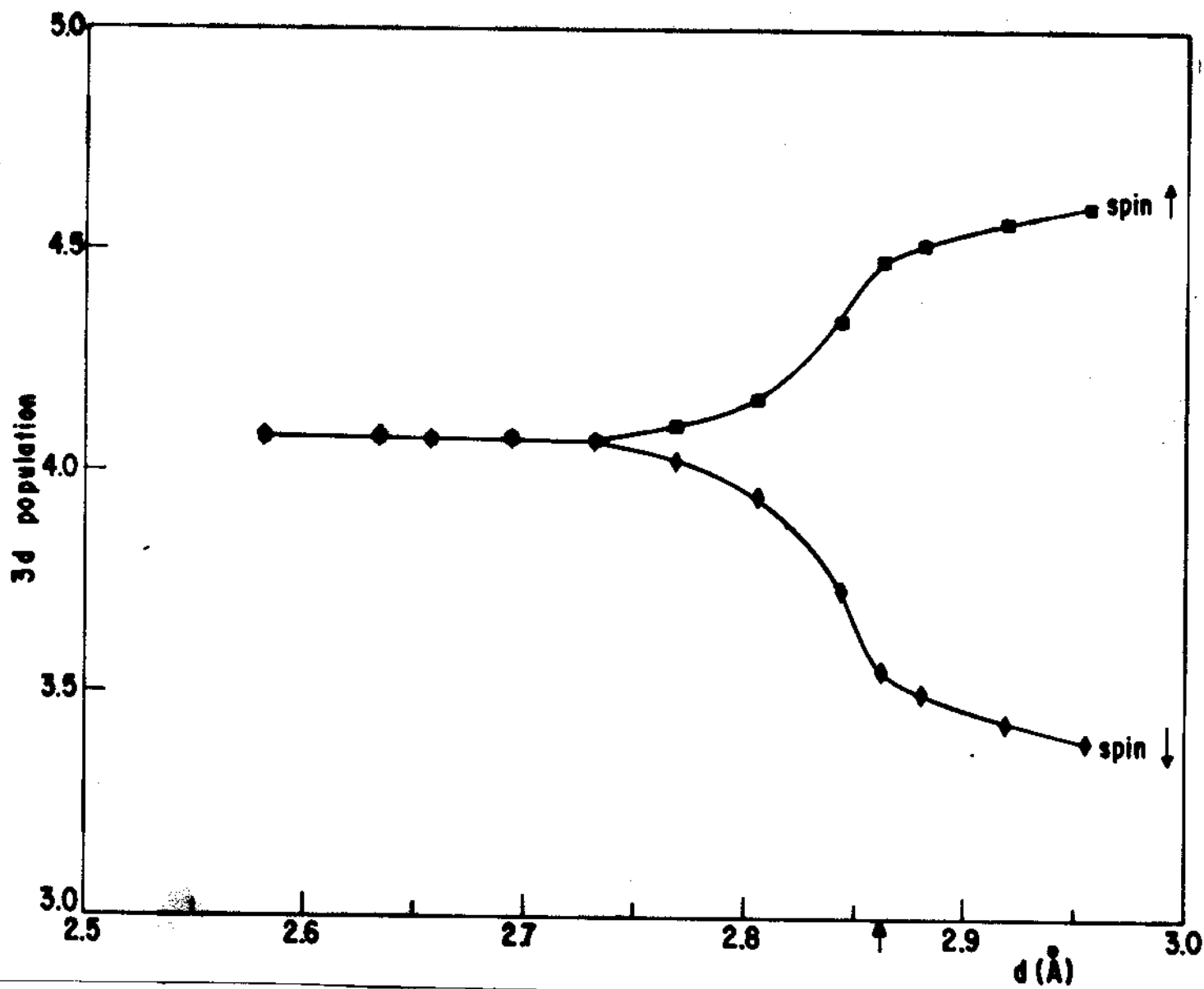
FIG. 3

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