

Hard-sphere properties of solid argon-xenon mixtures probed by recoilless resonant absorption

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The Mössbauer effect in ^{119}Sn was applied to obtain information on the local dynamical properties in frozen Ar-Xe mixtures. The results indicate a softening of the lattice in a composition range between 5% and 15% Xe in the mixture, and possible dealloying at higher concentrations of Xe. These results are in excellent agreement with hard-sphere model calculations and with the Hume-Rothery size rule for alloys.

The rare gases and their mixtures have been the subject of continuous interest as model systems to understand the mixing mechanism of simple interacting systems. Since the interatomic interaction for all rare gases is well known and the interatomic potentials have been well studied, much work both theoretical and experimental has been devoted to the study of rare-gas mixtures in the gas and fluid phase. On the other hand, very little is known about the solidification of these mixtures and their properties.

Only in recent years have several publications appeared on the subject of the crystalline properties and the local arrangement of rare-gas alloys relative to their respective atomic sizes and at various concentration ratios. Recent extended x-ray-absorption fine-structure (EXAFS) studies^{1,2} on Xe-Ar, Xe-Ne, and Kr-Ne mixtures have shown that xenon atoms in argon are statistically distributed on substitutional sites in the argon lattice up to a xenon concentration of 10%, while the krypton in neon demonstrates clustering already from concentration of 1%. Neutron diffuse and Bragg scattering³ measurements on Kr-Ar alloys show complete mixing of the components on the argon-rich side, while the results at 10% Ar in Kr show the existence of argon-rich microclusters. Earlier extreme uv absorption spectroscopy studies of solid rare-gas mixtures indicate partial dealloying in Xe-Ar mixtures somewhere between 40% and 60% Xe.⁴ Theoretical calculations on the freezing of binary hard-sphere mixtures at varying size ratios show a variety of phase diagrams for different ratios and predict immiscibility in accordance to the Hume-Rothery size rule.⁵ In view of all these results we have undertaken a study to obtain information about the microscopic dynamical properties of such mixtures by utilizing the Mössbauer spectroscopy.

For our first series of experiments we have chosen the Mössbauer effect in ^{119}Sn in a matrix-isolated molecule $\text{Sn}(\text{CH}_3)_4$ as our probe. This study was undertaken as part of an investigation of the behavior of a heavy impurity-like tetramethyltin in all the rare gases from Ne to Xe. The properties of tetramethyltin make it an ideal impurity for the study of rare-gas solids and their mixtures. The tin atom is surrounded by four methyl groups in a tetrahedral symmetry. The interaction between the molecules in the liquid and solid form is van der Waals and the Mössbauer parameters of the Sn atom are identical irrespective of the surroundings both in the case of the matrix-isolated molecule in all rare gases⁶ and their mixtures as in the crystal-

line solid.⁷ In the low-temperature region (below 80 K) all the internal degrees of motion of the molecule are frozen⁸ making the molecule rigid and giving it properties similar to a heavy rare-gas atom with a mass of 179 amu.

In this paper we report on our study of the Ar-Xe mixtures in the range from 100% Ar to 100% Xe. The experiments were performed as follows. The mixtures of high-purity rare gases were prepared in a container in molar ratios in the gas form. A small amount of tetramethyltin was added in 1% atomic concentration. This mixture was heated to about 60°C and evaporated through a needle valve on a beryllium window of an exchange gas chamber in a liquid-helium cryostat. During the evaporation the pressure in the vacuum shroud of the cryostat was allowed to rise to 6×10^{-5} Torr and the temperature of the substrate to rise to a maximum of 9 K. The temperature of the frozen absorber could be changed by a heater mounted on the beryllium substrate and the temperature was controlled with a Si diode in direct contact with the evaporated sample.

Mössbauer absorption spectra were obtained by using a standard 2-mCi $^{119\text{m}}\text{Sn}$ source in the chemical form of CaSnO_3 . Spectra were recorded at various temperatures in the temperature range between 7 and 27 K. This temperature range was chosen to insure that no sublimation takes place which would change the composition of the sample and to be far enough from the onset of internal vibrations in the tetramethyltin molecule. The composition of the mixtures which were studied started with pure argon and then varied with xenon concentrations of 5, 10, 15, 20, 30, 50, 70, and 100%.

