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THE STRAIN ENERGY OF A DISK-SHAPED GP ZONE

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ABSTRACT

A simplified form of Khachaturyan's solution to the problem of determining the strain energy of an arbitrarily-shaped coherent inclusion is found for the case of a disk-shaped inclusion. Specific strain energies are calculated as a function of the orientation of such an inclusion in lattices possessing various elastic properties. Some numerical results are presented. The salient features of the specific strain energy surface are found to depend only on the elastic properties of the lattice. From this, a relationship between an elastic anisotropy parameter, A, and the minimum strain energy orientation of a disk-shaped inclusion is observed. The strain energies of GP zones in Al-Cu and Cu-Be age hardening alloys are calculated. The minimum strain energy orientations of GP zones in these alloys agree with experimentally observed orientations.

1. INTRODUCTION

The clusters of solute atoms that often form during the first stage of solid solution decomposition in age hardening alloys are usually referred to as Guinier-Preston (GP) zones. GP zones are coherent with the surrounding matrix phase, thus any difference in atomic spacing between the precipitate and matrix phases results in coherency strain fields around the clusters. The strain field of each precipitate has an associated strain energy (self strain energy) and, in addition, the interactions of the strain fields of nearby clusters involve interaction strain energies. In general, the strain energy as well as any additional energy associated with the precipitate-matrix interface depend on the configuration (shape and orientation) of the precipitate whereas the bulk free energy change is configuration independent. GP zones are thus expected to form preferentially in configurations which minimize a combination of strain and interfacial energies, thereby minimizing the free energy of the clusters.

The self strain energy of an inclusion has been shown to depend on the shape of the inclusion both in the case where the precipitate-matrix interface is incoherent[1,2] and when it is coherent.[3] In addition, periodic arrays of coherent precipitates have been shown[4-9] to be energetically preferred over a random distribution owing to the interaction of the strain fields of the precipitates. The dependence of the self strain energy of nonspherical coherent precipitates on their orientation in an elastically anisotropic matrix has been examined by Schwellinger, Leamy and Warlimont[10] in the special case of two-dimensionally infinite misfitting precipitate sheets. Their analysis, however,

treated a nonequilibrium problem since strains were confined to the precipitate phase. The purpose of this study was to examine the anisotropy of the strain energy associated with disk-shaped inclusions of finite extent.

For calculation of the self strain energy of a coherent inclusion, several approaches are available. Eshelby[11] obtained a solution in terms of tabulated elliptic integrals for the case of an ellipsoidal inclusion in an isotropic elastic medium. This solution was subsequently extended to anisotropic media by Walpole.[12] A solution to the general case of an arbitrarily shaped coherent inclusion in an elastic medium of arbitrary anisotropy has been found by Khachaturyan.[13]

Presented here are the results of a study of the self strain energies associated with disk-shaped GP zones using Khachaturyan's solution. Strain energies were calculated as a function of the orientation of a disk-shaped coherent inclusion in various materials. The relationship between the minimum energy orientations and the elastic anisotropy of the matrix phase found by Schwellinger et al[10] is extended to the more general case of a coherent precipitate of finite extent in elastic equilibrium with the matrix phase.

2. THEORETICAL CONSIDERATIONS

2.1 Khachaturyan's Solution

Khachaturyan[13] obtained a solution of the general problem of determining the elastic strain energy of a new-phase coherent inclusion of arbitrary shape in an elastic medium of arbitrary anisotropy. The assumptions inherent in this solution require that the inclusion be isolated in an infinite elastic medium and that the elastic properties of the inclusion be identical with those of the surrounding matrix. The latter is equivalent to the assumption that the modulus effect is small with respect to the size effect.

Of primary importance in Khachaturyan's solution of this strain energy problem is a tensor which shall be referred to as the "free state strain tensor." Consider the volume which is to undergo transformation. Suppose it is removed from the elastic medium and allowed to transform free of the constraints normally imposed on it by this medium. The strains corresponding to the deformations it undergoes as it transforms in the absence of mechanical constraints define the matrix elements of the free state strain tensor.

Khachaturyan's solution to the problem may be expressed in the following form

$$E = \frac{1}{2} \lambda_{ijlm} \epsilon^{o}_{ij} \epsilon^{o}_{lm} V_T - \frac{1}{2} \int \frac{d^3\underset{\sim}{k}}{(2\pi)^3} |\theta(\underset{\sim}{k})|^2 A\left(\frac{\underset{\sim}{k}}{k}\right) \tag{1}$$

where E is the strain energy of the coherent inclusion, λ_{ijlm} is the elastic modulus tensor, ϵ^{o}_{ij} is the free state strain tensor, V_T is the volume which undergoes transformation and $\theta(\underset{\sim}{k})$ are the Fourier components

of $\theta(\underset{\sim}{r})$, the form function ($\theta(\underset{\sim}{r})$ being equal to zero outside the inclusion and unity inside it). $A\left(\frac{\underset{\sim}{k}}{k}\right)$ is defined by the following equation

$$A\left(\frac{\underset{\sim}{k}}{k}\right) = \left(\hat{\sigma}^{o}\,\underset{\sim}{k},\ \hat{G}^{-1}\hat{\sigma}^{o}\underset{\sim}{k}\right)$$

where (...,...) is the scalar vector product and $\hat{G}^{-1}$ is the reciprocal of the Green's function of the elastic equilibrium equations. The matrix elements of the operator $\hat{\sigma}^{o}$ are determined by the following relationship

$$[\hat{\sigma}^{o}]^{ij} + \lambda_{ijlm}\,\epsilon^{o}_{lm} = 0\ .$$

Finally, the matrix elements of the operator $\hat{G}^{-1}$ are defined by the equations

$$[\hat{G}]^{ij} = \lambda_{ijlm}\,k_l k_m$$

and

$$\hat{G}^{-1}\hat{G} = \hat{1}$$

where $[\hat{1}]^{ij} = \delta_{ij}$. In all of the above equations (and throughout this paper) summation over repeated indices is implied.

