PHYSICAL REVIEW B VOLUME 45, NUMBER 2 1 JANUARY 1992-II

Structure and thermodynamic properties of nanocrystalline metals

Michael Wagner
Werkstoffwissenschaften, Universität des Saarlandes, Fachbereich 15, Bau 43, D-6600 Saarbrücken, Germany

(Received 7 May 1991)

Nanocrystalline (nc) metals show significant differences in their thermodynamic properties, such as specific heat at constant pressure and thermal expansion, in comparison to polycrystalline metals. These properties are explained in terms of a macroscopic analysis. Based on a quasiharmonic approximation, the thermodynamic quantities are calculated as functions of the excess volume of the grain-boundary component in nc metals. The enhancements of the specific heat and the thermal expansion coefficient are accompanied by a reduction of the Debye temperature. The results show good agreement with experimental data.

INTRODUCTION

Nanocrystalline (nc) metals are polycrystals with a crystal size of a few nanometers (~ 10 nm) and a random texture.[1,2] Due to the small crystal size, up to 50% of the atoms are located at the intercrystallite boundaries. Holz and Patashinskii[3] describe nanocrystalline materials as two-component systems made up of a skeleton cluster of randomly oriented nanocrystallites (crystalline component) and a labyrinthine cluster, containing highly disordered material (grain-boundary component) (Fig. 1). Since grain boundaries affect the properties of materials, experiments on nanocrystalline metals show significant differences in thermodynamic and elastic properties: Rupp and Birringer[4] measured an increase of the specific heat at constant pressure of up to 30% and linear in T for nc-Cu and nc-Pd, confirmed by recent experiments on nc-Ir.[5] Measurements of the elastic properties of nc-Pd indicate a reduction of Young's modulus Y to 71.5% and of the shear modulus G to 74%,[6] which corresponds to a reduction of the bulk modulus B ($B=Y/[3(3-Y/G)]$) to 40%. And, as a last example, there is an increase of the coefficient of the linear thermal expansion by a factor of between 2 and 3 (Refs. 1 and 7) (nc-Cu, nc-Pd), although recent measurements suggest a smaller enhancement between 1 and 2 (nc-Pd).[8]

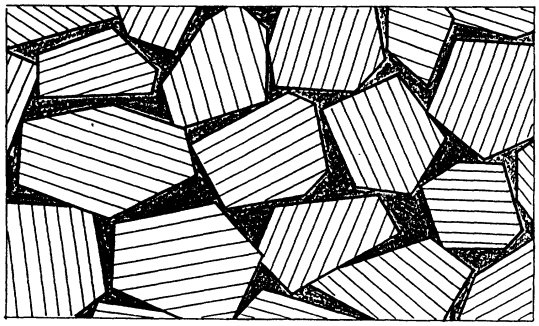

FIG. 1. Schematic illustration of a two-dimensional cross section through a three-dimensional nc material. The hatched areas represent the nanocrystals with different orientations. The dark regions separating the crystals are the disordered grain boundaries.

From a simple geometric estimate, the contribution of the grain-boundary component to the material is $3\delta/d$, where δ is the thickness of the grain boundary and d is the diameter of the crystallites. For nc-Pd with $d=9$ nm, about 30% of the material consists of the grain-boundary component. Keeping in mind that the density of nc-Pd is 90% (Ref. 2) of the polycrystalline Pd, we get for the excess volume ΔV of the grain-boundary component, $\Delta V \approx 30\%$. Consequently, ΔV seems to be a significant parameter for describing the grain-boundary component and for the nanocrystalline metals, too.

THEORY

In order to develop a simple method to describe the grain-boundary component of nc metals, some approximations have to be made. In a grain boundary, the number of nearest neighbors is reduced. This reduction can be calculated for each boundary atom in every type of grain boundary and can be used to estimate the energy and entropy of the grain boundaries (see, for instance, Ewing[9] and Provan and Bamiro[10]). Obviously, such calculations are useless in this case.