A typical absorption spectrum is shown in Fig. 1. The temperature dependence of the total intensity of absorption for one composition is presented in Fig. 2. Such results were obtained for each concentration and, as previously mentioned, the shape, linewidth, and isomer shift of all spectra at all concentrations and temperatures were identical. These parameters correspond closely to the parameters obtained in the solid tetramethyltin⁷ and indicate that there is no change in the local chemical environment of the tin atom.

The intensity of the resonant absorption is proportional to the probability of the recoilless emission and absorption of the γ radiation which is represented by the Debye-Waller factor. For an impurity case it is quite customary to evaluate the Debye-Waller factor in the Debye approxi-

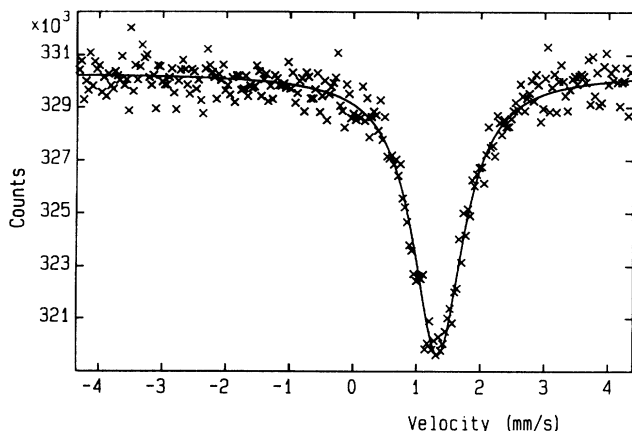


FIG. 1. Absorption spectrum of a CaSnO_3 source vs a matrix-isolated tetramethyltin absorber.

mation by assigning a characteristic Mössbauer temperature instead of the Debye temperature of the host lattice. This formalism was applied to extract the characteristic Mössbauer temperature for each composition from the temperature dependence of the absorption intensity. The experimental results were fitted by the following formula for the temperature dependence of the recoilless fraction in the Debye approximation:

$$\ln f = -\frac{6E_r}{k\Theta_M} \left[\frac{1}{4} + \left(\frac{T}{\Theta_M} \right)^2 \int_0^{\Theta_M/T} \frac{x}{e^x - 1} dx \right]. \quad (1)$$

Here E_r is the recoil energy of the recoiling impurity upon absorption of the Mössbauer γ energy and Θ_M is the characteristic Mössbauer temperature. The temperature dependence of the Mössbauer intensity for all compositions could be fitted satisfactorily with this model and the deviations were relatively small, as can be seen in the example of Fig. 2.

The results of the concentration dependence of the characteristic Mössbauer temperatures are presented in Fig. 3. A pronounced dip in the characteristic tempera-

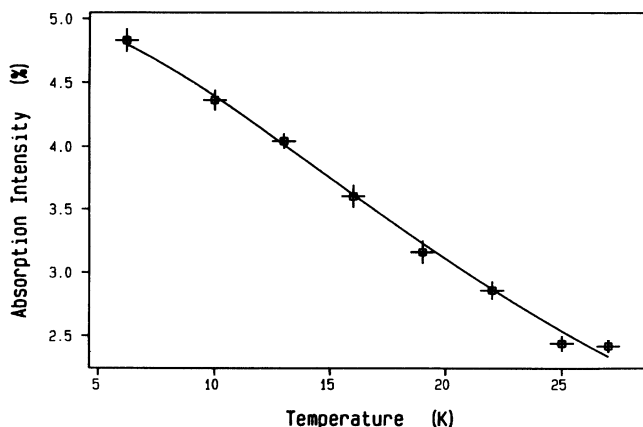


FIG. 2. Temperature dependence of the resonant absorption intensity for the 70% Xe mixture.