While the solution to this problem exists in principle, evaluation of equation (1) in the general case is difficult. A simplified expression may be obtained, however, for the special case of a disk-shaped inclusion.

2.2 Strain Energy of Disk-Shaped Inclusions

Consider the Fourier components of the form function in the case of a disk-shaped inclusion. The only non-zero components lie in a direction very nearly parallel to the normal vector of the disk. Thus, as was observed by Khachaturyan,[13] only $\underset{\sim}{k}$ vectors which are nearly parallel to

this normal vector will contribute significantly to the integral in equation (1). As is indicated by the functional form, the quantity $A(\frac{\underset{\sim}{k}}{k})$ is dependent only on the direction of $\underset{\sim}{k}$, not on its magnitude. Thus, if $A(\frac{\underset{\sim}{k}}{k})$ is a smooth and slowly varying function of $(\frac{\underset{\sim}{k}}{k})$, only a slight approximation will be incurred by replacing $A(\frac{\underset{\sim}{k}}{k})$ with $A(\underset{\sim}{n})$, where $\underset{\sim}{n}$ is a unit vector normal to the plane of the inclusion. $A(\underset{\sim}{n})$ being constant, it may be removed from the integral and the elastic energy of the disk-shaped inclusion may be re-expressed as

$$E \simeq \frac{1}{2} \lambda_{ijlm} \epsilon^{o}_{ij} \epsilon^{o}_{lm} V_T - \frac{A(\underset{\sim}{n})}{2} \int \frac{d^3\underset{\sim}{k}}{(2\pi)^3} |\theta(\underset{\sim}{k})|^2 .$$

This may be further simplified by making use of the identity

$$V_T = \int \frac{d^3\underset{\sim}{k}}{(2\pi)^3} |\theta(\underset{\sim}{k})|^2 .$$

Thus, in the case of a disk-shaped inclusion, Khachaturyan re-expressed equation (1) in the much simplified form

$$E \simeq \frac{V_T}{2} \left\{ \lambda_{ijlm} \epsilon^{o}_{ij} \epsilon^{o}_{lm} - A(\underset{\sim}{n}) \right\} . \qquad (2)$$

Numerical evaluation techniques were used to show that $A(\frac{\underset{\sim}{k}}{k})$ is, in fact, a smooth slowly varying function of $\frac{\underset{\sim}{k}}{k}$ so that the error introduced by the above approximation is small.

2.3 Evaluation of Calculational Parameters

From equation (2) it is immediately obvious that the strain energy of a disk-shaped coherent precipitate is directly proportional to the volume of the precipitate prior to transformation, V_T. Thus, the parameter of interest is the specific strain energy of the precipitate, $\frac{E}{V_T}$, which shall be donoted ε_V. The parameters required for calculation of ε_V for a GP zone in a cubic lattice are three independent elastic constants (C_{11}, C_{12} and C_{44}), the matrix elements of the free state strain tensor, and two parameters characterizing the orientation of the disk in the lattice. To see how these parameters are related to measurable quantities, consideration of a model of disk-shaped GP zones in binary alloys is necessary.

X-ray studies[14] and, more recently, high resolution electron microscopy[15,16] have suggested that the model proposed by Gerold[17] best describes the nature of GP zones in Al-Cu and Cu-Be alloys. This model, originally describing the GP zones which form in Al-Cu age hardening alloys, assumes that they are composed of a monolayer of Cu atoms in a matrix of nearly pure Al. Assuming that Gerold's model may be employed to describe GP zones in all binary alloys, the parameters required for the calculation of ε_V may be evaluated as follows for the case of a supersaturated solution of B in A.

The matrix surrounding a fully grown cluster is nearly pure A and it may be assumed that the residual concentration of B has only a slight effect on the elastic properties of the A matrix. The most readily accessible elastic constants appropriate to this case are therefore those of pure A.

Prior to transformation, the disk-shaped volume to be transformed contains a more or less random A-B solution. After the GP zone has formed, the volume contains pure B. In the unconstrained state, deformations must occur in the plane of the disk to change the lattice parameter from that of the A-B solid solution to that appropriate to a monolayer of B. Denote the strain corresponding to free state deformations in the plane of the disk ϵ_p. Similar deformations may be imagined in the direction normal to the precipitate disk. The strain coresponding to this deformation is denoted ϵ_n.

The free state strain tensor for a GP zone lying in the (001) matrix plane is easily seen to have the following matrix elements

$$\left(\epsilon^{o}_{ij}\right)_{001} = \begin{pmatrix} \epsilon_p & 0 & 0 \\ 0 & \epsilon_p & 0 \\ 0 & 0 & \epsilon_n \end{pmatrix} . \tag{3}$$

Assuming that the values of the transformation parameters (ϵ_p and ϵ_n) are isotropic, the free state strain tensor for a GP zone in any orientation may be easily obtained using coordinate transformation techniques. Thus, there remains only the evaluation of the transformation parameters ϵ_p and ϵ_n.

Lattice parameter measurements, traditionally used to determine atomic misfits, may not be used directly in this case since the crystal structure of the A-B solid solution and pure B are not necessarily the same. If the transformation parameters assumed to be isotropic, the cube root of the volume per atom, L_v, may be used as a measure of atomic size as well as the efficiency of atomic packing. The change in L_v from

an A-B random solution to pure B is a measure of the free state deformation which must occur in the plane of the disk during the transformation. The strain, ϵ_p, corresponding to this deformation is

$$\epsilon_p = \frac{L_v(B) - L_v(A\text{-}B)}{L_v(A\text{-}B)}$$

Along the axis normal to the plane of the precipitate disk one might reasonably suppose that after the transformation, L_v would be similar to that of a solid solution containing A and B in equal concentrations. The value of L_v for such a solid solution may be obtained by extrapolation of measured lattice parameters. The strain, ϵ_n, along the direction normal to the plane of the disk is thus given by

$$\epsilon_n = \frac{L_v\ (\text{extrapolated AB}) - L_v\ (A\text{-}B)}{L_v(A\text{-}B)}$$

In cases where the crystal structures of the A-B solid solution and pure B are the same, this method is equivalent to direct use of lattice parameter measurements.

