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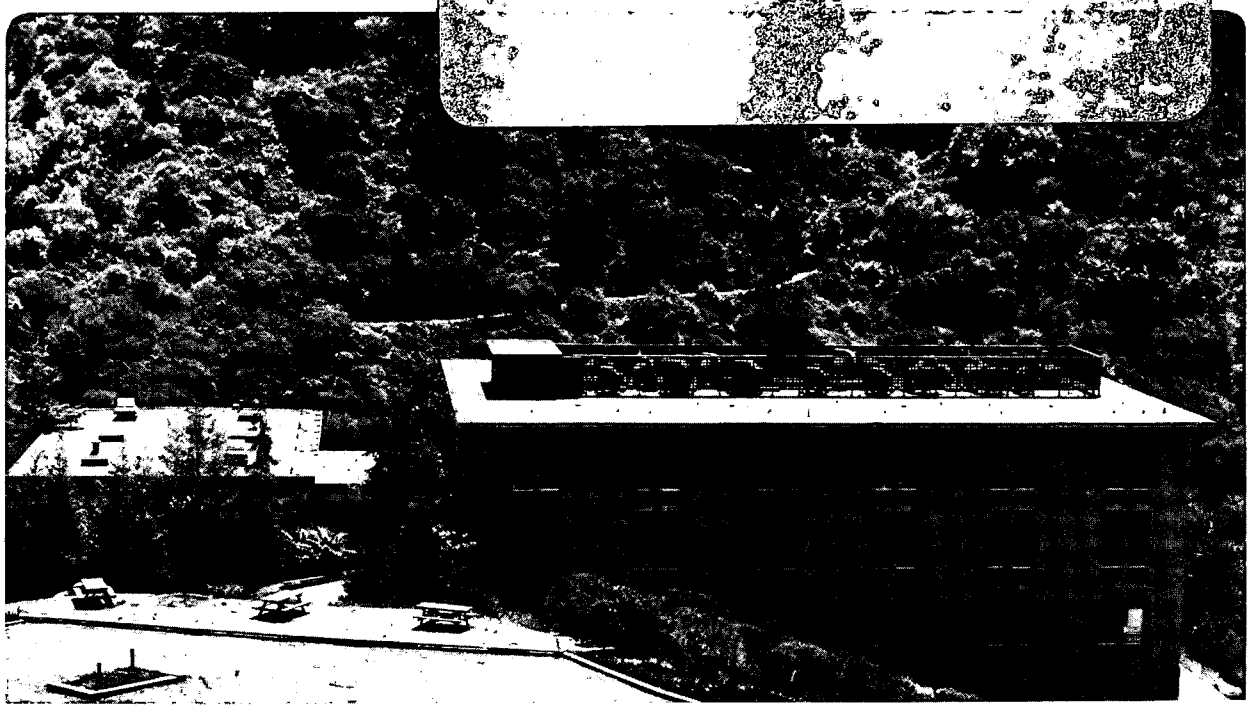

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ABSTRACT

Flinn's model of short-range order hardening in fcc binary solutions has been extended to take second-neighbor pair interactions into account. First and second-neighbor pair probabilities are evaluated in the Tetrahedron-Octahedron approximation of the cluster variation method as a function of concentration and temperature, and for various values of the ratio of pair interactions. Predictions of the present model are found to differ significantly from those of the Bragg-Williams model used heretofore.

1. INTRODUCTION

The idea that local order can contribute to the hardening of a solid solution was first proposed by Fisher [1] and its mathematical analysis was subsequently performed by Flinn [2]. These authors attributed the hardening effect, called short range order hardening (SROH), to the partial destruction of equilibrium short-range order across a slip plane due to a motion of a dislocation line. Flinn calculated the number of ordering pairs before and after a dislocation passage and estimated the hardening effect for a Cu_3Au crystal, finding the effect to be quite appreciable. Although the basic ideas of Fisher and Flinn were certainly valid, their pair interaction model should be reexamined in the light of modern treatments of local order. Such is the object of this paper.

