Molecular-dynamics calculation of the vibrational densities of states and infrared absorption of crystalline rare-gas mixtures

S. Gonçalves and H. Bonadeo

Departamento de Física, Comisión Nacional de Energía Atómica, Avenida del Libertador 8250, 1429 Buenos Aires, Argentina

Relaxations around defect sites, vibrational local densities of states, and absolute infrared absorptions are computed on the twelve possible crystal mixtures of Ne, Ar, Kr, and Xe in the highly diluted limit, using molecular dynamics. We found that the lattice deformation does not decay uniformly with the distance from the impurity, and that it plays an important role in determining the effective interactions. Vibrational local densities of states show that, except for Ar-Kr mixtures, light impurities give resonant bands and heavy impurities produce localized modes. Infrared-absorption calculations show a good agreement with the experimental data. The possibility of refining mixed-rare-gas interaction potentials by use of these systems as probes is discussed.

I. INTRODUCTION

Rare-gas crystals are among the simplest and most studied solids; their crystal energies and lattice modes are well reproduced using quite sophisticated interaction models.[1] Rare-gas mixtures have received much less attention: most calculations use Green's-function methods on highly diluted mixtures,[2-4] do not take into account the important relaxation of the bulk crystal around the impurity, and adopt the harmonic approximation. To our knowledge only Vermesse *et al.*[5] have used the molecular-dynamics (MD) method on these systems, studying Ar doped with Kr and Kr with Xe. For a review of the properties of inert gas crystals doped with impurities (including other rare gases) see Ref. 6.

Experimental results, in the form of impurity-induced far-infrared absorption spectra, are rather scarce, probably due to the difficulty of growing thick single crystals; furthermore, of the three papers published so far[7-9] only the last one, where Keeler and Batchelder[9] study Ar impurified with Kr and Ne, seems to provide reliable data.

In the present work we study all the rare-gas mixtures in the highly diluted limit, using MD. The MD method has the distinct advantage of providing results that are "exact" with respect to the interaction model adopted: in our case it automatically takes into account relaxations of the atoms around the impurity and the anharmonicity of the potential. We have used a Lennard-Jones (LJ) potential, fitted to reproduce crystal structure and cutoff frequency of the pure materials; the mixed interactions were taken from atomic collision experiments,[10] and so were the induced dipole model and parameters used to calculate the absorption spectra;[11] it is to be noted that they refer to interatomic distances quite different from crystalline spacings. One of the important objectives of this work is to promote experimental work on these systems: the comparison of data with calculations, and the correction of these to fit them will enable us to understand better the mixed rare-gas interactions. Although the importance of three-body interactions in these crystals is well established, we have preferred at the present stage to deal with an effective two-body force. In order to be able to introduce meaningfully more sophisticated models, with unknown parameters, much better and more complete experimental data are necessary.

The paper is organized as follows: in the next section we give the necessary details of the calculation; in Sec. III we describe the lattice relaxations, and the commonly used approximations associated with their neglect; Sec. IV is devoted to the vibrational power spectra, and in Sec. V we present the calculated absorption spectra, compare them with available experimental data, and attempt a refinement of the mixed-atom parameters, in order to establish the sensibility of impurity related vibrational frequencies to the mixed interaction parameters.

II. CALCULATION METHOD AND PARAMETERS

MD calculations were performed on a constant volume box containing 500 atoms, initially on fcc sites corresponding to the cell parameter of the bulk crystal at $T = 0$ K. One of the atoms is the substitutional impurity, and periodical boundary conditions are used.

To follow the relaxation, all the atoms are given initially zero velocities. The potential energy introduced by the impurity transforms into kinetic energy; every time this attains its maximum, all velocities are set again to zero. The procedure is repeated until the desired precision in the atomic positions is attained.