3. RESULTS OF STRAIN ENERGY CALCULATIONS

3.1 Dependence of the Specific Strain Energy on Elastic Properties

Calculations from lattice parameter measurements[18] for a variety of age hardening alloy systems in which disk-shaped GP zones form have shown that the absolute values of ϵ_p and ϵ_n generally fall between 0.04 and 0.15. In addition, the value of ϵ_n is usually somewhat smaller than than that of ϵ_p. For investigation of the dependence of the specific strain energy on the elastic properties of the matrix, the typical values $\epsilon_p = 0.10$ and $\epsilon_n = 0.07$ will be used. All calculations referred to in this section employed these values of ϵ_p and ϵ_n.

The specific strain energy was calculated as a function of GP zone orientation using the elastic constants corresponding to several different metals. It is not suggested that disk-shaped GP zones are observed in alloys based on all these metals, they have been used for comparison purposes only. Some of the results are plotted in Figures 1, 2 and 3. In these plots, the direction associated with the radial vector is parallel to the GP zone normal and the magnitude is proportional to ε_v for that orientation. These radial plots are planar profiles of the specific strain energy surface of a GP zone in the particular elastic medium.

Many profiles of the specific strain energy surface were investigated for the case of a GP zone in an Fe (bcc) lattice. The elastic constants corresponding to Fe are given in Table 1. Figure 1 shows the variation of the specific strain energy upon rotation of the normal vector of a GP zone in the (100) lattice plane. Owing to the four-fold symmetry of the (100) plane, the plot is symmetric about the [011] axis. Figure 2 is also an ε_v surface profile for an Fe lattice. In this case the GP zone normal

has been confined to the $(1\bar{1}0)$ lattice plane. As a result of this study of the ε_v surface for a GP zone in an Fe lattice, it was found that the GP zone orientations with the normal vector parallel to a <100> direction correspond to minimum values of ε_v, saddle points are associated with the <110> orientations and the <111> orientations correspond to maxima on the specific strain energy surface.

The effect of a change in the elastic constants on the specific strain energy surface can be seen by comparing Figures 2 and 3. Figure 3 is a plot of the same rotation plane as Figure 2, however, the elastic constants have been changed to those corresponding to Nb (see Table 1). As before, the <100> , <110> and <111> orientations correspond to extrema on the specific strain energy surface. The roles of the <100> and <111> orientations, however, are clearly reversed when the elastic constants of Fe are replaced by those of Nb.

Table 1 summarizes the results of calculations involving the elastic constants of a number of metals but retaining the same values of ϵ_p and ϵ_n. In all cases it was found that the <100> , <110> and <111> orientations correspond to extrema on the specific strain energy surface. The values of ε_v for these orientations thus characterize the surface and they are presented in Table 1. Perhaps the most significant general feature of this table is the relationship between the elastic anisotropy parameter A, defined as

$$A = \frac{2C_{44}}{C_{11}-C_{12}},$$

and the orientation corresponding to the minimum specific strain energy.

Table 1. Numerical results for the critical orientations with fixed values of ϵ_p and ϵ_n.

Element & Reference	Elastic Constants 10^{11} dynes/cm^2			A	Specific Strain Energy for Indicated Orientation 10^2 eV/A^3			Strain Energy Ratios	
	C_{11}	C_{12}	C_{44}		<100>	<110>	<111>	$\frac{\mathcal{E}_v<110>}{\mathcal{E}_v<100>}$	$\frac{\mathcal{E}_v<111>}{\mathcal{E}_v<100>}$
Cu (19)	16.84	12.14	7.54	3.21	0.716	1.455	1.629	2.031	2.274
Ag (19)	12.4	9.34	4.61	3.01	0.479	0.962	1.084	2.010	2.264
Au (19)	18.6	15.7	4.20	2.90	0.487	1.027	1.177	2.110	2.420
Ni (19)	24.65	14.73	12.47	2.51	1.359	2.225	2.430	1.637	1.788
Fe (20)	23.7	14.1	11.6	2.42	1.312	2.103	2.294	1.603	1.748
Al (21)	10.82	6.13	2.85	1.22	0.624	0.693	0.714	1.110	1.144
W (19)	50.1	15.14	19.8	1.13	3.501	3.679	3.735	1.051	1.067
I_1 *	24.0	10.0	7.0	1.00	1.602	1.602	1.602	1.000	1.000
I_2 *	20.0	12.0	4.0	1.00	1.099	1.099	1.099	1.000	1.000
Mo (19)	46.0	17.6	11.0	0.775	3.129	2.795	2.672	0.893	0.854
Cr (22)	35.0	6.78	10.08	0.714	2.44	2.17	2.06	0.889	0.844
Nb (23)	24.6	13.4	2.87	0.813	1.461	1.042	0.879	0.714	0.602

*I_1 and I_2 are two hypothetical isotropic materials with cubic lattices.

For the particular values of ϵ_p and ϵ_n used in these calculations, the <100> orientations are minima when A > 1 and the <111> orientations are minima for A < 1. This is the same relationship found by Schwellinger et al[10] in their study of two-dimensionally infinite misfitting sheets. For the purposes of this paper, however, it is not yet a general statement since the shape of the specific strain energy surface may also depend on the values of the transformation parameters.