It is important to specify what kind of atomic interactions stabilize the local order of the system. If multibody interactions are important, changes of multiatom atomic configurations associated with a dislocation slip should be taken into consideration in addition to changes due to pairs. Even if pair interactions are dominant, which pair interactions (first neighbor, second neighbor ...) should be involved in the estimation of the SROH is another important issue. In this study, we shall investigate the effects of first and second neighbor pair interactions in fcc solid solutions.

The reason for selecting these interactions is provided by ground state analysis of the fcc lattice [3-6]: rigorous results indicate that most experimentally observed fcc-based ordered structures (superstructures) can be stabilized by 1st and 2nd n.n. pair interactions only. In fact, eight stable

superstructures have been thus determined, the stability of each depending on the concentration and on the ratio α of 2nd to 1st n.n. pair interactions. In the light of these results, it can be reasonably assumed that the SROH of fcc solid solutions, whose ground states contain these ordered phases, can be evaluated by a 1st and 2nd n.n. pair interaction model. Since Flinn's original calculation was limited to 1st n.n. pair correlations, it is important to extend his analysis to include at least 2nd n.n. pair correlations.

The calculation of pair correlations depends largely on the thermodynamic model used. Flinn's calculation was based on the Bragg-Williams (BW) approximation which is the simplest one available and which is known as a single site approximation. In order to properly evaluate pair probabilities, however, it is indispensable to employ a more sophisticated model. In fact, the BW approximation does not provide correct results, except at high temperatures.

Recently, a more elaborate thermodynamic model has been developed, based on the Cluster Variation Method (CVM) [7]. The reliability and superiority of the CVM over the BW approximation have been amply demonstrated through phase diagram computations [8-12], and short range order diffuse intensity calcuations [13]. In particular, the Tetrahedron-Octahedron approximation of the CVM (T-O CVM) [8-13] yields ten kinds of correlation functions, including multisite correlations, in addition to 1st and 2nd n.n. pair correlations. With the T-O CVM, seven fcc-based prototype phase diagrams were constructed, with 1st and 2nd n.n. pair interactions covering the entire range of α values [8-12].

In the present study, we make use of the T-O CVM to calculate pair probabilities more accurately and to clarify the effect of 2nd n.n. pairs on

the SROH of an fcc solid solution. An outline of the calculation procedure is provided in the next section. Main emphasis is placed on the calculation of the change in energy due to dislocation motion in terms of pair probabilities. Since the CVM derivation of the equilibrium fraction of ordered pairs is not the main purpose of this study, the interested reader should refer to the authors' previous papers [8-12]. The main results are presented in the last section and the physical implications are discussed.

2. CALCULATION PROCEDURE

During glide of a dislocation with Burgers vector $\mathbf{b}=\frac{1}{2}a_0\langle 101\rangle$, ($a_0$ is the fcc lattice parameter), atomic bonds across a $\{111\}$ slip plane are broken and new ones created. The increment of energy per atom, ΔE, associated with the change of atomic bonding can be related to the SROH resolved shear stress τ in the following way [2]:

$$\tau = 4\,\frac{\sqrt{(2/3)}}{a_0^{\,3}}\,\Delta E \qquad (1)$$

This equation can be readily derived by converting ΔE to the energy increment per unit area on a slip plane and equatingthis to the work τb done by a moving dislocation. The dislocation could be dissociated, but the end effect of the passage of partials would be the same.

The calculation of ΔE has been performed in the following way. Consider 1st n.n. pairs; of the three neighborsof a given atom across a slip plane, one will be replaced by a 2nd n.n. atom, another by a different 1st n.n. and the third by a more distant one which is regarded as uncorrelated to the original

atom. Similarly, for 2nd n.n. pairs, among the three pairs across a slip plane, two of the three are randomized and the other is replaced by a 1st n.n. pair. For an atom at position a in Fig.1, the replacements of bonding pairs before and after slip are indicated in Table 1.