An alternative approximation is as follows. The reduction of the number of nearest neighbors in the grain boundary results in a decrease of the density ρ of the system. The density ρ is taken as the main feature of grain boundaries which are approximated by a perfect crystal structure having an enhanced nearest-neighbor separation compared to the equilibrium atom-atom distance of the crystal, in such a way that the densities of the grain boundary and of the dilated crystal are equal. The properties of the grain-boundary component are then estimated by the properties of the dilated crystal. The calculation of the dilated crystal is carried out for a simple central force model in the quasiharmonic Debye approximation.[11] The free energy $F(T,V)$, with $V \sim \rho^{-1}$, is then given by

$$F(T,V)=\phi+3Nk_BT\ln(1-e^{-\Theta/T})-Nk_BTD(\Theta/T)\ , \tag{1}$$

where ϕ is the total potential energy, N is the number of atoms, k_B is Boltzmann's constant, Θ is the Debye temperature, and

$$D(\Theta/T)=3(T/\Theta)^3\int_0^{\Theta/T}\frac{x^3}{e^x-1}dx$$

is the Debye function.

The potential energy is given by

$$\phi=\frac{N}{2}\sum_{i\neq j}^{N}\varphi(|r_i-r_j|)\ , \qquad (2)$$

where $|r_i-r_j|$ is the distance between atoms i and j and, as the pair potential function $\varphi(r)$, we choose the Morse function[11]

$$\varphi(r)=D(e^{-2b(r-a)}-2e^{-b(r-a)})\ . \qquad (3)$$

Regarding only the nearest-neighbor interaction, Eq. (2) is simplified to

$$\phi=6N\varphi(r)\ , \qquad (2')$$

where r is the nearest-neighbor separation. The potential constants are calculated to fit the energy of sublimation and the coefficient of linear thermal expansion:

	D (J)	a (m)	b (m^{-1})
Cu	9.4×10^{-20}	2.553×10^{-10}	1.3×10^{10}
Pd	1.04×10^{-19}	2.75×10^{-10}	1.4×10^{10}
Ir	1.8×10^{-19}	2.715×10^{-10}	1.45×10^{10}

Since the pressure is given by $P=-(\partial F/\partial V)_T$, Eq. (1) leads to the equation of state

$$P=-\frac{1}{3cr^2}\frac{\partial\phi}{\partial r}+\frac{3\gamma Nk_BT}{V}D(\Theta/T) \qquad (4)$$

with $V=cr^3$, $c=1/\sqrt{2}$ for fcc crystals, and γ is the Grüneisen parameter. Equations (3) and (4) are used to calculate the thermodynamic quantities[12]

$$C_V=-T\left[\frac{\partial^2F}{\partial T^2}\right]_V\ , \qquad (5)$$

$$B=-V\left[\frac{\partial P}{\partial V}\right]_T\ , \qquad (6)$$

$$\alpha_L=\left[\frac{\partial P}{\partial T}\right]_V\Big/3B\ , \qquad (7)$$

C_V, B, α_L are the specific heat at constant volume, the bulk modulus, and the coefficient of linear thermal expansion respectively. The specific heat at constant pressure is given by

$$C_P=C_V+9BV\alpha_L^2T\ , \qquad (8)$$

or, with $3\alpha_L=\gamma C_V/(BV)$,

$$C_P=C_V+(\gamma^2C_V^2/BV)T\ . \qquad (8')$$

In this simple model, the Debye temperature and the Grüneisen parameter only depend on r and are written as[13]

$$\Theta(r)=[\varphi''(r)/\varphi''(a)]^{1/2}\Theta_0\ . \qquad (9)$$

(Θ_0 means the Debye temperature for $r=a$, $\Theta_0=340$, 280, 420 for Cu, Pd, Ir, respectively,[14] and $\varphi''=\partial^2\varphi/\partial r^2$) and

$$\gamma(r)=-(r/6)\varphi'''(r)/\varphi''(r) \qquad (10)$$

(with $\varphi'''=\partial^3\varphi/\partial r^3$).

Now we are able to describe the various thermodynamic properties of the grain-boundary component in terms of the excess volume $\Delta V=V/V_0-1$, where $V_0=ca^3$ is the volume of the corresponding crystalline state at $P=0$ and $T=0$. For given T, $P(V)$ or $B(V)$ indicate the stability limit of the system. The critical excess volume ΔV_c is reached where $P(V)$ has its negative maximum value corresponding to $B(V)=0$ (see Fig. 2). At the critical excess volume ΔV_c, the grain-boundary component becomes mechanically unstable resulting in crack formation. Measurements of the elastic constants resulting in the reduced bulk modulus B[6] and calculation of the ex-

