

Interpretation of Solid Solution Hardening with Vibrational Spectra

J. N. Plendl, P. J. Gielisse, L. C. Mansur, S. S. Mitra, A. Smakula,
 and P. C. Tarte

Solid solution hardening has been reviewed with respect to existing experimental data. It is shown with the aid of new experimental data on two inorganic systems (NiO-CoO and CaF₂-SrF₂) that the large increase in hardness of intermediate compositions correlates qualitatively and can also be quantitatively justified by the use of selected values of the parameters in a previously developed atomistic hardness formula. The key parameters are the variations in the unit cell dimensions, the eigenfrequency, and anharmonic factor of the structure.

Introduction

Physical expressions of hardness have been formulated by Friedrich,¹ Goldschmidt,² and Powarjonnych.³ No formulation has given hardness a physically meaningful dimension, however.

Plendl and Gielisse⁴ have developed a physical quantity, the volumetric cohesive energy, which is linearly related to physical hardness. The volumetric cohesive energy has dimensions of a force per square centimeter and can be conceived of as an energy per volume, or the ratio between input energy and the volume removed or displaced during hardness testing. The validity of the relationship has been substantiated for some eighty-eight nonmetallic solids of twenty-two different structure types. As a result an expression was found involving well-defined characteristics or measurable physical parameters which was applicable over the entire hardness range, regardless of bond type. A similar expression was later developed by Plendl *et al.*⁵ for the compressibility of solids.

It has already been indicated that hardness variations within a crystal such as are caused by anisotropy, solid solution hardening, and temperature dependence could be predicted with the new formulation.⁶ Because of lack of proper experimental data no proof could be given. Such data are now available. Specific reference

is made herein to an atomistic hardness formula^{4,6} which remains valid for directional effects as well as the effect of composition on hardness.

Solid Solution Hardness

The increase of mechanical strength of metals through formation of solid solution alloys has been known for a long time. Nonlinear diagrams showing a maximum of indentation hardness for the systems Ag-Au and Ag-Cu have been reported by Sachs,⁷ Kuntze,⁸ and Winkler.⁹ A comprehensive study of mechanical properties of metallic solid solutions as a function of composition was carried out by Koester and Rauscher.¹⁰ A nonlinear increase of compressive yield strength vs composition was observed on dielectric solid solutions of MgO-MnO and MgO-NiO by Liu *et al.*¹¹ Nonlinear effects on the microhardness of solid solution single crystals of binary dielectrics have been observed for a limited number of cases. They primarily involve the systems K₂SO₄-(NH₄)₂SO₄,¹² a series of alkali halides,^{13,14} group II oxides,¹⁵ the III-V compound solid solution InP-GaP,¹⁶ and the systems CaF₂-SrF₂, SrF₂-BaF₂,^{17,18} and NiO-CoO.¹⁷

Although several of these systems lend themselves to spectral analysis, only two of them (NiO-CoO and CaF₂-SrF₂) are treated here in detail, because only for them are all physical quantities necessary for analysis available.

The atomistic expression of hardness may be given as⁶
 $H = U/V$ or

$$H = \frac{1}{2} Z \frac{m_r}{V} \left(\frac{\omega_0 r_0}{\Psi(A)} \right)^2 \quad (1)$$

When $2\pi\nu_c = \omega_c$ and $V = 2r_0^3$ are used for the molecular volume of a solid with the NaCl structure but

J. N. Plendl and L. C. Mansur are with AFCRL, Bedford, Massachusetts 01730; P. J. Gielisse and S. S. Mitra are with the Department of Chemical Engineering of the University of Rhode Island; A. Smakula is with the MIT Crystal Physics Laboratory; and P. C. Tarte is with the Institute of Chemistry of the Université de Liège.

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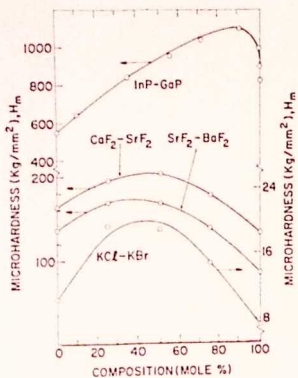


Fig. 1. Variation of hardness as a function of composition for several solid solution systems. For references, see text.

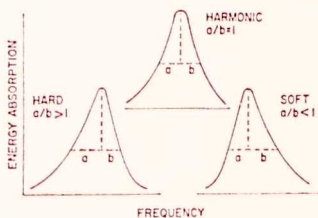


Fig. 2. Schematic presentation of energy absorption curves for solids with a hard ($a/b > 1$) or a soft ($a/b < 1$) anharmonic factor. A fully symmetric energy absorption curve would be obtained for the linear case, where the anharmonic factor is unity.