Power spectra are usually obtained by giving random velocities to the atoms at their equilibrium positions, thermalizing the system, and Fourier transforming the velocity autocorrelation functions, averaged over sufficiently long (a rather loose definition) intervals, and over several runs; the autocorrelation functions are apodized using Gaussians, which is equivalent to a Gaussian convolution of their Fourier transform. The different runs correspond to different random initializations of the atom's

velocities. The problem is that unless the statistics are extremely good, spurious peaks appear, obscuring the true shape of the power spectrum.[5] We have found[12] that an alternative method is by far more effective: only one particle is initially given nonzero velocity; the time evolution of its velocity is Fourier transformed, and this is repeated for the nonequivalent directions around the atom to yield the local-power spectrum. In turn, all nonequivalent atoms in the crystal may be so excited, and this can be shown to correspond to equally exciting all the system's modes. This method yields unbiased, smooth, and well-defined power spectra, at a much reduced cost,[12] since to start with the thermalization steps are avoided. The time intervals used for Fourier transforms were chosen to smooth out the discrete states of the 500 atoms of the MD cell; in our case this gives a resolution of about 14% of the maximum frequency of the pure-crystal phonon bands. Although it is possible to use more atoms and a better resolution, we thought it unnecessary for our qualitative general results.

The infrared absorption spectra were obtained from the dipole moment autocorrelation function; the model and parameters for the induced dipoles were taken from the work by Bar-Ziv and Weiss.[11] As we were interested in obtaining quantitative results, the computations were performed with the crystal energy near the zero-point energy, since at the temperatures involved in actual experiments the crystal is mostly in its fundamental state. In Table I we show the LJ parameters used in the calculation.

III. LATTICE RELAXATION

Using the method outlined above with interactions including up to fourth neighbors, equilibrium positions are obtained with as few as 150 MD steps and about 10 coolings, with fluctuations of about 0.1% in the atomic positions.

The distortions around the substitutional impurity are limited by the fcc symmetry: calling its pth neighbors (pN), some allowed directions are 1N:[110], 2N:[100], 3N:[x11], and 4N:[110]. The magnitudes and signs of the distortions are determined by the relative sizes of

TABLE I. Parameters for the LJ potential used in the present calculation; $V(r) = \epsilon[(\sigma/r)^{12} - 2(\sigma/r)^6]$. k is the Boltzman constant.

	σ (Å)	ϵ/k (K)
Ne-Ne	3.25	28.3
Ne-Ar	3.43	71.9
Ne-Kr	3.58	74.5
Ne-Xe	3.75	75.0
Ar-Ar	3.87	114.1
Ar-Kr	3.88	164.0
Ar-Xe	4.10	190.0
Kr-Kr	4.11	156.4
Kr-Xe	4.18	229.0
Xe-Xe	4.46	215.1

the host and impurity atoms, and by geometric considerations. For a large impurity, the 1N are driven outwards by the impurity and push 4N in the same direction, while the 2N, not affected by the 1N (which are their first neighbors) because they move perpendicularly to the 1N-2N direction, relax towards the impurity attracted by it, although their relaxations are smaller. The 3N's are pushed by the 1N's (their first neighbors) but not as drastically as the 4N's, because they are not in the direction of movement of the 1N's. Obviously all signs are reversed in the case of a light impurity or a vacancy. The fact that the relaxation of the 2N is determined exclusively by their interaction with the impurity is confirmed by the results of a nearest-neighbor interaction calculation: all relaxations except those of the 2N's, which do not move, remain qualitatively the same.

We have calculated the displacements of 1N's to 4N's for all rare-gas combinations; beyond 4N's they are very small although 9N's, in line with the impurity, and 4N's, in some cases, move more than 2N's. The displacements of the 1N's range from 0.3% of the nearest-neighbor distance in Ar-Kr, to 10% in Ne-Xe; in the same cases, 2N's vary from 0.1% to 1.6%, the 3N's from 0.1% to 2.9%, and the 4N's from 0.1% to 4.7%. The changes in the effective impurity-1N force constant, when going from the undistorted to the distorted geometry are very significant; the percentage change is as large as 80% for the Ne-Xe system. We also found that a small impurity creates larger distortions than a vacancy; this is so because the former exerts an attractive force on its neighbors.