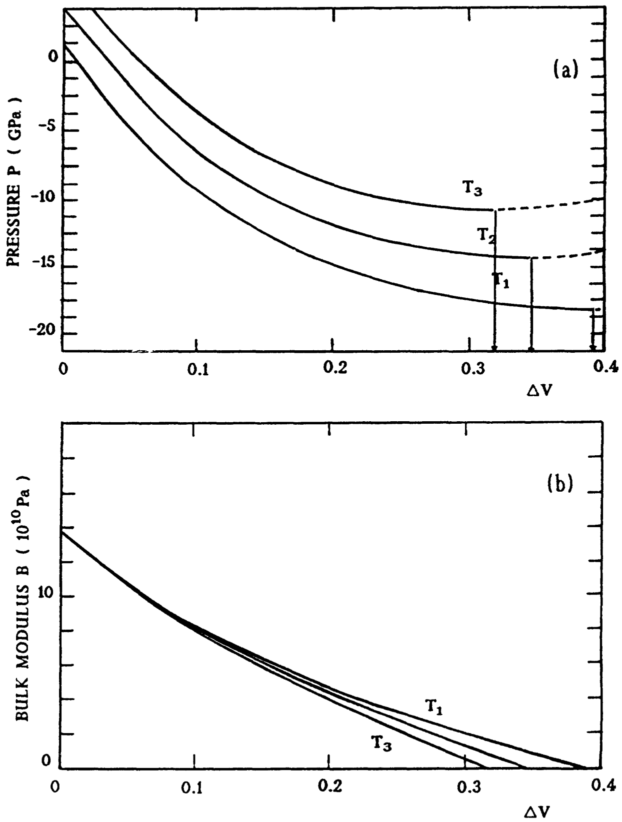

FIG. 2. The stability of grain boundaries of Pd as a function of excess volume ΔV ($\Delta V=V/V_0-1$, where V_0 is the volume of the crystal at $P=0$ and $T=0$) for three different temperatures $T_1=300$ K, $T_2=800$ K, $T_3=1300$ K. (a) the equation of state $P(V,T)$. The stability limit ΔV_c is given by the maximum negative pressure and indicated by arrows. (b) The bulk modulus $B(V,T)$. ΔV_c is given by $B(\Delta V_c,T)=0$.

cess volume of nc-Pd from density measurements agree with these estimates.

In Fig. 3 the Debye temperature und the Grüneisen parameter are shown as functions of excess volume ΔV_c. Due to the increase of the averaged atom-atom distance, the phonon spectrum becomes softer indicated by a reduction of the Debye temperature. Experimental evidence for such a reduction is given by Herr *et al.*[15]

The dependence of C_P and α_L on ΔV is calculated using Eqs. (8) and (8'). For conventional polycrystals ($\Delta V \approx 0$), the second term leads to a contribution in the order of magnitude of $(10^{-5}-10^{-4})k_B/K$ for each atom and therefore it only plays a role at high temperature. However, for a large excess volume we expect an essential contribution due to the fact that B tends to zero. The same argument is valid for α_L. The first term, C_V, of Eq. (8) provides the constant value of $3k_B$ for each atom in the harmonic approximation at high temperature and is independent of ΔV. Anharmonic contributions to the free energy have been previously discussed in the literature.[16-18] A model also based on the nearest-neighbor interaction with Morse potentials was introduced by Shukla and MacDonald.[19] In this model the anharmonic contribution to C_V can be easily calculated, but will only give about $10^{-5}k_B/K$ for each atom and will not change essentially for varying ΔV. Only at low temperature is there a dependence of C_V on ΔV due to influence of ΔV on the Debye temperature. In the harmonic case, C_V is written as

$$C_V = 3Nk_B \left[4D(\Theta/T) - \frac{3\Theta/T}{\exp(\Theta/T)-1} \right] . \tag{11}$$

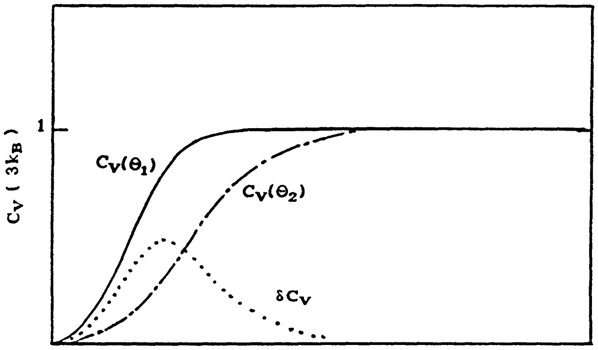

FIG. 4. Schematic illustration of the specific heat at constant volume for two Debye temperatures $\Theta_1 < \Theta_2$ and the difference $\delta C_V = C_V(\Theta_1) - C_V(\Theta_2)$.