3.2 Dependence of the Strain Energy on the Transformation Parameters

That ε_v for a particular orientation must depend on the transformation parameters if evident from the limiting case. As ϵ_p and ϵ_n go to zero, ε_v must also go to zero. For all sets of elastic constants listed in Table 1, however, it has been found that the ratios ε_v <110> / ε_v <100> and ε_v <111> / ϵ_v <100> are independent of the values of the parameters ϵ_p and ϵ_n. This is significant because it shows, for all the cases in Table 1, that the salient features of the specific strain energy surface are independent of the parameters characterizing the transformation. For these cases the shape of the ε_v surface depends only on the elastic properties of the matrix phase.

4. DISCUSSION

4.1 Relationship between Minimum Energy Orientations and Elastic Anisotropy

In the previous section it was observed that for all cases listed in Table 1, the shape of the specific strain energy surface is independent of the transformation parameters ϵ_p and ϵ_n. Since the <111> or <100> orientations correspond to the minimum value of ε_v in all cases investigated, the ratio ε_v <111> / ε_v <100> reflects an essential feature of the surface. Figure 4 is a plot of this ratio vs the anisotropy parameter A. Inferring from Figure 4 that this approximate linear relationship is valid in all cases, one observes that for A > 1 the ratio ε_v <111> / ε_v <001> is also greater than one, implying that the <001> orientations are minima on the ε_v surface. For A <1 this ratio is less than one so that the <111> orientations correspond to minima on the ε_v surface. This linear relationship is valid for any disk-shaped coherent inclusion provided that the free state strain tensor has the form of (3). In cases where the interfacial and interaction energies are isotropic (or where the self strain energy is the dominant term), disk-shaped GP zones will form preferentially on the <100> planes if A > 1 and the <111> planes if A < 1. Simple calculations for GP zones of typical size indicate, however, that the anisotropy of the interfacial energy would also be important if the interfacial energy density exceeded a few hundred ergs/cm^2.

4.2 The Case for Al-Cu

The Al-Cu binary alloys are the basis of many technologically important alloys meriting special consideration of this case. The elastic constants of Al are given in Table 1 and the transformation parameters computed from lattice parameter measurements[18] are $\epsilon_p = 0.108$ and $\epsilon_n = 0.0595$.

Vigier et al[24] report that the GP zones in an Al-1.74 $^a/o$ Cu alloy have diameter of about 80 A and the pre-transformation thickness of a monolayer may be taken as half of an Al lattice parameter, about 2 A.

A plot of the variation of the strain energy for a GP zone of the above dimensions with the normal vector confined to the $(1\bar{1}0)$ plane is shown in Figure 5. The <100> orientations correspond to the minimum strain energy which is the observed GP zone orientation in Al-Cu alloys.[25] In Figure 5 the minima are broad and shallow (A being only slightly greater than one) and from this, one might expect some variation in the observed orientation of the GP zones. Since no variation is observed, one could speculate that interfacial energies or strain field interactions might be important in this case.

In Al-1.74 $^a/o$ Cu alloys, GP zone densities of the order of 5×10^{17} cm^{-3} are commonly observed.[25] Assuming that all of the GP zones are in (or very near to) the minimum strain energy orientation and ignoring interactions between strain fields, the strain energy associated with the GP zones in this alloy is 8.6 cal per mole alloy.

4.3 The Case for Cu-Be

Similar calculations may be made for another important alloy in which disk-shaped GP zones are observed, Cu-Be. The elastic constants for Cu are given in Table 1 and values of ϵ_p and ϵ_n calculated from lattice parameter measurements[18] are -0.118 and -0.0433, respectively. For a Cu-12.37 $^a/o$ be alloy,[16] the observed GP zone diameter is about 60 A and the thickness is taken as one half a Cu lattice spacing, 1.85 A.

A plot of the variation of the strain energy when a GP zone normal is confined to the $(1\bar{1}0)$ plane is shown in Figure 6. Again the minimum strain energy orientation is <100> which corresponds to the observed GP zone orientation in this alloy.[25] Comparison of Figures 5 and 6 re-emphasizes the dependence of the shape of the strain energy surface on the anisotropy parameter A. Unlike the case for Al-Cu, the minima in Figure 6 are fairly sharp and deep so one would expect other factors to be less necessary in surpressing variations in the observed GP zone orientations in this alloy.

5. CONCLUSIONS

1. An approximate expression for the specific strain energy of an isolated disk-shaped inclusion is obtained from Khachaturyan's solution to the general problem. Numerical results are presented for a number of metallic elements with varying elastic properties.

2. It is found that the shape of the specific strain energy surface is independent of the transformation parameters ϵ_p and ϵ_n.

3. The relationship between the anisotropy parameter A and the GP zone orientation of minimum strain energy proposed by Schwellinger et al[10] also found for the case of finite disk-shaped precipitates. An approximate linear relationship between the ratio of the strain energies for the <111> and <100> orientations and the anisotropy parameter A is observed.

4. Profiles of strain energy surfaces are presented for Al-Cu and Cu-Be alloys. The minimum energy orientations agree with the experimentally observed GP zone orientations in these alloys.

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FIGURE CAPTIONS

Figure 1. Variation of the specific strain energy of a GP zone in an Fe lattice where the normal vector has been confined to the (100) plane.