Then, by refering to the Table 1,one may write the increment of the energy per atom ΔE as •

$$\begin{aligned}\Delta E &= [(P_{AB}^{(2)} + P_{AB}^{(1)} + P_{AB}^{(r)}) - (3P_{AB}^{(1)})]v_1 \\ &\quad + [(2P_{AB}^{(r)} + P_{AB}^{(1)}) - 3P_{AB}^{(2)}]v_2 \\ &= (-2P_{AB}^{(1)} + P_{AB}^{(2)} + P_{AB}^{(r)})v_1 \\ &\quad + (P_{AB}^{(1)} - 3P_{AB}^{(2)} + 2P_{AB}^{(r)})v_2 \end{aligned} \tag{2}$$

where $P_{AB}^{(i)}$ (i=1,2) is the fraction of i-th AB pair in thermodynamic equilibrium, $P_{AB}^{(r)}$ is the fraction of AB pair in the random state, and v_i (i=1,2) is one-half the energy required to rearrange configurations so as to form two A-B bonds from one A-A bond and one B-B bond, which is one-half the negative i-th effective pair interaction energy $\varepsilon_{2,i}$ (i=1,2)

$$\varepsilon_{2,s} = -2v_s \tag{3}$$

The pair fractions $P_{AB}^{(i)}$ (i=1,2) and $P_{AB}^{(r)}$ are most conveniently described by correlation variables in the following way [8]:

$$\begin{aligned} P_{AB}^{(1)} &= x_{AB}^{(1)} + x_{BA}^{(1)} = 2\,\frac{1}{2^2}\,(1 - \xi_{2,1}) \\ P_{AB}^{(2)} &= x_{AB}^{(2)} + x_{BA}^{(2)} = 2\,\frac{1}{2^2}\,(1 - \xi_{2,2}) \\ P_{AB}^{(r)} &= x_{AB}^{(r)} + x_{BA}^{(r)} = 2\,\frac{1}{2^2}\,(1 - \xi_1^2) \end{aligned} \tag{4}$$

where $X_{AB}^{(i)}$ and $X_{BA}^{(i)}$ are, respectively, i-th A-B and B-A pair cluster probabilities, ξ_1 is a point correlation function and $\xi_{2,i}$ (i=1,2) are i-th pair correlation functions the rigorous definition of which can be found in previous publications [8]. Substitution of Eq.(4) into the Eq. (2) yields the final formula of ΔE:

$$\Delta E = \frac{1}{2}(2\xi_{2,1} - \xi_{2,2} - \xi_1^2)v_1 + \frac{1}{2}(-\xi_{2,1} + 3\xi_{2,2} - 2\xi_1^2)v_2$$

$$= \frac{1}{4}(-2\xi_{2,1} + \xi_{2,2} + \xi_1^2)\varepsilon_{2,1} + \frac{1}{4}(\xi_{2,1} - 3\xi_{2,2} + 2\xi_1^2)\varepsilon_{2,2} \qquad (5)$$

where α was previously defined as theratio of 2nd to 1st n.n. pair interaction energies. The equilibrium values of correlation functions ξ_1, $\xi_{2,1}$ and $\xi_{2,2}$ for a given concentration and temperature were calculated by the T-O CVM.

3. RESULTS AND DISCUSSION

The temperature dependence of SROH at composition c = 1/2 is shown in Fig. 2 in reduced coordinates: the ordinate represents the hardening effect given by ΔE normalized by the first pair interaction energy $\varepsilon_{2,1}$, and the abscissa is the reduced temperature normalized by the same parameter. The case α = 0.0 is the one that maybe compared directly to that treated by Flinn; it is seen that the curve ofSROH of the present analysis is consistently above that of Flinn's (dashed curve). This effect can be explained as follows: acccording to Flinn's model, two of the three 1st n.n. pairs across a slip plane are "randomized" after passage of a dislocation while the rest retain

their 1st n.n. pair correlation. According to the present model, however, as is indicated in Table 1, only one pair is randomized while the remaining two pairs retain their 1st and 2nd n.n. correlations. Because of the tendency of the solution (with $\alpha = 0$) to enhance 1st n.n. unlike pair concentrations, like 2nd n.n. pairs will predominate. Hence,the replacement of a 1st n.n. by a 2nd n.n. pair will tend to raise the energy compared to that resulting from randomization.

With $\alpha = -0.2$, the probability of finding like 2nd n.n. is further enhanced, and the resulting energy change ΔE is even more pronounced. On the contrary, with $\alpha = 0.35$ and 0.55, like 2nd n.n. pair probabilities are decreased, with resulting lowering of ΔE compared to the case of vanishing 2nd n.n. interaction. Curves in Fig. 2 may intersect because the temperature dependences of 1st and 2nd n.n. correlations differ from one another and from that predicted by the BW model.

