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MOLECULAR DYNAMICS STUDY OF SILVER

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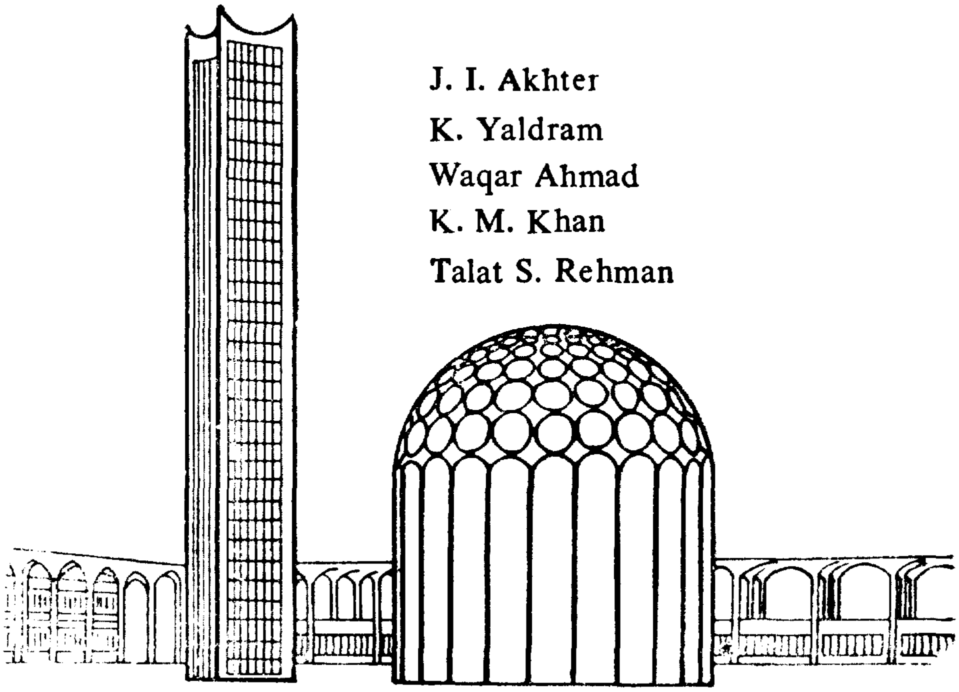
Talat S. Rehman



Nuclear Physics Division
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J.I. Akhter, K. Yaldram, Waqar Ahmad, K.M. Khan
NPD, PINSTECH

and Talat S. Rehman
Dept. of Physics, Kansas State University, U.S.A.

Abstract

We present results of molecular dynamics study using the embedded atom potential to examine the equilibrium bulk properties of Ag. We calculate the total energy and the lattice parameters as a function of temperature. From these we determine the specific heat and linear coefficient of thermal expansion. The comparison with experimental results of these two quantities is found to be excellent. We have also calculated the mean square displacement of the atoms in the three directions. As expected because of symmetry the displacements in the three directions are comparable and increase with increasing temperature.

1. INTRODUCTION

Molecular Dynamics (M.D.) and Monte Carlo (M.C.) computer simulation methods have become very important tools for the study of equilibrium and transport properties of model condense matter systems. The M.C. method has been used extensively at PINSTECH for the study of different physical systems of interest. These include catalytic surface reactions, single chain polymers, phase separation in alloys, order-disorder phenomena, annealed and quenched binary alloys etc. So far very little working experience in M.D. exists either in PINSTECH or elsewhere in the country. In the present work we have used the M.D. technique to study the bulk properties of Ag, like the temperature dependence of the lattice constant, internal energy, coefficient of thermal expansion, specific heat and atomic displacements. The aim of the study is to gain familiarity with the M.D. technique, rather than to do any novel research. Ag was chosen because of the easy access to experimental results with which ultimately we hope to compare our results.

2. MOLECULAR DYNAMICS

In the M.D. method, one investigates the time evolution of positions and velocities of atoms and molecules which constitute the system. This is done by constructing a suitable intermolecular potential model, and solving the equations of motion of these particles with a suitable numerical algorithm. The simulations are done on an insolated system so that the number of particles and the total energy E is conserved as the system moves along its trajectory in phase space. During the simulation the temperature and pressure or temperature and volume or volume and energy of the system can be kept constant. The simulation gives a detailed information about the velocities and positions of the particles of the system at different times. This information can then be used to study the equilibrium as well as non-equilibrium properties of the system.

The proper choice of a potential is extremely important and depends upon the type of system under consideration. We have used the Embedded Atom Method, which is based on density functional ideas, for Ag. This method is discussed in detail in the section that follows. In M.D. we always work with a limited number of particles. This restriction is imposed due to the limitations of the computer speed and memory. To partly overcome the effects introduced by the finiteness of the system Periodic Boundary Conditions are imposed. This is discussed in the subsequent section. Another important aspect to be considered in M.D. simulations is the solution of the equations of motion for each particle to determine their positions and velocities at regular intervals of time. The dynamical integration schemes in particular the Nordsieck scheme is described in section 5. To mimic the real system we had to make an appropriate choice of different parameters. Section 6 discusses this and also gives a comprehensive picture of the computational scheme. Finally we present and discuss results obtained for bulk Ag.

3. EMBEDDED ATOM METHOD (EAM)

Historically the problems of atomic interactions have been addressed with various pair-potential models like Lennard-Jones potential, Morse potential, etc. With these potentials the energetics of an arbitrary arrangement of atoms can be calculated efficiently. However there are some significant problems associated with the application of pair potential specially when N-body interactions are considered which limits its use. Some of these limitations are listed below.

i) When the local environment is substantially different from the uniform bulk, pair-potential results are not accurate. This is because the pair potentials are defined for a perfect crystal. Any change in environment of an atom is not accounted for in the potential. This includes such problems like surfaces, grain boundaries, voids, fractures, etc. [1].

ii) While determining the elastic properties of metals, the total energy requires the use of a volume dependent energy term, to balance the so called Cauchy pressure. This volume dependent term, on the other hand, restricts the use of pair potential to situations where volume is definable. Such ambiguities arise in calculations involving surfaces because the exact termination of the volume on atomic scale at the surface is ambigious. In such cases results could be invalid [3].

iii) In pair potential, vacancy formation energy is always found to be equal to the cohesive energy but experimentally it is about one-third of cohesive energy as given in the experimental data table by M.W. Finnis and J.E. Sinclair [2].

iv) Whereas the pair potentials have been used successfully to treat inert impurities such as helium in metals, the method is not applicable to chemically active impurities. Particularly the energy of hydrogen atom in a transition metal cluster cannot be represented by pair interaction whereas the energy of helium atom can be so represented [3].