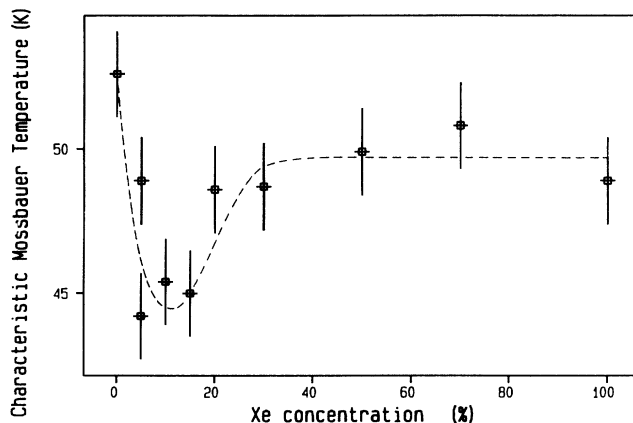


FIG. 3. The dependence of the characteristic Mössbauer temperature on the mixture composition for the argon-xenon system. The curve is only a guide for the eye.

ture in the concentration range between 5% and 15% of Xe, and at higher concentrations the characteristic temperature is constant and equal to the value obtained for 100% Xe.

To check the stability of the frozen mixtures at all compositions, the samples were cooled down after the measurement at 27 K and remeasured in a second series. In all cases this yielded the same characteristic temperatures, indicating the absence of any kind of local rearrangement.

The relation of the impurity characteristic Mössbauer temperature to the lattice-dynamical properties of the crystalline host is very complex.⁹ It involves a change in the phonon distribution, localized modes, and anharmonicity. The theoretical treatment of this problem is limited to monoatomic cubic crystals in the Debye approximation and no treatment of alloys and mixtures is available. Therefore it is not possible to deduce quantitative values on the host lattice-dynamical parameters. However, we can assume that the Mössbauer characteristic temperature is coupled to the frequency moments of the phonon distribution of the host and that changes in the phonon distribution of the host crystal will affect the impurity. In this context we can relate the lowering of the impurity Mössbauer characteristic temperature in the observed concentration range with the softening of the host lattice and local disorder due to size mismatch.

In view of the existing literature on this subject, we can interpret our results as follows. The atomic size ratio for Ar and Xe is 0.87. This is very close to 0.85, which the Hume-Rothery size rule defines as being the limiting value for a stable alloy in a large concentration range.¹⁰ By applying the density-functional theory for the study of the freezing of hard-sphere mixtures Barrat, Baus, and Hansen⁵ have shown that at ratios approaching 0.85, the solubility of the large spheres in the small spheres is decreasing very fast and the crystalline matter becomes more disordered. On the large sphere side of the phase diagram they predict phase separation into pure small sphere crystals and large sphere-rich crystals. We believe that our results fit this model extremely well.

Assuming that our probe molecule ($r \approx 3.6 \text{ \AA}$) (Ref. 11) is behaving in the mixture like a large Xe atom, it will

follow the Xe atoms in the separation process and our results show that in the small-atom-size-rich part of the phase diagram the phonon spectrum of the frozen mixture shows softening. This softening coincides exactly with the region derived for ratios of 0.9 by Barrat, Baus, and Hansen,⁵ a region at which they predict an eutectic alloy with low melting temperature.

Already at a concentration of 20% Xe we observe a recovery of the characteristic temperature to the value of solid Xe. This may be explained by the segregation of the mixture into argon microcrystals and Xe-rich regions that contain our probe molecule. Indication for such a segregation have been observed by Haensel *et al.*⁴ in their optical studies on rare gas mixtures.

In summary, we have demonstrated that by utilizing the

Mössbauer effect important information on the behavior of rare-gas solid mixtures can be obtained. For the case of xenon-argon mixtures the results can be interpreted qualitatively by the hard-sphere model and show that geometrical consideration is the governing cause for the crystallization of systems as similar as the rare-gas atoms.

This work begins a series of studies in which we intend to probe by similar methods the behavior of other pairs of rare-gas mixtures with different radii ratios. A particularly interesting case will be the Ar-Ne mixture for which the atomic size ratio is 0.82, setting this mixture below the limiting value of the Hume-Rothery size rule. In future work we intend to employ ⁸³Kr and possibly ¹²⁹Xe as rare-gas probes for this kind of study.

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