The concentration dependence of SROH is illustrated in Fig. 3 (high temperature) and Fig. 4 (lower temperature). Again, the curves calculated from the TO-CVM model lie above those calculated by the BW model (dashed curves), for the reasons explained above. The degree of SRO vanishes at c=0 (pure solid) and reaches a maximum at c=1/2. Since concentration-independent pair interactions are used, the curves must be symmetric about the mid-concentration.

At the lower temperature ($k_BT/\epsilon_{2,1} = 1.320$), the SROH curves for $\alpha = 0.0$ and -0.2 are quite complicated-looking because, at this reduced temperature, the fcc solution orders into the $L1_2$ and $L1_0$ structures [12]. In Fig. 4, the portions of the corresponding curves for which the solid solution is the stable phase are shown as full lines. The portions shown dotted refer to a metastable solid solution. As pointed out elsewhere [12], whenever reliable

theoretical estimates of poperties are required, it is imperative to use a free energy model from which a topologically correct phase diagram can be constructed. The CVM provides such amodel, the BW, which Flinn used to derive his SROH curves, does not.

Recently, Buttner and Nemback [14] performed simultaneous measurements of critical resolved shear stress (CRSS) and short-range order (SRO) in polycrystalline Cu-10at.%Au solid solutions. These authors found no correlation of SROH with SRO, and concluded that Flinn's model overestimates the contribution of the destruction of SRO to CRSS by a factor of about 10. This conclusion was based on the observed0.9% scatter of the data for the CRSS in which the authors claim the SROH effect must lie buried. From these measurements, it does appear that the *variation* of SROH with SRO is much less than theoretically expected, but it does not necessarily follow that the *magnitude* of the influence of SRO on the CRSS is small. Actually, Buttner and Nemback offer no explanation for the rather large value of the CRSS in these partially ordered alloys.

Moreover, the measurements were made on low-concentration polycrystalline specimens at low temperature. The variation of the CRSS with degree of SRO would surely have been more apparent at higher concentrations, which would have necessitated deforming specimens in a single phase region at higher temperatures. Also, the degree of SRO was measured by the first Warren-Cowley parameter only.

Clearly, the simple models of SROH proposed by Flinn, and elaborated upon here, do not do justice to the complixities of the initiation of plastic flow in real materials posessing short-range order. Nevertheless, it was deemed important to present as accurate a picture as possible of the simple SROH mechanism, that offered by the TO-CVM, before proceeding with the

incorporation of other complicating factors.

4. SUMMARY

The T-O approximation of the CVM has been used to calculate first and second-neighbor pair probabilities in binary fcc solutions as a function of average concentration and temperature, and for various values of the ratio α of second to first neighbor pair interactions. The resulting short-range order hardening effect has been calculated and compared to earlier results of Flinn based on the Bragg-Williams approximation with first-neighbor pairs only. The inclusion of second-neighbor interactions and the use of a more accurate thermodynamic functional results in significant differences in the predictions of the two models. Good agreement between theoretical and experimental values of critical resolved shear stress is still an elusive goal, however.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Fig.1 Perspective view of a (111) slip plane of an fcc lattice and the atomic arrangement in its vicinity. Atom a is below the slip plane and atoms b.....j are above the slip plane.

Fig.2 Temperature dependence of the SROH at c=0.50 for different α values, α being defined as the ratio of 2nd to 1st n.n. pair interaction energies. Temperature axis is normalized by the first n.n. pair interaction energy $\epsilon_{2,1}$. The vertical axis is SROH (resolved shear stress) normalized by

$$4/(2/3)\ a_0^{-3}\ \epsilon_{2,1}.$$

Fig.3 Concentration dependence of SROH at $k_BT/\epsilon_{2,1} = 6.096$.

Fig.4 Concentration dependence of SROH at $k_BT/\epsilon_{2,1} = 1.320$. Dotted line indicates the ordered phase region in which SROH is no longer meaningful.