To overcome these difficulties, Daw and Baskes [4] developed a new method known as Embedded Atom Method (EAM). This method has been applied successfully to such problems as phonons, structure of liquid metals, defects, dislocation propagation, alloys, impurities, interdiffusion in alloys, fracture, surface structures, segregation, order-disorder transition, hydrogen interaction with metals, etc. [5]. Moreover the computational requirements of EAM are not significantly more than that required for pair potential calculations. So EAM provides a powerful technique for atomistic calculation of metallic systems.

3.1 Theory

This method is based on density-functional theory as derived by Stott and Zaremba [6] in quasiatom approach and Norskov and Lang [7] in effective-medium approach. In these approaches energy required to place an impurity atom in a lattice is taken solely as a function of the electron density at that particular site. Each atomic species therefore has a unique energy function which is in turn a function of just the electron density. So an impurity is assumed to experience a locally uniform, or slightly non-uniform, environment [8]. In its simplest form, the energy of quasiatom is given by

$$E_{quas} = E_z(\rho_h(r))$$

where $\rho_h(r)$ is the electron density of host without impurity at r, the site where an impurity is to be placed and E_z is the quasiatom energy of an impurity with atomic number Z.

Based on this quasiatom scheme, EAM is developed where all atoms are viewed as being embedded in host consisting of all other atoms. The embedding energy is density dependent where the density is always definable and so the problem of defining the volume is circumvented. This makes it possible to treat chemically active as well as inert impurities and alloying additions in one unified theory that can handle crystal surfaces and cracks.

Since each atom can be viewed as an impurity in the host of other atoms, following form of the total energy can be taken based on quasiatom concept

$$E_{tot} = \Sigma_i F_i(\rho_{h,i})$$

where F_i is the embedding energy, $\rho_{h,i}$ is the density of host at position r_i without atom i and the total energy is sum of the individual contributions.

To include the core-core repulsion, the above equation is assumed to include a short-range pairwise potential term. Thus the resulting energy for N-atom system is

$$E_{tot} = \sum_{i} F_i (\rho_{h,i}) + \frac{1}{2} \sum_{i,j}{}' \phi_{ij} (r_{ij}) \tag{3.1}$$

where ϕ_{ij} is the short range core-core pair repulsion between atoms i and j separated by distance r_{ij}.

Since the host electron density $\rho_{h,i}$ is very small as compared with the atomic charge density of atom i, by making the simplification that this background electron density is constant, it can reasonably be approximated by the linear superposition of contribution from the individual atoms. i.e.

$$\rho_{h,i} = \sum_{i,j}{}' \rho_j^{a} (r_{ij}) \tag{3.2}$$

where ρ_j^{a} is contribution to the density by atom j as a function of distance from its center.

Although EAM is used very efficiently for alloy studies, but for simplification and to minimize the number of functions involved in calculations, the case of monatomic metal is considered. Then the eq. (3.1) and (3.2) when applied to perfect crystal containing N atoms, can be simplified to

$$E = F(\rho) + \frac{1}{2} \sum_{m} S_m \phi (r_m) \tag{3.3}$$

and

$$\rho = \sum_{m} S_m \rho^{a} (r_m) \tag{3.4}$$

Here E is the energy per atom i.e $E = E_{tot}/N$, r_m is the distance of mth neighbor with respect to given atom and S_m is the number of atoms in mth shell. If the perfect crystal structure is maintained then all neighbor distances are multiple of the nearest neighbour distance, i.e.

$$r_m = P_m r_1 \tag{3.5}$$

where the factor P_m depends on the type of the crystal structure e.g. for fcc crystal, $P_m = \sqrt{m}$. Then the embedding energy is only a function of nearest neighbor distance, so equation (3.3) can be written as

$$F(\rho(r_1)) = E(r_1) - \frac{1}{2} \sum_m S_m \phi (r_m) \tag{3.6}$$

In early EAM calculations, the embedding function was determined by a complex fitting procedure. Foils [1] introduced a straight forward scheme which is used here.

Rose et al [6] has shown that, for a broad range of materials, the energy as a function of nearest neighbor distance (or any length parameter in the lattice) is well approximated by the relation.

$$E (r_1) = - E_c \left[1 + \alpha \left[\frac{r_1}{r_{1e}} - 1 \right] e^{-\alpha \left[\frac{r_1}{r_{1e}} - 1 \right]} \right] \tag{3.7}$$

with

$$\alpha = \left[\frac{9 B_e \Omega_e}{E_c} \right]^{1/2} \tag{3.8}$$

where B is the bulk modulus, Ω is the atomic volume, E_c is the cohesive energy and $\frac{r_1}{r_{1e}}$ is the deviation from equilibrium. The subscript 'e' indicates evaluation at equilibrium.

However, combining eq. (3.6) and (3.7), $F(\rho(r_1))$ becomes $F(r_1)$ as there is no 'ρ' on R.H.S.

so

$$F(r_1) = -E_C\left[1+\alpha\left(\frac{r_1}{r_{1e}} - 1\right)\right] e^{-\alpha\left(\frac{r_1}{r_{1e}} - 1\right)} - \frac{1}{2}\sum_m S_m\, \phi(r_m) \qquad (3.9)$$

i.e. embedding energy becomes a function of distance only but the potential should be density dependent.

In order to obtain analytic function $F(\rho)$, $\rho\ (r_1)$ is expected to be simple enough to give r_1 as an analytic function of ρ.