It must be noted that all previous calculations do not take into account the effects of lattice relaxations, at least consistently. They are usually ignored, assumed to be small, or at least assumed not to appreciably affect the vibrational properties,[2-4,13] based on calculations on vacancies such as Refs. 14 and 15, where only 1N's and 2N's are allowed to relax. Burton and Jura[16] performed a minimum-energy calculation on vacancies and substitutional Ne and Kr in Ar. On the hypothesis (here proved wrong) of a uniform decay of the distortion with distance, they free 1N's, 2N's and 3N's, leaving the rest of the crystal fixed. They find, in general, smaller distortions than we do, since in our case only the atoms on the boundary of the MD cell (13N's) are fixed. It is clear from our results that relaxation effects should by no means be neglected; the present results also show that a discussion of the dynamics of these systems in the quite usual[2] terms of a mass parameters $\epsilon = 1 - M'/M$ and a force constant parameter $\lambda = 1 - k'/k$, where the unprimed and primed quantities refer to host and impurity atoms respectively, may be qualitatively adequate, but is necessarily incomplete: the displacements of the impurity neighbors cause changes in the interactions with their neighbors, and, furthermore, since atoms are no longer at the minima of the LJ potential, first derivatives of the potential contribute to the effective force constants.

IV. VIBRATIONAL POWER SPECTRA

In Fig. 1 we show the local vibrational power spectra at the impurity, corresponding to the systems, where
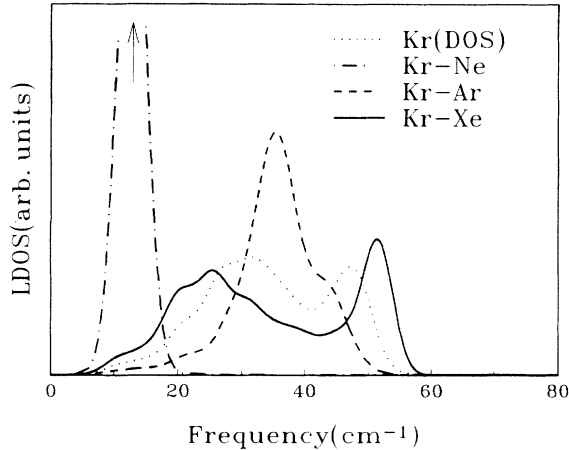
FIG. 1. Local vibrational densities of states (LDOS) at the impurity for Kr-impurity systems, compared with the density of vibrational states (DOS) of the corresponding pure crystal.

Kr is the host, which are representative of the different situations we encountered. In Table II we list the relevant data for all the rare-gas mixtures. We have used nearest-neighbor interactions here, after checking that the vibrational properties change negligibly when longer-range forces are neglected. It can be seen that excitations in the local densities of states fall into the three possible categories: (a) resonant modes, (b) localized modes, and (c) broad bands. (a) Ar-Ne, Kr-Ne, Xe-Ne, Xe-Ar, and Xe-Kr are systems in which the impurity is lighter than the host, but as a consequence their interaction is weaker, and the net result is to produce a resonance below the host's cutoff frequency. (b) Ne-Ar, Ne-Kr, Ne-Xe, Ar-Xe, and Kr-Xe are systems complementary to those in (a). The interaction strength upsets the mass effect, and localized modes beyond the majority bands are ob-

TABLE II. Frequencies in cm^{-1} of the main peaks in the power spectra of the twelve systems. In parentheses the same quantities divided by the cutoff frequency of the corresponding pure crystal.

	ν_1	ν_2	Type
Ne-Ar	20.6(0.37)	68.4(1.24)	b
Ne-Kr	16.3(0.29)	66.5(1.20)	b
Ne-Xe	11.6(0.21)	69.5(1.26)	b
Ar-Ne	18.2(0.27)		a
Ar-Kr	27.0(0.41)	62.1(0.94)	c
Ar-Xe	22.7(0.34)	70.2(1.06)	b
Kr-Ne	12.8(0.25)		a
Kr-Ar	35.4(0.70)		c
Kr-Xe	25.3(0.50)	51.5(1.02)	b
Xe-Ne	2.5(0.06)		a
Xe-Ar	28.0(0.64)		a
Xe-Kr	24.6(0.57)		a

^{a}Resonant mode.
^{b}Localized mode.
^{c}Broad band.

tained. At the same time there are contributions to the main band, and a peak associated with large wavelength modes, where the mass effect predominates. (c) Kr and Ar are relatively alike, and their mixed-crystal spectra are intermediate between cases (a) and (b); the impurity couples with the host lattice modes, giving rise to a broad band.