TABLE

Table 1. Changes of atomic pair configurations across a slip plane (Fig.1 should be referred to). The third column indicates the correlation with atom at position a. (Correlations beyond the second neighbor are assumed to vanish.) $P_{AB}^{(i)}$ is the fraction of i-th A-B atomic pair in a thermal equilibrium; $P_{AB}^{(r)}$ is the fraction of A-B pair in a random state.

	Original Bonding	after a slip		
		Bonding	corr.with a	incr. A-B pair
1st. n.n.	ab	ae	2nd. n.n.	$P_{AB}^{(2)} - P_{AB}^{(1)}$
	ac	ad	1st. n.n.	$P_{AB}^{(1)} - P_{AB}^{(1)}$
	ad	ah	random	$P_{AB}^{(r)} - P_{AB}^{(1)}$
2nd. n.n.	ae	ai	random	$P_{AB}^{(r)} - P_{AB}^{(2)}$
	af	ab	1st. n.n.	$P_{AB}^{(1)} - P_{AB}^{(2)}$
	ag	aj	random	$P_{AB}^{(r)} - P_{AB}^{(2)}$

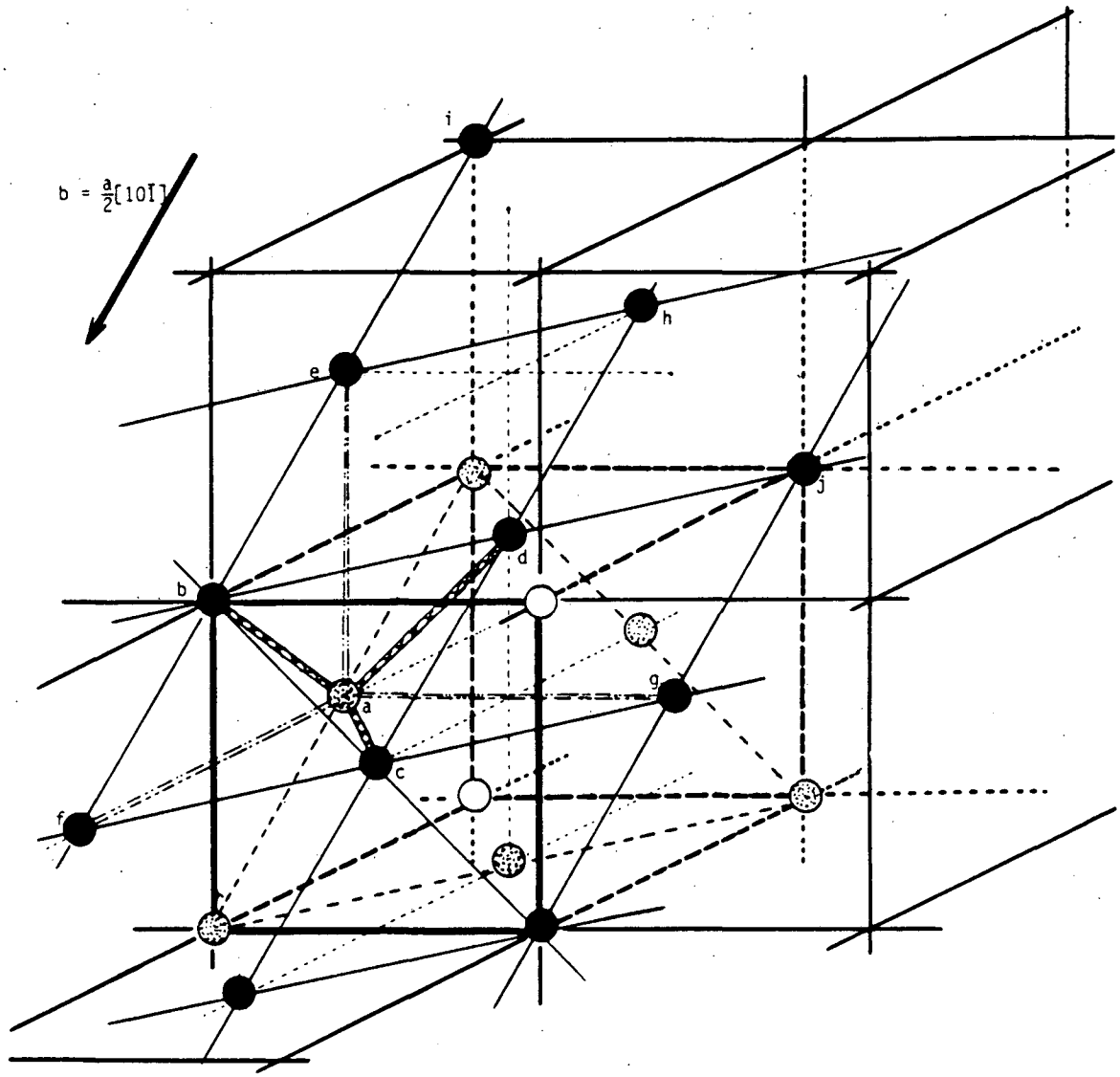

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Fig. 1

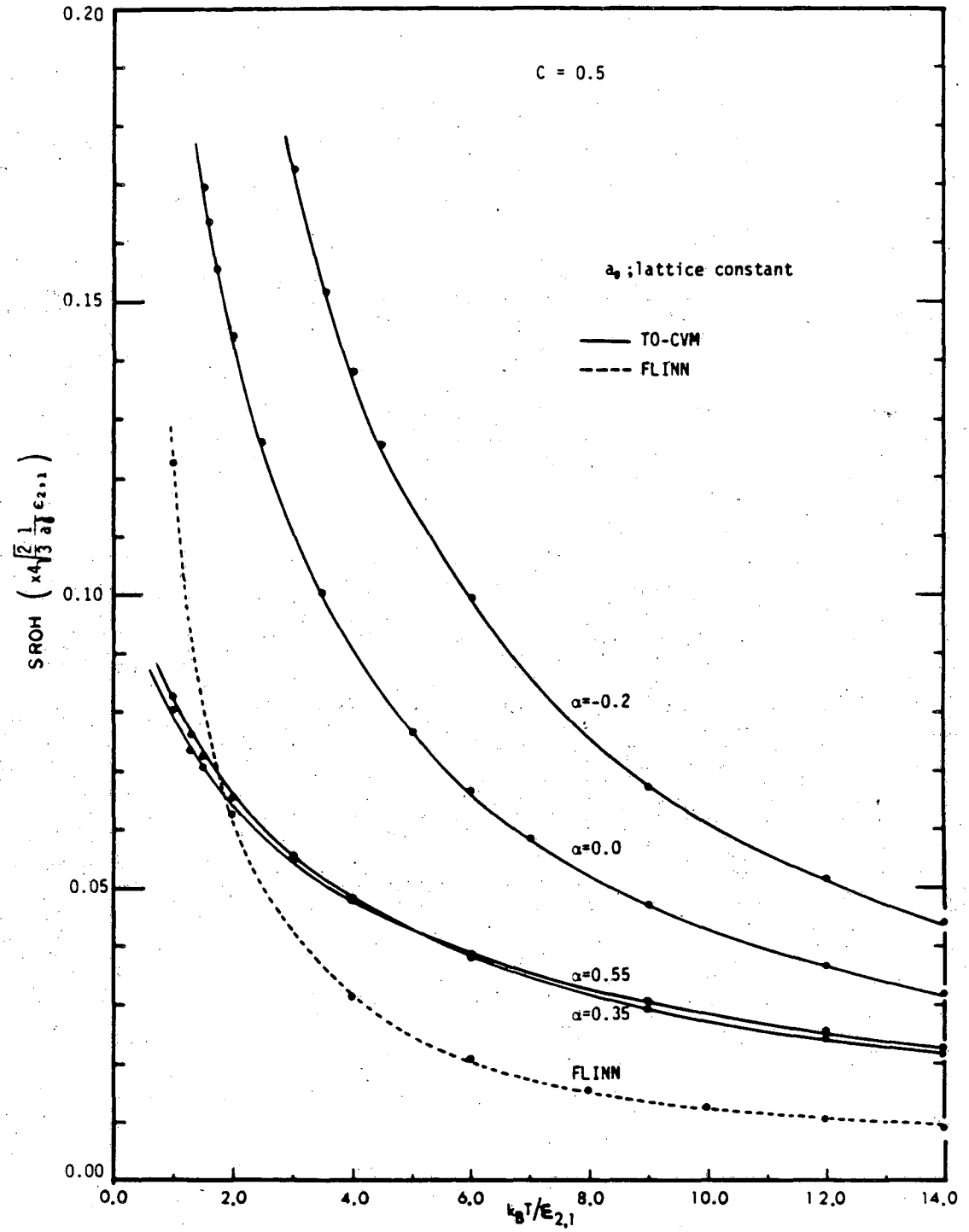