For decreasing Θ, C_V reaches its limiting value $3Nk_B$ at lower temperatures (see Fig. 4).

The dependence of C_P and α_L on ΔV is shown in Figs. 5(a) and 5(b), respectively. Both of them diverge at the

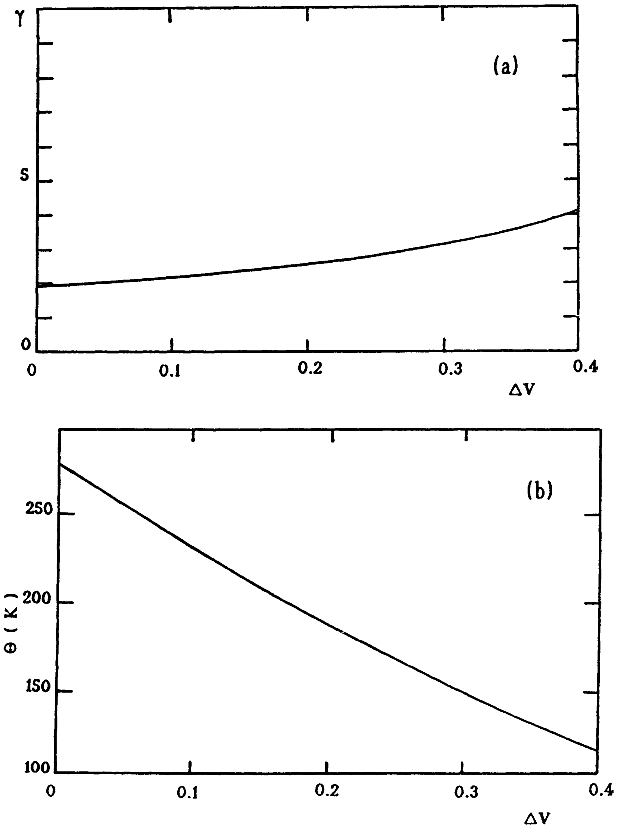

FIG. 3. (a) The increase of the Grüneisen parameter and (b) the decrease of the Debye temperature as functions of the excess volume.

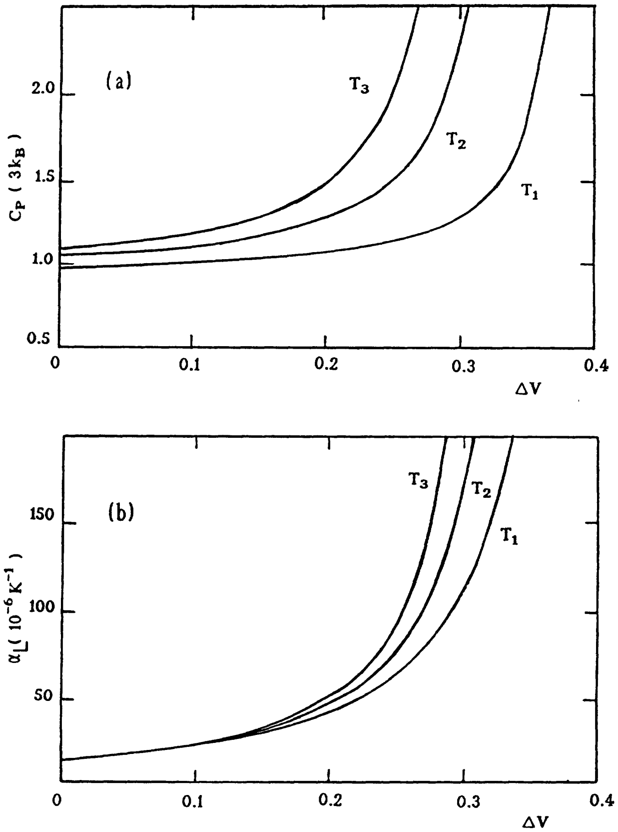

FIG. 5. The divergences of (a) the specific heat at constant pressure C_P and (b) the thermal expansion coefficient α_L as functions of the excess volume indicate the instability if the critical volume is reached.