By taking the atomic charge densities from Hartree-Fock calculations in Atomic Nuclear Data Tables, it is found that $\rho(r_1)$ could be well approximated by an exponential decay when r_1 is not far away from equilibrium value r_{1e} [10]. So it is assumed that

$$\rho = \rho_e\, e^{-\beta\left(\frac{r_1}{r_{1e}} - 1\right)} \qquad (3.10)$$

where ρ_e and β can be determined from fitting the calculated electron density

Combining eq. (3.4) and (3.10)

$$\sum S_m\, \rho^a(r_m) = \rho_e\, e^{-\beta\left(\frac{r_1}{r_{1e}} - 1\right)} \qquad (3.11)$$

It is clear from this equation that ρ cannot have the same form as ρ^a when the interaction beyond the first nearest neighbor is considered. So for generality, atomic charge densities are replaced with a parameterized function.

$$\rho^a(r) = \rho_e^a \sum_{l=0}^{k} C_l \left[\frac{r_{1e}}{r}\right]^l \tag{3.12}$$

With this assumption $\rho^a(r)$ has the same form as in eq.(3.4), so Combining equation (3.5), (3.11) and (3.12)

$$\sum_m S_m \rho_e^a \sum_{l=0}^{k} C_l \left[\frac{r_{1e}}{r_1}\right]^l P_m^{-l} = \rho_e \, e^{-\beta\left[\frac{r_1}{r_{1e}} - 1\right]}$$

Similarly two body potential $\phi(r)$ can take the form as in eq.(3.7) i.e.

$$\phi(r) = -\phi_e\left[1+\delta\left[\frac{r}{r_{1e}} - 1\right]\right] e^{-\gamma\left[\frac{r}{r_{1e}} - 1\right]} \tag{3.13}$$

Using eq.(3.5), (3.9), (3.10) and (3.13)

$$F(\rho) = -E_c\left[1 - \frac{\alpha}{\beta}\ln\left[\frac{\rho}{\rho_e}\right]\right]\left[\frac{\rho}{\rho_e}\right]^{\alpha/\beta} + \frac{1}{2}\phi_e \sum_m S_m \, e^{-(P_m-1)\gamma}$$

$$\cdot\left[1+\left[P_m-1\right]\delta - P_m\frac{\delta}{\beta}\ln\left[\frac{\rho}{\rho_e}\right]\right] + \left[\frac{\rho}{\rho_e}\right]^{P_m(\alpha/\beta)}$$

This analytic embedding function is easy to use in computer simulation. In principle it can be used for any crystal structure. There are only five parameters to be determined ρ_e, ϕ_e, β, δ and γ. Since only the ratios of electron density occurs, so ρ_e cancels from the model, β can be obtained from fitting atomic charge densities and other three parameters can be determined from fitting the unrelaxed vacancy formation energy and the elastic constants.

4. PERIODIC BOUNDARY CONDITIONS

In computer simulation, in general one is interested in the computation of a property in the thermodynamic limit. The thermodynamic limit is that in which the number of particles goes to infinity. However, computer simulations allow system sizes which are small compared to the thermodynamic limit, so that there are possible finite-size effects. In order to reduce the finite-size effects periodic boundary conditions are used.

Let the system under study consist of N particles. We restrict ourselves to properties of the bulk at a specific density ρ. In order to retain a constant density we must introduce a volume i.e the M.D cell. If the system is in thermal equilibrium then the shape of the volume is not relevant for liquid and gas states [11]. However, for system in a crystalline state the shape does make a difference. We take a cubic volume for computational simplicity. Let L be the linear size of the M.D cell with its volume L^3. The introduction of the box creates six surfaces. Particles hitting these surface walls would be reflected back into the interior of the cell or be lost in void. Especially for system with a small number of particles (specific to M.D simulation where usually 10^2- 10^4 particles are considered), important contribution to any property would come from the surface. We impose periodic boundary conditions to reduce these surface effects. The basic cell (cubic box) is repeated identically an infinite number of times throughout space to form an infinite lattice. For computer simulation it is assumed that if a particle moves in the basic cell, its periodic image in each of the neighbouring cells moves exactly in the same way. As a particle crosses surface of the basic cell, one of its image enters through the opposite side. There are no walls at the boundary of the basic cell and no surface particles. This cell simply forms a convenient reference for measuring the coordinates of the N particles. The assumption made in this is that the small volume is embedded in a bulk.

If we consider the origin to lie at the centre of the cube then all coordinates lie in the range $-\frac{1}{2}$ L to $+\frac{1}{2}$ L. As the simulation proceeds, these molecules move about the infinite periodic system. When the molecule leaves the box by crossing one of the boundaries attention is switched to the image molecule entering the box by simply adding L to or subtracting L from the appropriate coordinate. For bulk simulation boundary conditions are applied along X, Y, and Z directions. However, for surface simulation boundary conditions are imposed in only two directions, the third direction is kept free.

4.1 Minimum Image Convention

M.D programs involve the calculation of the potential energy (P.E) of particular configuration and the forces acting on all particles. We know that in a basic cell there are N particles. In order to calculate force on particle 1 (or contribution to the P.E involving particle 1), we must include interactions between particle 1 and every other particle j in the simulation cell. There are N - 1 such particles in the cell. We must also, in principle, include all interactions between particle 1 and images lying in the neighbouring cells. This will be, of course, infinite number of terms and impossible to calculate in practice. We restrict this summation by considering particle 1 to be at the center of a region which has the same size and shape as the basic simulation cell. Particle 1 interacts with all the particles whose center lie within this region, that is the closest periodic images of the other N - 1 particles. This technique, which is natural consequence of the periodic boundary condition is called minimum image convention [12].

The minimum image convention may be coded in the same way as the periodic boundary adjustment.

4.2 Potential Truncation

Despite introducing minimum image convention, the calculation of the P.E due to interactions involves $\frac{1}{2}$ N(N - 1) terms. This may be a very substantial calculation for a system of 1000 particles. To overcome this, further approximation is used which is called potential truncation. The potential is set to zero for $r \geq r_c$, where r_c is the cutoff distance. For $r > r_c$ the potential is small and can be ignored. The cutoff distance must be less than L/2 for consistency with the minimum image convention.