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Fig. 2

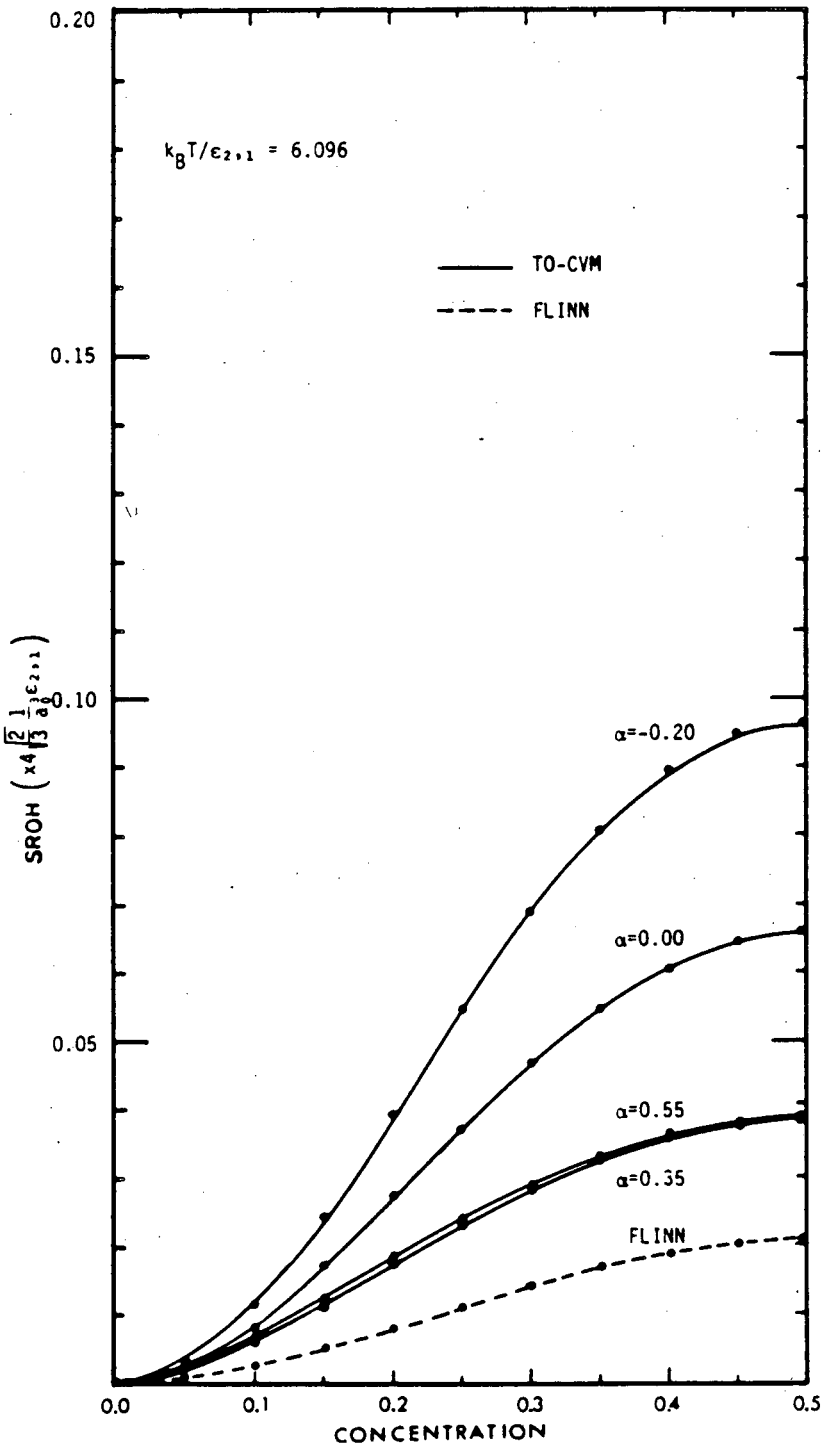

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Fig. 3

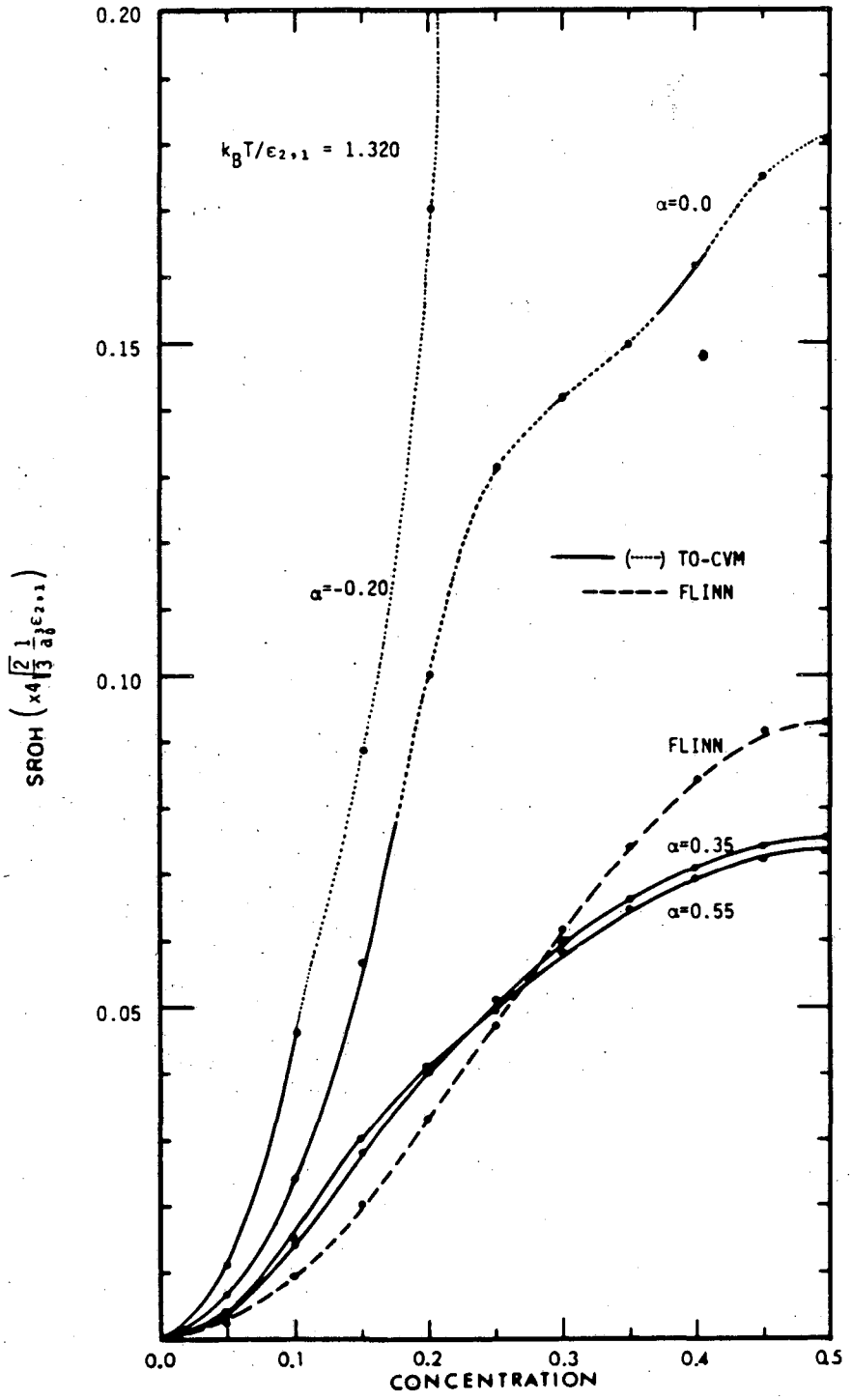

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Fig. 4

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