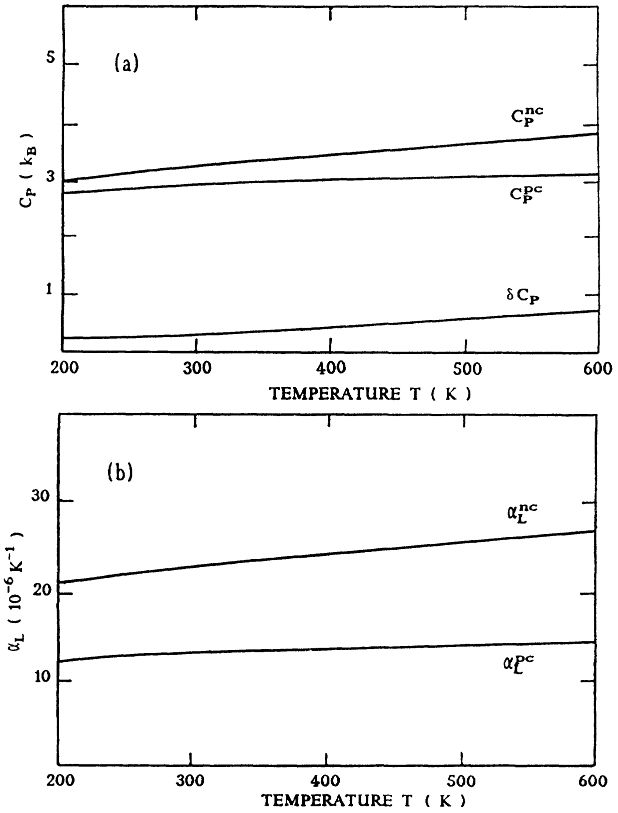

FIG. 6. (a) The specific heat of nc-Pd with a crystallite size of 9 nm as a function of the temperature in comparison to polycrystalline Pd (also calculated in the quasiharmonic approximation). The excess specific heat $\delta C_P = C_P^{nc} - C_P^{pc}$ shows a linear dependence on T. (b) The enhancement of the thermal expansion coefficient α_L of nc-Pd in comparison to polycrystalline Pd.

critical excess volume ΔV_c due to the vanishing bulk modulus B. By describing nanocrystalline metals as a two-component system with a crystalline component and a grain-boundary component with a large excess volume of about $\Delta V \approx 0.3-0.35$, their specific heat and thermal expansion can then be estimated by appropriate scaling of the grain-boundary contribution. As an example, this is done for nc-Pd with a crystallite size of 9 nm. Following the geometrical estimates noted above, we obtain a grain-boundary concentration of about 30% and an excess volume $\Delta V \approx 0.3$ of the grain-boundary component. The results are shown in Figs. 6(a) and 6(b). The specific heat shows an enhancement of about 10–25 % in comparison to polycrystalline Pd, for α_L we obtain an increase of factor between 1.7 and 1.85. Both of the values agree well with experimental data.[4,5,7,8]

DISCUSSION

It was shown in the section above that the excess volume ΔV of the grain-boundary component of nc metals is the suitable parameter to describe the thermodynamic properties of nc metals. ΔV was used as an averaged parameter. The grain-boundary component was approximated by a dilated crystal structure instead of a description of all the possible grain-boundary structures contained in nc metals. At first sight, this method seems to be a crude approximation. However, the model has the advantage that the method is easily applied and leads to reasonable results. Instead of the quasiharmonic approximation, Fecht[20] uses the universal equation of state (EQS) developed by Smith *et al.*[21] and gets similar results for C_P and α_L. But the divergence of these quantities is stronger in his model, which is caused by a divergence of the Grüneisen parameter γ. This also leads to a divergence of the vibrational entropy and to an entropy stabilization of the grain boundary which is not observed in experiments. Agreement between these two models is obtained if the Slater formula[22] $\gamma = 0.5\partial B/\partial P - \frac{1}{6}$ in Fecht's model is replaced by the formula developed by Dugdale and MacDonald:[23]

$$\gamma = -1 - 0.5V \left[\frac{\partial^2 P/\partial V^2 - 10P/9V^2}{\partial P/\partial V + 2P/3V} \right]$$

because the Slater formula is valid at $P = 0$ only and not at the large negative pressure appearing in Fecht's calculation. In Fig. 6 the calculations are made up to 600 K. In reality nc metals start to relax at about 400 K resulting in a small increase of the averaged grain size. Although the model cannot describe this structural relaxation, it is also valid for the relaxed structure.