5. DYNAMICAL METHOD INTEGRATION SCHEMES

Dynamical method computer experiments are used to simulate the movement of individual atoms in an assembly of N atoms on the basis of Newtonian mechanics. If the initial position and velocity vectors for each atom in the assembly are given, the dynamical history of the assembly is generated by numerically integrating the 3N simultaneous equations of motion for the coordinate components of N atoms in the assembly. In this numerical integration process, the 3N velocity components for the N atoms are also determined. Hence, the dynamical method generates a phase space point trajectory for N atom assembly as a function of time.

A number of numerical integration schemes are available to solve the differential equations. If molecular positions, velocities and other dynamic information at a time t is known, then the positions, velocities and accelerations are obtained at a later time $t+\Delta t$, to a sufficient degree of accuracy, through these algorithms. Differential equations are solved on a step by step basis where time step Δt depends on the method of solution. However the time step is significantly smaller than the time taken for a molecule to travel its own length. The general scheme of a stepwise MD simulation, based on a predictor corrector algorithm may be summarized as follows:-

(a) Predict the positions, velocities, accelerations etc., at a time $t+\Delta t$, using current values of these quantities.
(b) Evaluate the forces, and hence accelerations $\bar{a}_i=\bar{f}_i/m$, from the new positions.
(c) Correct the predicted positions, velocities, accelerations, etc., using the new accelerations.
(d) Repeate the process till the predicted and corrected quantities are within specified limits of each dt.
(e) Calculate any variables of interest, such as energy, order parameter, ready for the accumulation of time averages, before returning to (a) for the next step.

A successful simulation algorithm might have the following desirable qualities.

i) It should be fast and require little memory.
ii) It should permit the use of long time step Δt.
iii) It should satisfy the known conservation laws of energy and momentum, and be time reversible.
iv) It should be simple in form and easy to program.

Four different numerical integration schemes are available to solve the differential equations and they are

I. Nordsieck Methods [13]
II. Central Difference [14]
III. Eular - Cauchy [15]
IV. Simple predictor - corrector [16]

The Nordsieck method is self starting and capable of utilizing a variable integration time step without loss of either stability or accuracy. Nordsieck method is used in our calculation and its details are given below.

5.1 Nordsieck method of Newton's equations

Nordsieck (1962) [13] developed a scheme to integrate ordinary differential equations. Let x(t) be the atom coordinate and let the first five scaled time derivatives of x be

$$U_1 = \frac{dx}{dt} \cdot \Delta t$$

$$U_2 = \frac{d^2x}{dt^2} \frac{(\Delta t)^2}{2!}$$

$$U_3 = \frac{d^3x}{dt^3} \frac{(\Delta t)^3}{3!}$$

$$U_4 = \frac{d^4x}{dt^3} \frac{(\Delta t)^4}{4!}$$

$$U_5 = \frac{d^5x}{dt^5} \frac{(\Delta t)^5}{5!}$$

The predicted values of x(t) and Un at time (t+Δt) are given by

$$x(t+\Delta t)=x(t)+\frac{\partial x}{\partial t} \Delta t+\frac{\partial^2 x}{\partial t^2} \frac{(\Delta t)^2}{2!}+\frac{\partial^3 x}{\partial t^3} \frac{(\Delta t)^3}{3!}+\frac{\partial^4 x}{\partial t^4} \frac{(\Delta t)^4}{4!}+\frac{\partial^5 x}{\partial t^5} \frac{(\Delta t)^5}{5!}$$

etc.

i.e.

$$x(t+\Delta t) = x(t) + U_1 + U_2 + U_3 + U_4 + U_5 \qquad (5.1)$$

$$U_1(t+\Delta t) = U_1(t) + 2U_2(t) + 3U_3(t) + 4U_4(t) + 5U_5(t) \qquad (5.2)$$

$$U_2(t+\Delta t) = U_2(t) + 3U_3(t) + 6U_4(t) + 10U_5(t) \qquad (5.3)$$

$$U_3(t+\Delta t) = U_3(t) + 4U_4(t) + 10U_5(t) \qquad (5.4)$$

$$U_4(t+\Delta t) = U_4(t) + 5U_5(t) \qquad (5.5)$$

$$U_5(t+\Delta t) = U_5(t) \qquad (5.6)$$

The predicted value of $x(t+\Delta t)$ is then used to compute the force $F(t+\Delta t)$ and the displacement function

$$\phi = \frac{1}{2}\left[\frac{F}{m}\right](\Delta t)^2 - U_2(t+\Delta t) \tag{5.7}$$

The corrected values for x and U_n are then given by

$$x^C(t+\Delta t) = x(t+\Delta t) + C_0\phi \quad (C_0 = 3/16)$$

$$U_1^C(t+\Delta t) = U_1(t+\Delta t) + C_1\phi \ (C_1 = 251/360)$$

$$U_2^C(t+\Delta t) = U_2(t+\Delta t) + C_2\phi \ (C_2 = 1)$$

$$U_3^C(t+\Delta t) = U_3(t+\Delta t) + C_3\phi \ (C_3 = 11/18)$$

$$U_4^C(t+\Delta t) = U_4(t+\Delta t) + C_4\phi \ (C_4 = 1/6)$$

$$U_5^C(t+\Delta t) = U_5(t+\Delta t) + C_5\phi \ (C_5 = 1/60)$$

This is the fifth order method and the values of constants C_0, C_1, - - - C_5 are valid for this order only. Stability of the numerical solution can be checked by monitoring the total energy which does not drift during the solution.

6. COMPUTATIONAL TECHNIQUE

It is important to chose a configuration that can relax rapidly to the structure and velocity distribution appropriate to the solid (liquid) under investigation. In our case the simulations were started from a perfect FCC lattice, containing 256 atoms. Periodic Boundary Conditions were used in all three directions. The initial velocities were chosen randomly from a Gaussian distribution, with magnitudes conforming to the required temperature corrected so that there is no overall momentum. Nordsiecks algorith with a time step 10^{-15}s was used to solve Newtons equations of motion for all the atoms in the M.D. cell.

Left to itself the system evolves in such a way as to conserve energy (NVE Molecular Dynamics). It is however desirable to be able to fix the temperature (NVT) or some other quantity like Pressure and temperature (NPT). This can be done by an appropriate rescaling of some variable. For the NVT simulation the velocities are rescaled at each time step so as to keep the temperature constant, through the use of the equipartition theorem i.e.

$$T_o = \frac{m}{3Nk} \sum_{i=1}^{N} V_i^2$$

where k is the Boltzman constant, and N is the number of atoms. If the required temperature is T, then the velocities are rescaled by a factor (T_o/T).