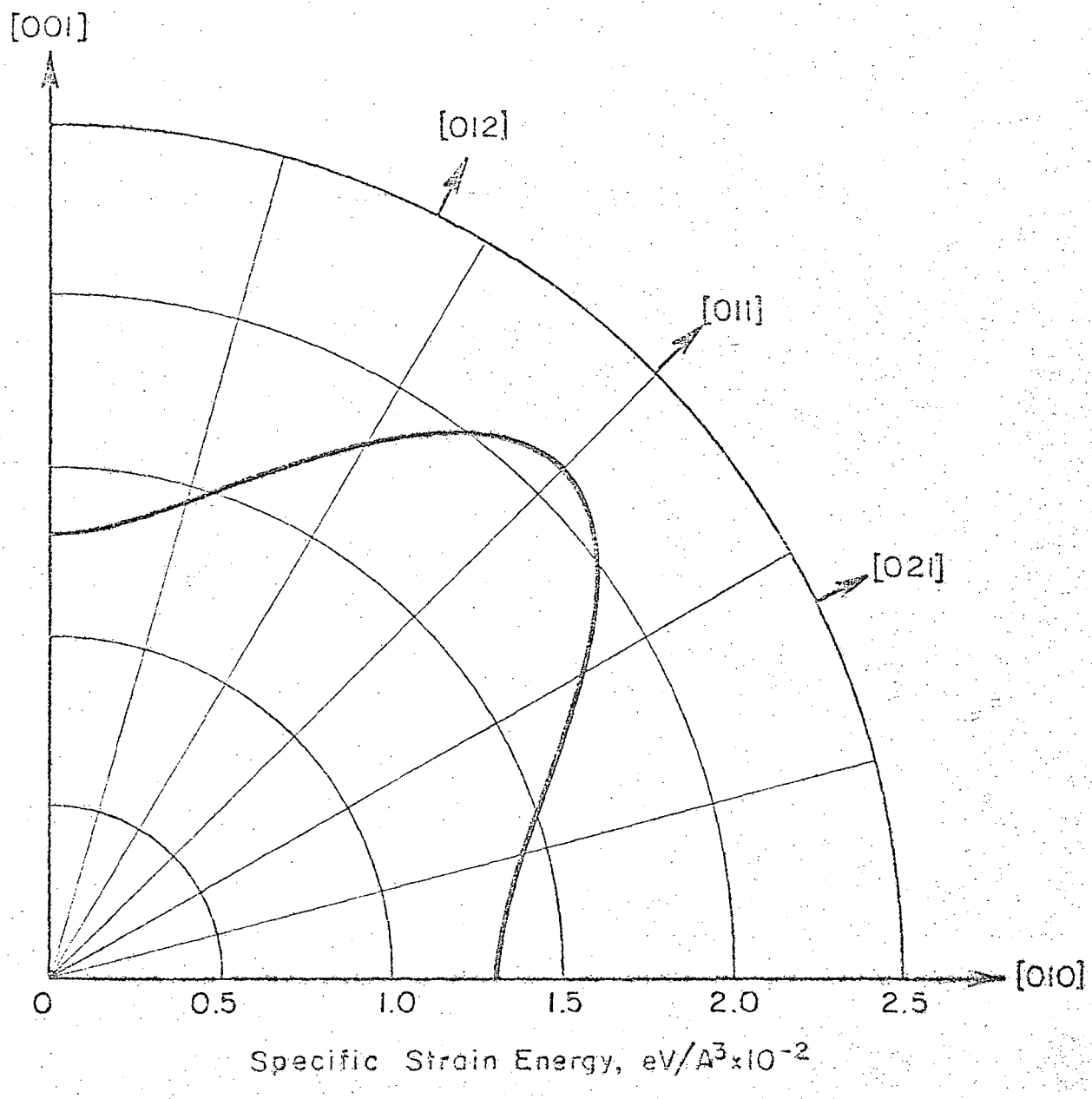
Figure 2. Variation of the specific strain energy of a GP zone in an Fe lattice where the normal vector has been confined to the $(1\bar{1}0)$ plane.

Figure 3. Variation of the specific strain energy of a GP zone in an Nb lattice where the normal vector has been confined to the $(1\bar{1}0)$ plane.

Figure 4. The relationship between the ratio ε_v <111> / ε_v <100> and the elastic anisotropy parameter A.

Figure 5. Variation of the strain energy of a GP zone in a Al-Cu alloy where the normal vector has been confined to the $(1\bar{1}0)$ plane.

Figure 6. Variation of the strain energy of a GP zone in a Cu-Be alloy where the normal vector has been confined to the $(1\bar{1}0)$ plane.



XBL 749-7327

Fig. 1.