ACKNOWLEDGMENTS

I am very grateful to Professor H. Gleiter, Professor A. Holz, Dr. R. Birringer, and Dr. S. Müller for stimulating discussions. I also want to thank A. Tschöpe for helpful discussions and access to his unpublished results and Greg McMahon for critically reading the manuscript.

---

[1] H. Gleiter, Phase Trans. **24-26**, 15 (1990).
[2] H. Gleiter, Prog. Mater. Sci. **33**, 223 (1989).
[3] A. Holz and A. Z. Patashinshii (private communication).
[4] J. Rupp and R. Birringer, Phys. Rev. B **36**, 7888 (1987).
[5] A. Tschöpe (private communication).
[6] D. Korn, A. Morsch, R. Birringer, W. Arnold, and H. Gleiter, J. Phys. (Paris) Colloq. **49**, C5-769 (1988).
[7] R. Birringer and H. Gleiter, *Encyclopedia of Material Science and Engineering Suppl.*, edited by R. W. Cahn (Pergamon, New York, 1988), Vol. 1, p. 339.
[8] M. Klingel (private communication).
[9] R. H. Ewing, Acta Metall. **19**, 1359 (1971).
[10] J. W. Provan and O. A. Bamiro, Acta Metall. **25**, 309 (1977).
[11] L. A. Gerifalco and V. G. Weizer, Phys. Rev. **114**, 687 (1959).
[12] L. D. Landau, and E. M. Lifshitz, *Lehrbuch der theoretischen Physik Band V, 6. Auflage* (Akademie-Verlag, Berlin, 1984).
[13] P. Brüesch, *Phonons: Theory and Experiments I,* Solid-State Sciences Vol 34 (Springer-Verlag, Berlin, 1982).
[14] E. A. Brades, *Smithells Metals Reference Book,* 6th Ed. (Butterworth, Washington, D.C., 1983).
[15] U. Herr, J. Jing, R. Birringer, U. Gonser, and H. Gleiter, Appl. Phys. Lett. **50**, 472 (1987).

[16] W. Ludwig, J. Phys. Chem. Solids **4**, 283 (1958).

[17] G. Leibfried and W. Ludwig, Solid State Phys. **12**, 275 (1961).

[18] A. A Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfell, Ann. Phys. **15**, 337 (1961); **15**, 360 (1961); P. A. Flinn and A. A. Maradudin, *ibid.* **22**, 223 (1963).

[19] R. C. Shukla and R. A. MacDonald, High Temp. High Pressure **12**, 291 (1980); R. C. Shukla, Int. J. Thermophys. **1**, 73 (1980).

[20] H. J. Fecht, Phys. Rev. Lett. **65**, 610 (1990); Acta Metall. Mater. **38**, 1927 (1990).

[21] J. H. Rose, J. R. Smith, F. Guinea, and J. Ferrante, Phys. Rev. B **29**, 2963 (1984); P. Vinet, J. R. Smith, J. Ferrante, and J. H. Rose, *ibid.* **35**, 1945 (1987).

[22] T. H. K. Barron, J. G. Collins, and G. K. White, Adv. Phys. **29**, 609 (1980).

[23] J. S. Dugdale and D. K. C. MacDonald, Phys. Rev. **89**, 832 (1953).

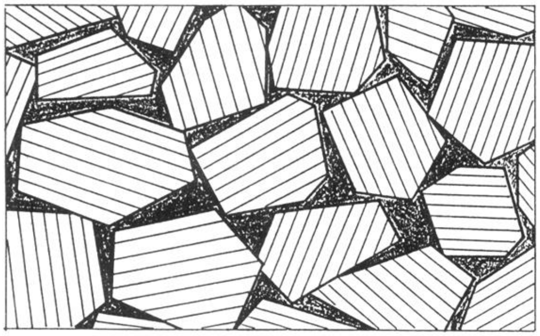

FIG. 1. Schematic illustration of a two-dimensional cross section through a three-dimensional nc material. The hatched areas represent the nanocrystals with different orientations. The dark regions separating the crystals are the disordered grain boundaries.