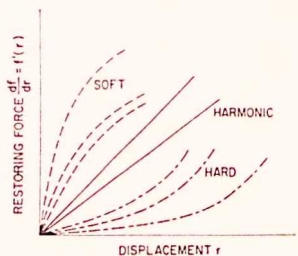


Fig. 3. Definition of soft and hard force characteristics as deviations from linear behavior. The two type behavior is classically characterized by different trends of the force characteristic as a function of displacement (see, e.g., Stoker²⁴). ---, Soft force characteristic; —, harmonic force characteristic; - - -, hard force characteristic.

$V = (\pi/2)\tau_0^3$ is used for CaF_2 structure,¹⁹ where r^0 represents the nearest-neighbor distance, this becomes $H = \pi^2 Z m_r \nu_c^2 / \tau_0 \Psi(A)^2$ for NaCl structure and $H = 4\pi Z m_r \nu_c^2 / \tau_0 \Psi(A)^2$ for CaF_2 structure, where Z = valency, m_r = reduced mass, ν_c = centro-frequency, and $\Psi(A)$ = anharmonic factor.

In solid solutions the primary variables in this formula are the quantities ν_c , τ_0 , and $\Psi(A)$. If linear variation in the preceding variables between the end members were the case, the hardness would vary monotonically from one end member to the other. Experimental evidence indicates, however, that hardness values for intermediate compositions of a solid solution series are as much as 100% higher than either end member. Figure 1 shows typical data for a limited number of systems which have so far been investigated. The first systems on which our experiments were conducted, KCl-NaCl and CoO-NiO, showed the maxima of the hardness anomalies at approximately the 50% composition point. This was felt to be due to the great similarity between the end members of these systems, KCl-NaCl and NiO-CoO. Reference to information on systems shown in Fig. 1 proved this to be true. In the InP-GaP system the maximum in the hardness curve lies as far over as the composition $(\text{In}_{0.10}\text{Ga}_{0.90})\text{P}$ and, as is the case for other similar systems, apparently always on the side of the harder end member.

The compositional variation of ν_c , τ_0 , and $\Psi(A)$ might have maxima and minima which may or may not coincide compositionally. The resulting quantitative hardness values may be consistent with either possibility. Present data are, however, not sufficient to unequivocally indicate the quantitative relation. Data such as are presented here for the NiO-CoO system or the CaF_2 - SrF_2 system would therefore be of particular interest on a system such as InP-GaP where the end members of the solid solution are sufficiently different to justify conclusions with regard to compositional coincidence of the maxima or minima.

The unit cell dimensions in solid solution systems generally vary linearly with composition (Vegard type solid solutions), as is the case in the CaF_2 - SrF_2 system. The NiO-CoO system shows a negative deviation from linearity, although positive deviations may also be possible. Generally the magnitude of the deviation does not exceed a few percent. In the case of NiO-CoO this would tend to produce an increase in hardness. How-

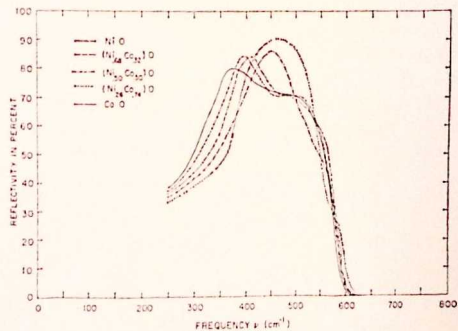


Fig. 4. Infrared reflectivity spectra in the area of the fundamental lattice vibrations for five members of the NiO-CoO solid solution system.²²

ever, this in itself does not explain the large observed hardness. The explanation will therefore have to be sought, in addition, in the variation of both ν_c and $\Psi(A)$.

The variation of ν_c , the characteristic vibrational frequency of the structure, can be conveniently obtained from evaluation of spectroscopic data such as the reflection or absorption spectrum of the solid in the lattice vibrational area of the spectrum. A method recently developed by one of us combines reflection and absorption data to yield an absorbed energy spectrum.²⁰ In dielectrics, its main absorption frequency is assumed to represent the transverse mode frequency, which has been verified by calculation of the frequency from elastic constants derived from sound velocity measurements in the (110) direction (ν_T). These frequency values are used in the hardness formula since they are clearly defined as a function of composition.

Structures with harmonic vibrations have symmetric energy absorption curves. The anharmonic factor²¹ $\Psi(A)$ may be obtained from the asymmetry of the energy absorption curves by the two relations²⁰ $\Psi(A) = 1 + (1/\pi)[1 - (b/a)]$ for a *hard* anharmonic force characteristic, and $\Psi(A) = 1 - (1/\pi)[1 - (a/b)]$ for a *soft* anharmonic force characteristic, where a and b are defined as in Fig. 2. This gives solids an anharmonic factor of $\Psi(A) > 1$ or $\Psi(A) < 1$. This classification is similar and related to Stoker's classical definition²⁴ of nonlinear vibrations into two categories with an anharmonic soft and anharmonic hard force characteristic. The behavior of systems with the two types of anharmonic force characteristics is shown schematically in Fig. 3, where the relation between restoring force $f'(r)$ and displacement length r differentiates between them.