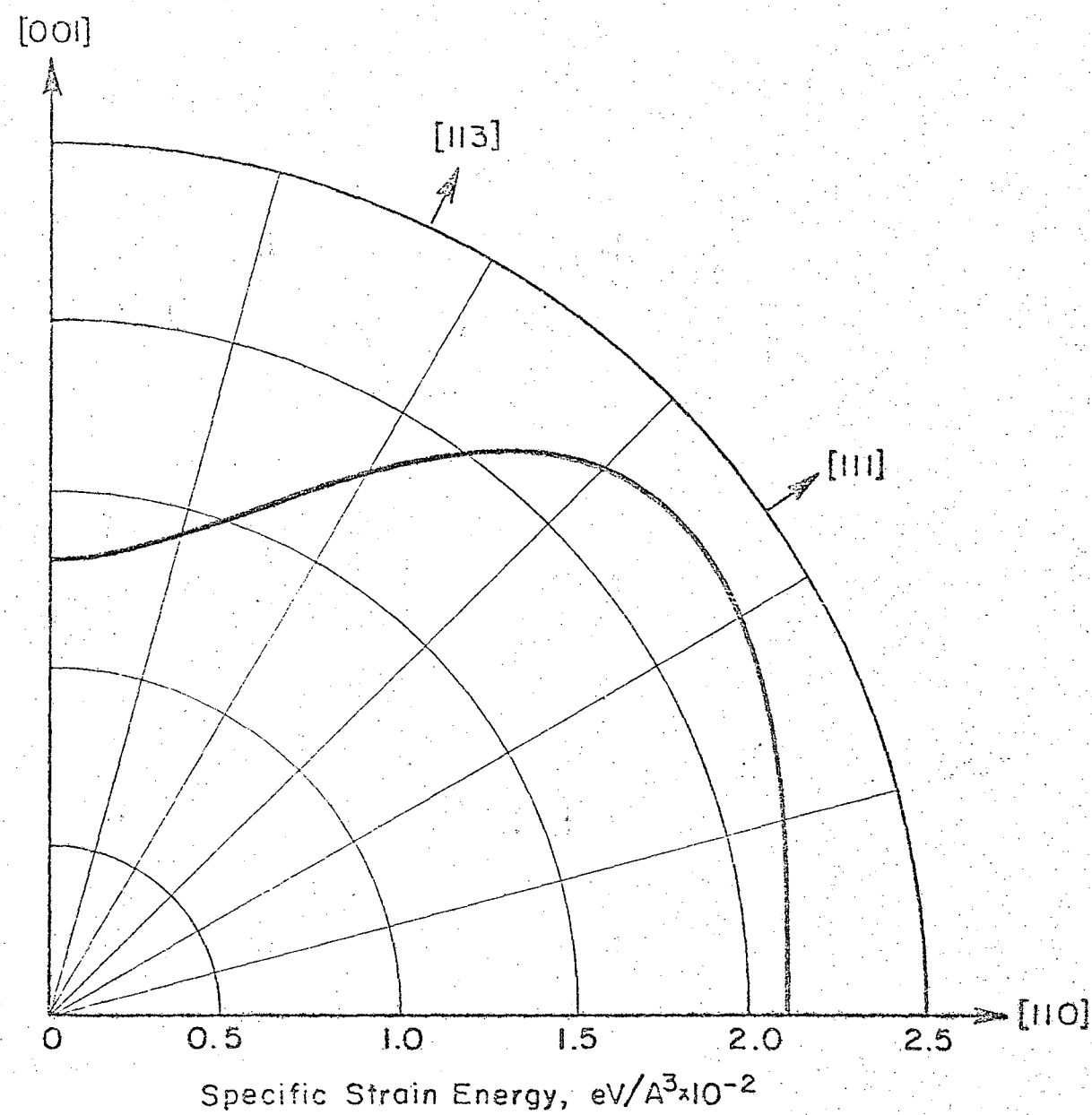


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Fig. 2.