To generate on isobaric-isothermal ensemble (NPT) the quantity to be rescaled is the coordinates of the atoms.

The constant pressure simulation (NPT) of Evans and Morriss [17] was used on bulk silver to calculate the lattice parameter at a given temperature. The input lattice parameter for any temperature is taken from a previous run which is performed at a slightly lower temperature. One can make a rough guess of the input lattice parameter by adding to this a small correction.

For further calculations the M.D. cell is generated from the lattice parameter calculated above. The system is first equilibrated to a desired temperature for 10 ps under the condition of constant volume and temperature (NVT). To obtain the internal energy at a given temperature a small simulation run is performed at constant energy (NVE) till the total energy (Kinetic + Potential) settles down to a constant value.

The third quantity of interest that we have measured from the NVE simulations is the mean square vibrational amplitudes of the atoms. For this we use the following equation

$$<U_{j\alpha}^2> = \frac{1}{N_j} \sum_{i=1}^{N} < \left[r_{i\alpha}(t) - < r_{i\alpha}(t-\sigma) > \right]^2 >$$

where α represents the direction (x, y or z) and $r_{i\alpha}$ is the instantaneous position of atom i along α. We perform a run for about 80 ps at constant energy and volume (NVE). After ignoring the initial 10 ps we retain configurations after every 0.02 ps. After 20 ps we calculate the mean square displacement. Using the configurations thus generated we can continue the run to calculate the mean square displacements after every 20 ps. We prefer this piecemeal process to one continous run as we can check our values at regular intervals and also as a buffer against computer failure.

7. RESULTS AND DISCUSSION

In Fig.1 we have plotted the internal energy as a function of temperature. We have fitted the data to a third order polynomial

$$E(T) = -2.85 + 0.32 \left[\frac{T}{Tm}\right] - 0.0021 \left[\frac{T}{Tm}\right]^2 + 0.042 \left[\frac{T}{Tm}\right]^3 \quad (7.1)$$

E is in eV and Tm=1234K.

By taking the derivative of equation (7.1) with respect to temperature, we obtain the heat capacities at constant pressure C_p. This has been plotted in Fig.2. The agreement with the experimental results [18] is quite good.

The lattice parameter (in Å) as a function of temperature is plotted in Fig.3. Again we have fitted a third order polynomial to these points

$$a(T) = 4.09 + 0.104 \left[\frac{T}{Tm}\right] - 0.02 \left[\frac{T}{Tm}\right]^2 + 0.047 \left[\frac{T}{Tm}\right]^3 \quad (7.2)$$

From this polynomial one can obtain the linear coefficient of thermal expansion $\left[\frac{1}{a(T)}\frac{da(T)}{dT}\right]$. This is plotted as a function of temperature in Fig.4. The dots show the experimental values [19,20,21,22]. Again the agreement of our simulation results with experiment is found to be reasonably good. The experimental results obtained from different sources show quite a scatter in the values at the same temperature. This difference in the values could arise due to various factors, the main one being the purity of the sample. The introduction of impurities can change the value of α from sample to sample. In MD simulations it must be noted that one works with pure samples.

Finally in Table 1 we have shown the mean square displacements for the three directions. These are found to be the same (with in statistical errors) for the three directions, a result which was expected because of the symmetry of the bulk sample. With temperature the mean square displacements show the expected increase in amplitudes. Fig.5 shows these displacements plotted as a function of temperature.

8. CONCLUSIONS

This was a first attempt at PINSTECH to run MD programme for study of different metals and alloys. Silver was chosen for easy comparison of our results with the experimental ones as well as with the results of earlier attempts with MD. The results we obtained on internal energy, lattice parameters, specific heat, expansion coefficient and mean square displacements compare favourably well with other experimental and simulation results. This is very encouraging since we now plan to use this technique for investigating some surface phenomena like melting, roughening and interlayer relaxations on Ag(111) surfaces. We also plan to study static properties like energy of single and divacancy formations, defects etc.

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Table 1: Mean square displacements (0.1A^2) of bulk Ag as a function of temperature (°K).

Temperature	$<U_x^2>$	$<U_y^2>$	$<U_z^2>$	$<U^2>$
300	0.791	0.757	0.723	0.757 ± 0.034
600	1.733	1.753	1.724	1.737 ± 0.016
900	3.341	3.111	3.144	3.199 ± 0.14
1100	4.273	4.361	4.523	4.386 ± 0.137