Experimental Results

Qualitative

The preparation of single crystals in the system NiO-CoO was described in an earlier paper.²² Also reported were the infrared reflectivity data, which are shown in Fig. 4. Transmission measurements were made on powders of the mixed crystals embedded in polyethylene disks in the region 30 cm^{-1} to 250 cm^{-1} in four different scans with the usual interchange of appropriate gratings and filters. The disks were hot-pressed at about 90°C and pressures up to 15 tons cm^{-2} for about 5 min. The exact details of the polyethylene disk method may be found elsewhere.²³ Spectral results are shown in Figs. 4 and 5 for the system NiO-CoO and in Figs. 6 and 7 for the system CaF_2 - SrF_2 . The evaluation of the reflectivity and transmissivity data yield, as previously mentioned, the absorbed energy spectra²⁰ and are shown in Figs. 8 and 9. From them the frequencies of maximum energy absorption ν_0 and the data of the anharmonic factor $\Psi(A)$ have been derived as a function of composition. Their ratio squared, $[\nu_0/\Psi(A)]^2$, forms a spectral parameter. Being proportional to the bond strength it is a convenient determinant for calculation of hardness [see Eq. (1)]. The values of this parameter are listed in Tables I and II for the compositions considered. They are further shown in Figs. 10 and 11 as

a function of composition together with measured data of microhardness. The two different data have an almost parallel trend, both showing maximum values at close to the 50/50 composition.

Quantitative

From the data of this spectral parameter and from valency and interatomic distance, values of atomic

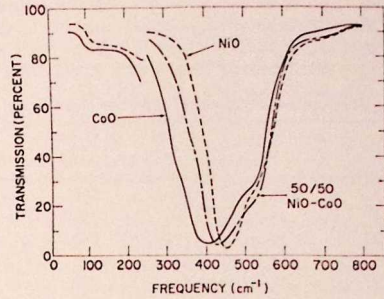


Fig. 5. Infrared transmission spectra for three compositions of the NiO-CoO solid solution system.

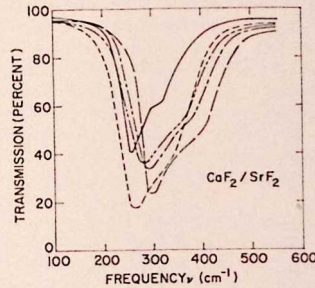


Fig. 6. Infrared transmission spectra for five compositions of the CaF_2 - SrF_2 solid solution system.

Composition (percent):	CaF_2	SrF_2
— — — —	100	0
- - - -	75	25
--- ---	50	50
- - - -	25	75
— — — —	0	100

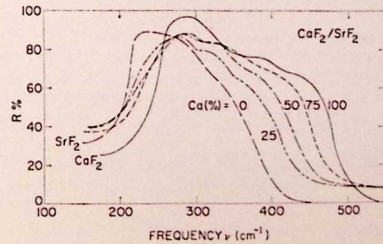


Fig. 7. Infrared reflectivity spectra for five members of the CaF_2 - SrF_2 solid solution system.

Table I. Data Used in the Evaluation of the Systems NiO-CoO and CaF₂-SrF₂

Solid	r_0 , 10 ⁻⁸ cm	V , cm ³	$\nu_{T0(110)}$, cm ⁻¹	$\Psi(A)$	$\Delta\nu/\nu_0$	Exptl. $H_{(110)}$, kg mm ⁻²	Calc. $H_{(110)}$, kcal cm ⁻³	Calc. $MH_{(100)}$, kg mm ⁻²	$[\nu_0/\Psi(A)]^2$, cm ⁻² × 10 ⁴
NiO	2.09	11.0	450	0.88	0.18	575	110	605	26.2
CoO	2.13	11.65	390	0.82	0.39	315	93	515	28.2
NiO/CoO	2.11	11.3	413	0.78	0.26	605	119	655	22.6
CaF ₂ /SrF ₂									
100:0	2.36	—	291	0.87	0.12	166	28.0	170	112
75:25	2.39	—	290	0.825	0.23	199	32.0	195	122
50:50	2.43	—	281	0.82	0.18	208	31.8	195	118
25:75	2.46	—	268	0.85	0.23	180	27.8	170	100
0:100	2.50	—	252	0.84	0.20	137	25.6	155	88

Table II. Mechanical Properties of Solids Used to Establish Proportionality Between Physical and Measured Hardness Data