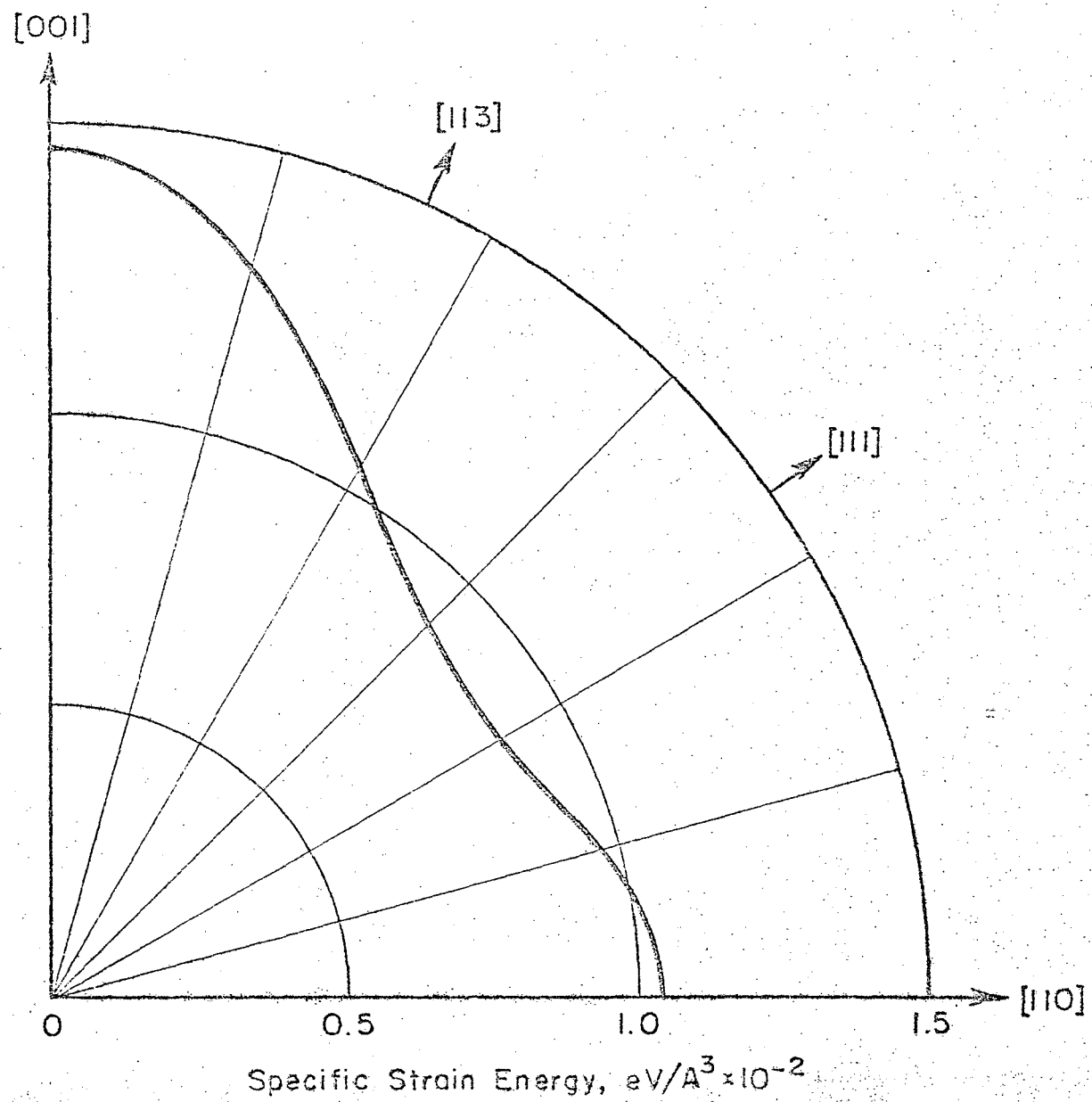

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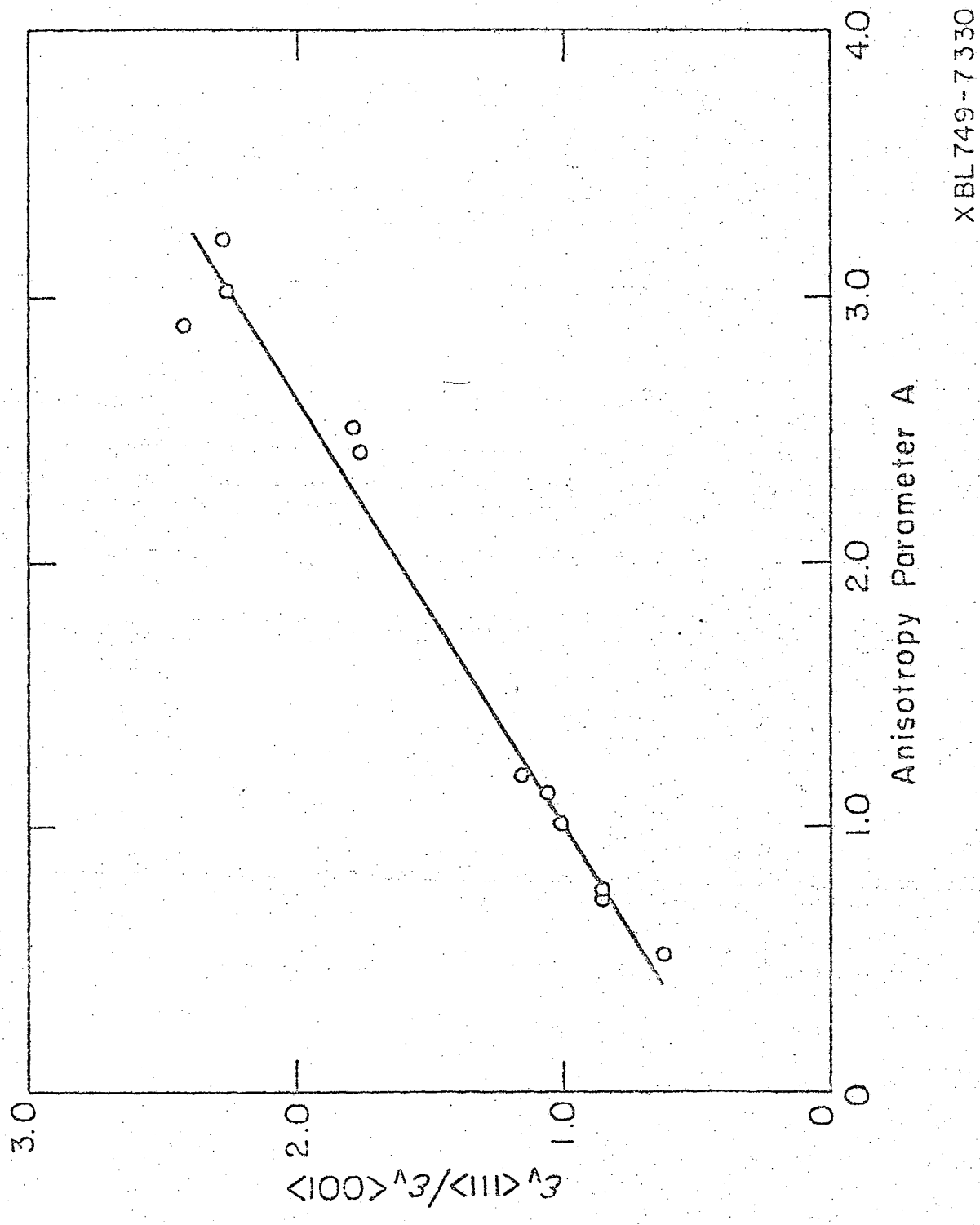
Fig. 3.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2.0
1.0
0
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0
1.0
2.0
3.0
4.0
Anisotropy Parameter A
XBL 749-7330

Fig. 4.