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Figure Captions

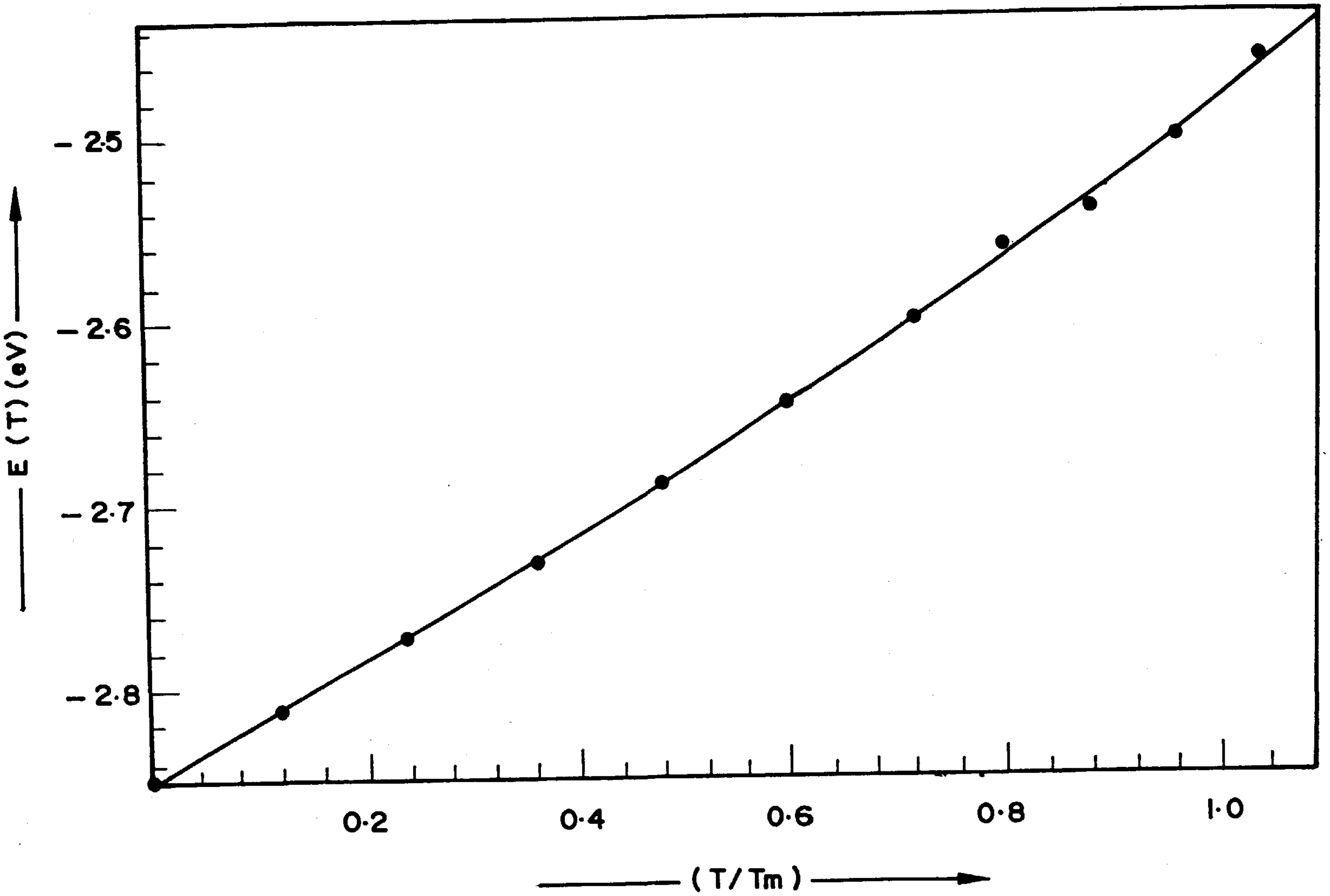
Fig.1: Internal energy per atom as a function of temperature for Ag from MD simulations. The data has been fitted to a third order polynomial curve.

Fig.2: Specific heat per atom at constant pressure plotted against temperature. The experimental data [18] of C_p is shown as solid circles.

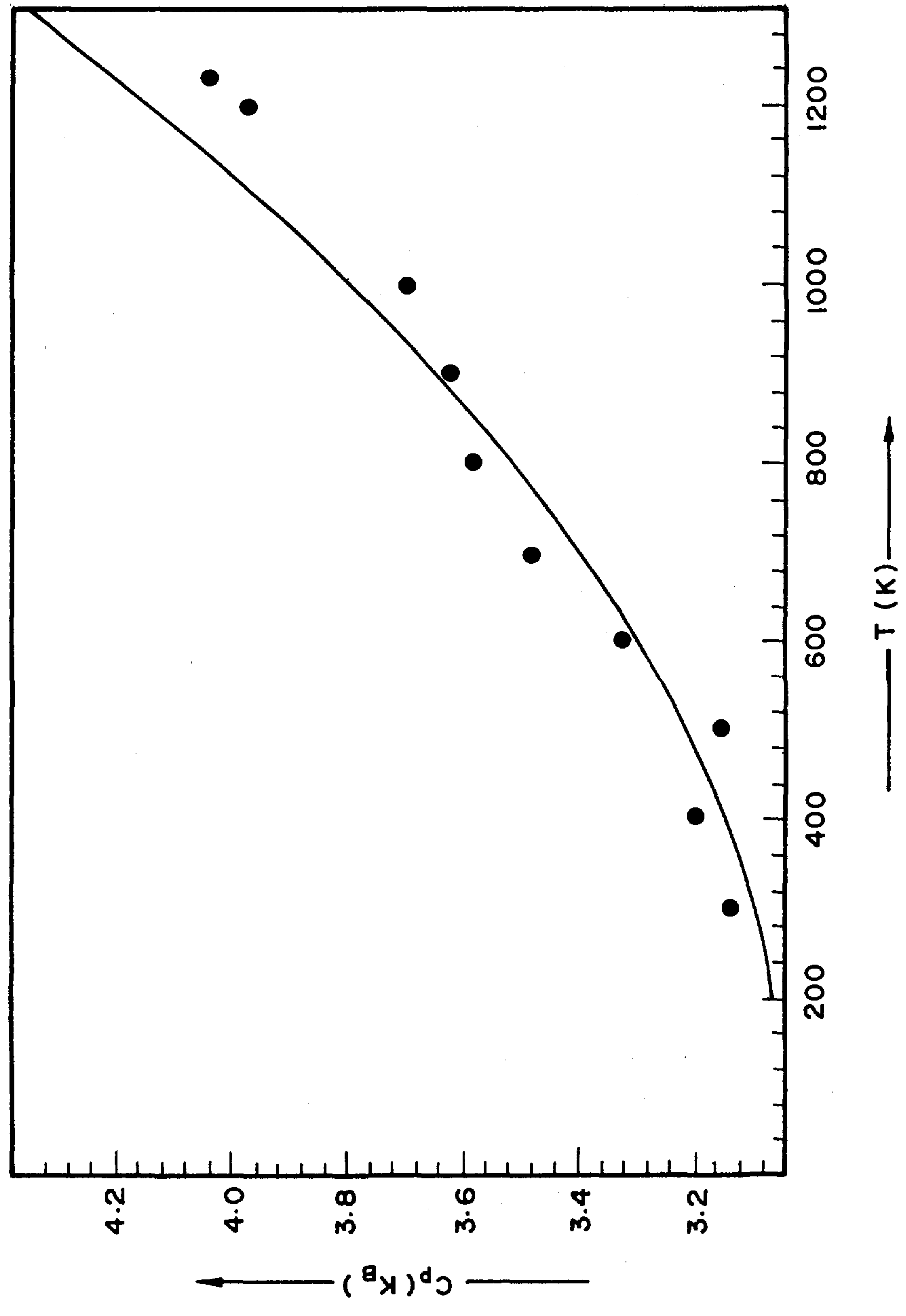
Fig.3: Lattice parameter as a function of temperature for Ag. The data has been fitted to a third order polynomial curve.