Solid	Structure	U , kcal mole ⁻¹	V , cm ³	U/V , kcal cm ⁻³	U/V , kbar	MH , kg mm ⁻²	K , kbar
BaF ₂	Fluorite	550	35.8	15.5	650	80	570
SrF ₂	Fluorite	590	29.3	20	830	135	650
CaF ₂	Fluorite	630	24.5	25.5	1070	163	900
CaCO ₃	Calcite	710	36.9	19.5	810	135	700
ZnS	Zinc blende	795	24.1	33	1370	205	800
SiO ₂	Quartz	3150	22.7	138	5800	750	2000
Ge	Diamond	3500	2 × 13.6	129	5400	700	—
Si	Diamond	4400	2 × 12.1	182	7500	1000	—

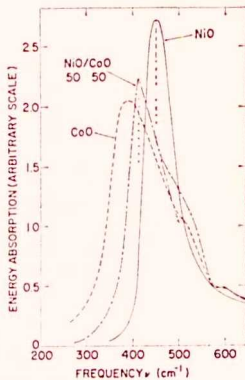


Fig. 8. Characteristic energy absorption spectra for three compositions in the solid solution system NiO-CoO.²⁰

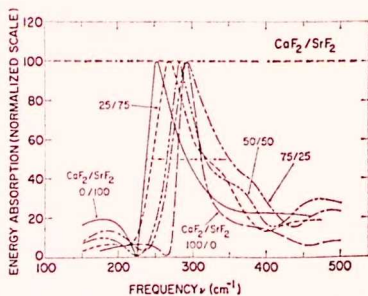


Fig. 9. Characteristic energy absorption spectra for five compositions in the solid solution system CaF₂-SrF₂.²⁰

hardness (kcal cm⁻³) have been calculated (see Table I). They are converted into microhardness data by using the calibration curve of Fig. 12. These data are plotted vs composition (curves *c*) in Figs. 10 and 11 for NiO-CoO and CaF₂-SrF₂. The calculated values are only slightly different from the measured hardness data. The agreement may be considered good when it is recalled that the percent deviation falls well within the inaccuracies of the hardness values themselves and that the graphically derived proportionality factor between U/V and MH has an accuracy of no better than 10%. In the case of NiO-CoO (Fig. 10) two different series of hardness measurements are shown, one for the (110) direction (of the indenter), curve *a*, and one for a different direction, curve *b*. The good agreement obtained between measured and calculated hardness data suggests that the spectral parameter $[\nu_0/\Psi(A)]^2$ correctly describes the change of bond strength, and thus of hardness, with varying composition. This result may prompt further exploration of the characteristic energy absorption spectra, aiming at a strictly atomistic interpretation of solid solution hardening.

Figure 12 shows the measured indentation hardness vs calculated atomistic hardness data for eight solids. It facilitates direct comparison between the external pressure applied through the indenter (to obtain permanent deformation in the sample) and the internal cohesive pressure (by which the atoms are held together in the solid state). The straight-line relationship obtained suggests a dimensionless factor of proportionality, since the two hardness values (MH and U/V) have the same dimension, expressed as either the volumetric cohesive energy or pressure per cm². In the case of Fig. 12, the ratio of internal pressure to external pressure is 75. In other words, the external pressure necessary for perma-

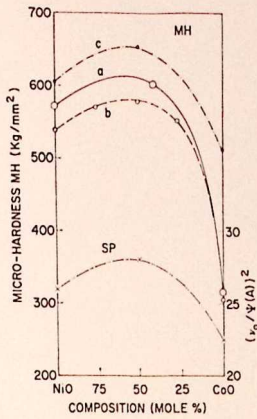


Fig. 10. Comparison between experimental hardness values (curves a and b) and those calculated with the proposed method (curve c) for the solid solution system NiO-CoO. The variation of the spectral parameter $(\nu_0/\psi(A))^2$ is also indicated (see SP).

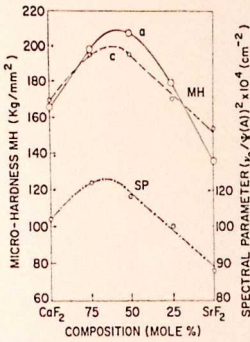


Fig. 11. Comparison between experimental hardness values (curve a) and those calculated with the proposed method (curve c) for the solid solution system CaF₂-SrF₂. The lower curve indicates the variation of the spectral parameter in this system (SP).

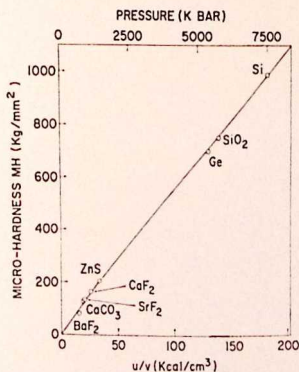


Fig. 12. Identification hardness vs volumetric lattice energy (physical hardness) for eight pertinent solids.

ment deformation, through an indenter, is only a small fraction of the internal cohesive pressure of the materials.

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