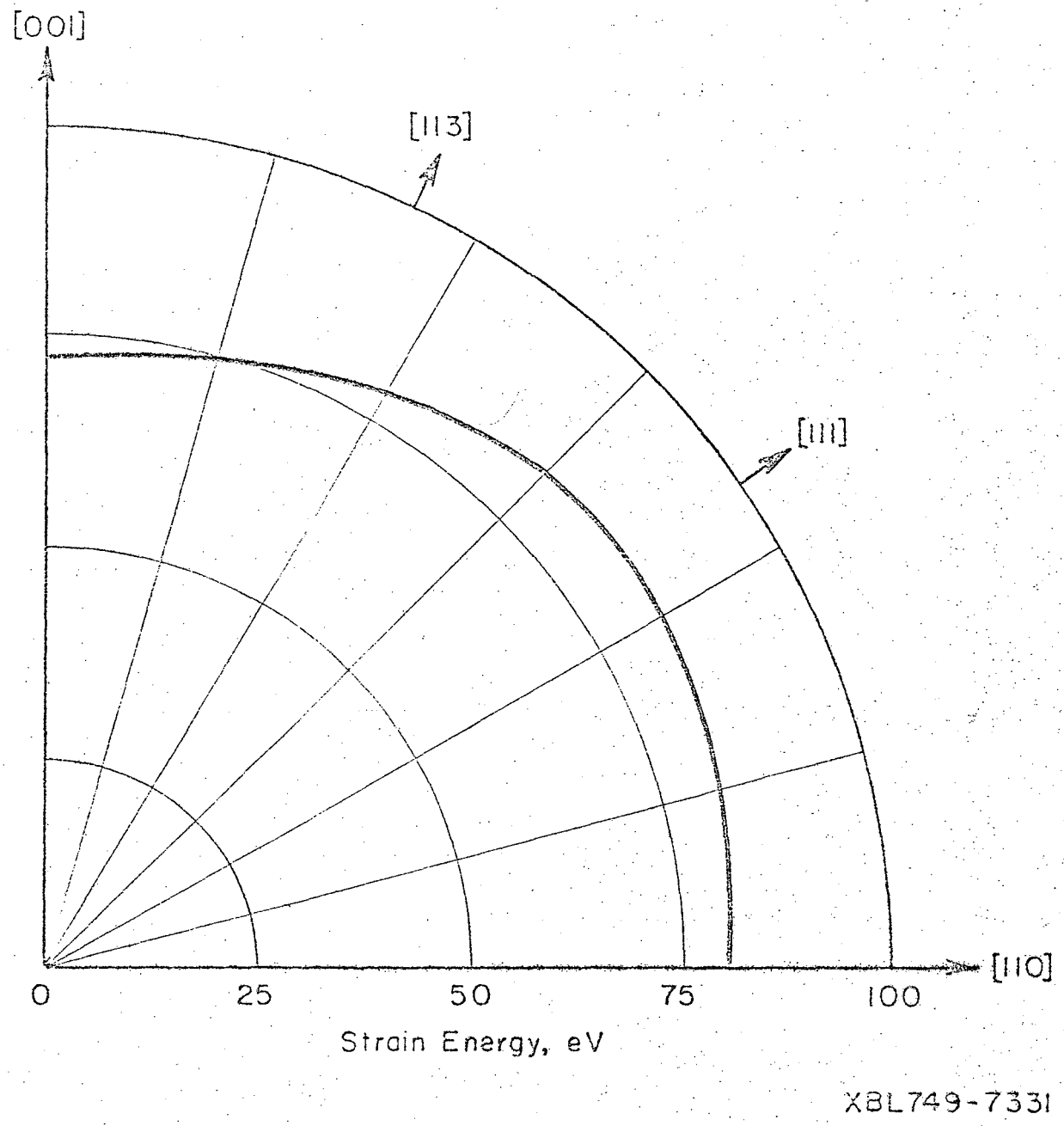

Fig. 5.

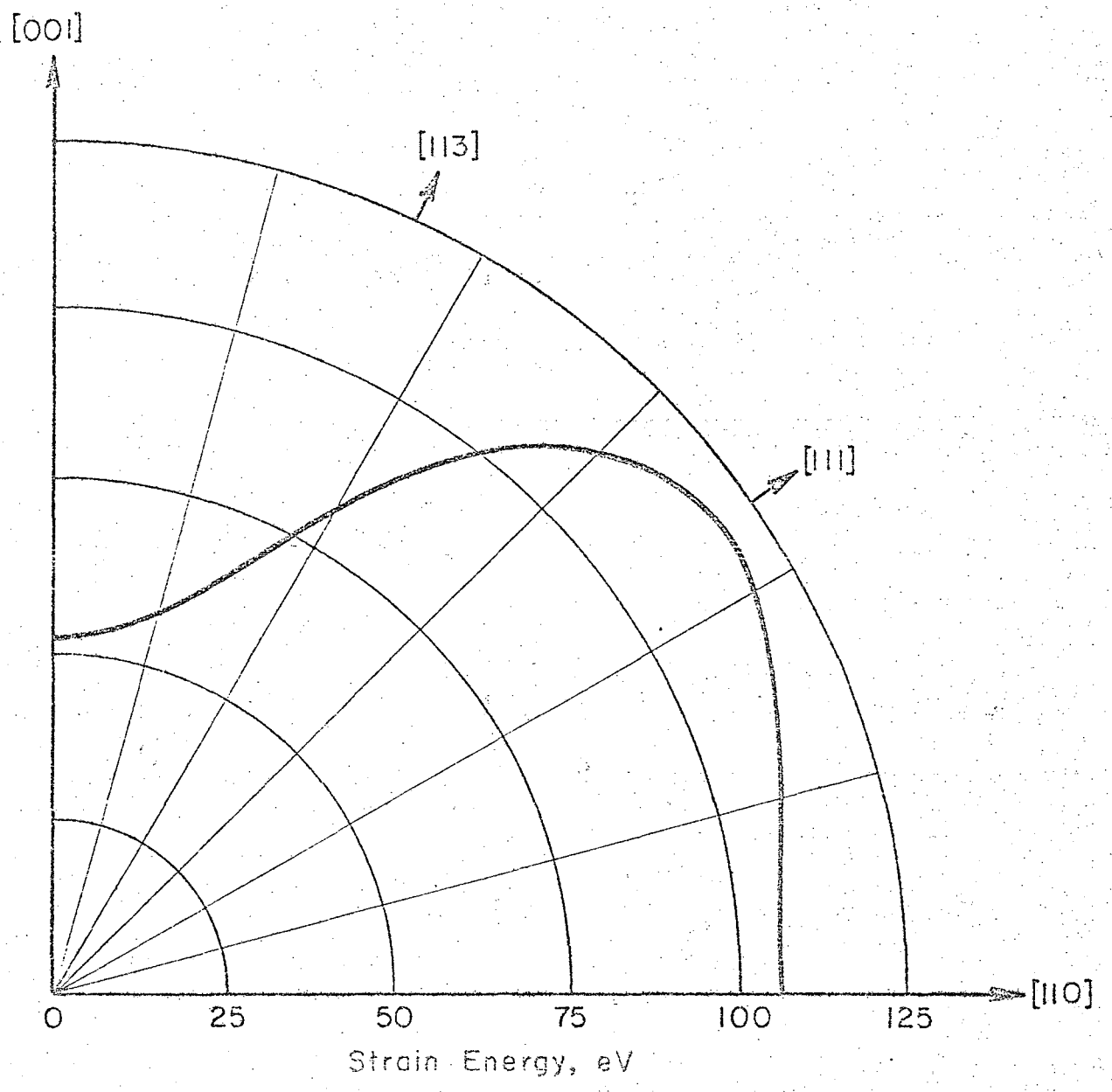

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Fig. 6.

0 0 0 0 4 2 0 1 5 8 7

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