Fig.4: Linear coefficients of thermal expansion α plotted against temperature T. The experimental data [19,20,21,22] of α is shown as solid circles.

Fig.5: Mean square displacements of Ag as a function of temperature.



Fig·1


4.2
4.0
3.8
3.6
3.4
3.2
Cp (KB)
200
400
600
800
1000
1200
T (K)

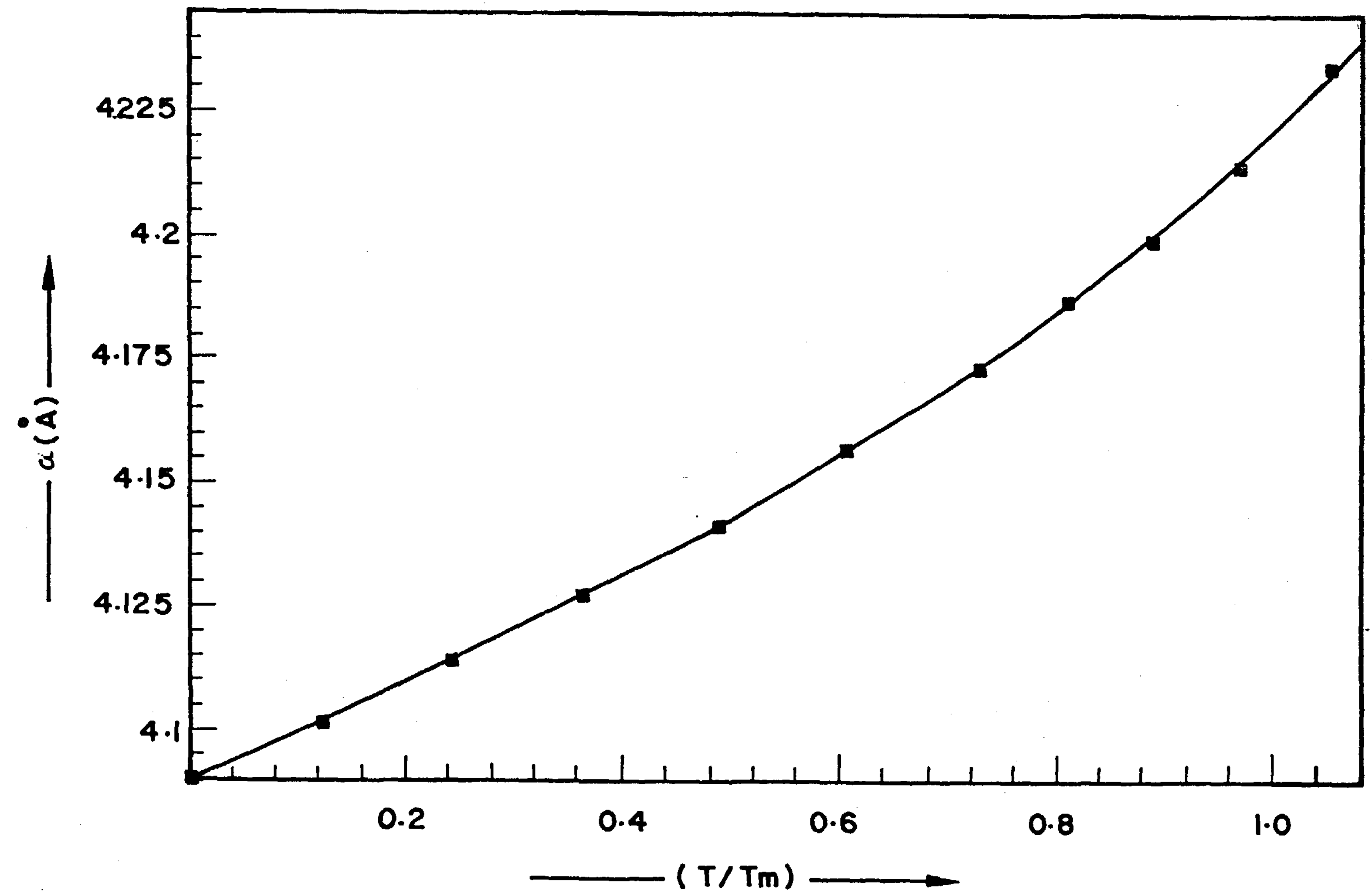


Fig. 3

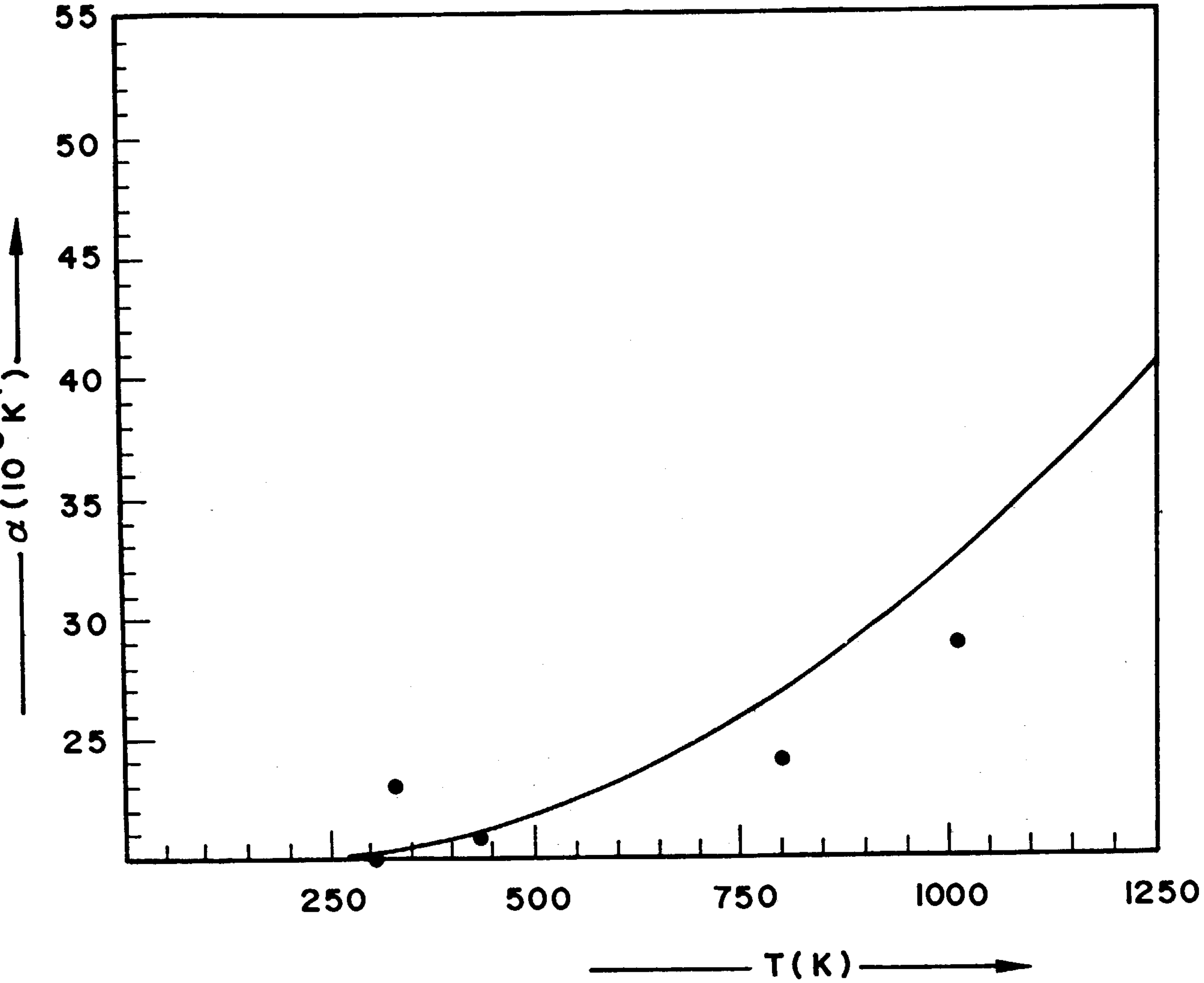


Fig. 4

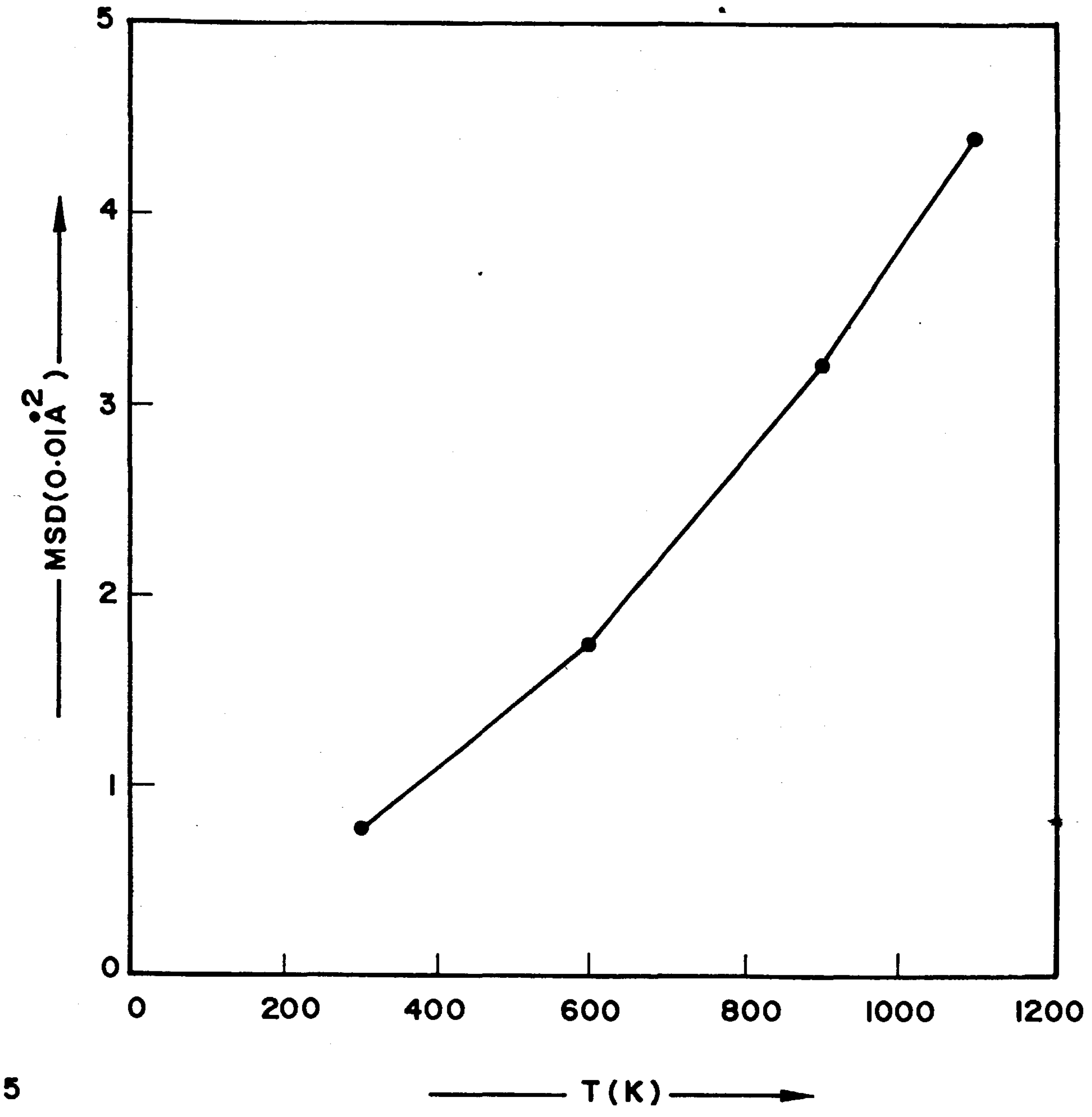


Fig. 5