V. INFRARED ABSORPTION

The infrared absorption of a sample of unit thickness due to the transition between states i and f is given by[17]

$$\alpha_{fi}(\omega) = \frac{4\pi^2\omega}{3\hbar c}(N_i - N_f)|\langle f|\mathbf{M}|i\rangle|^2\delta(\omega - \omega_{fi}) , \qquad (1)$$

where N_i and N_f are the populations per unit volume, of the initial and final states respectively, $\mathbf{M}$ is the electrical dipole moment operator, and $\omega_{fi} = (E_f - E_i)/\hbar$. The absorption coefficient is obtained by summing over all possible transitions. In the classical limit it is possible to show that[17]

$$\alpha(\omega) = \frac{2\pi\omega}{3\hbar c}\frac{1}{V}[1 - \exp(-\beta\hbar\omega)]$$

$$\times \int_{-\infty}^{+\infty} \exp(-i\omega t)\langle\mathbf{M}(0)\cdot\mathbf{M}(t)\rangle dt, \qquad (2)$$

where $\beta = 1/kT$, V is the volume of the sample and $\langle\mathbf{M}(0)\cdot\mathbf{M}(t)\rangle$ is the autocorrelation function of the electrical dipole moment. In the pairwise approximation, the interaction between the impurity and an atom of the host induces a dipole moment

$$\bar{\mu}(r) = \mu(r)\cdot\hat{\mathbf{r}},$$

where r is the distance between the pair and $\hat{\mathbf{r}}$ is a unit vector along the interatomic axis, and the sum over all pairs yields $\mathbf{M}$. It is possible to calculate $\langle\mathbf{M}(0)\cdot\mathbf{M}(t)\rangle$ using the MD results, provided a law for $\mu(r)$ is given. Such a law has been proposed by Bar-Ziv and Weiss,[11] based on ir absorption spectra activated by collisions between rare-gas atoms and has been used, together with the corresponding parameters, in this work.

In all previous work on these systems, the absorption spectra have been evaluated in arbitrary units, or only the Fourier transform of $\langle\mathbf{M}(0)\cdot\mathbf{M}(t)\rangle$ has been reported. Since we are interested in promoting experimental work, and in improving the existing models, we must produce quantitative results.

The equivalence between Eqs. (2) and (1) is correct at high temperatures, but shows serious problems at low temperatures; for instance, it is seen immediately that at 0 K, where the crystal certainly absorbs, the atoms are classically at rest, and $\langle\mathbf{M}(0)\cdot\mathbf{M}(t)\rangle = 0$. To correct for quantum effects we do the following: the dipole moment autocorrelation function is calculated for the crystal at low temperature T, and the absorption coefficient thus obtained is renormalized with the coefficient $\langle x^2\rangle_Q/\langle x^2\rangle_C$, where $\langle x^2\rangle_Q$ and $\langle x^2\rangle_C$ are the theoretical quantum and classical mean square amplitudes of a

harmonic oscillator with the frequency of the main peak. Each absorption spectra involves 4000 MD steps (about 200 periods of the host cutoff frequency), the first 1000 for thermal equilibration and the rest to obtain the dipole moment autocorrelation function.

Figure 2 shows the absorption coefficient of the Kr-impurity systems calculated at 0 K with the method outlined above, for an atomic impurity concentration of 1%, and Table III the positions of the peaks of all the rare-gas mixtures and their integrated absorption. For the localized mode systems, the resonant bands are strongly reduced from the vibrational densities of states, as expected, since they correspond to long wave modes.

Of the three experimental papers concerning the far-infrared absorption of the systems, we will only consider the results of Keeler and Batchelder. The other works, as has already been discussed,[4] yield doubtful or inconsistent results, due to the lack of appropriate instrumentation at the time they were completed.

Keeler and Batchelder studied Ne and Kr in an Ar matrix, at concentrations of 0.15% and 1%, respectively; they grew large single crystals and used interferometric techniques. In Fig. 3 we reproduce their infrared absorption spectra.

For Ar-Kr, the results are completely different from ours, since we calculated a broad band, and they found a well-defined localized mode at 63 cm^{-1}. Furthermore, the intensity is the lowest calculated by us, much lower than the observed one; this is so because the potential parameter for the mixture is similar to those of the pure crystals, and the impurity moves in a region where the induced dipole is near its minimum. Clearly, the interaction potential used is too soft and must be modified. We have increased the LJ parameter σ by 3%, and obtained the result shown in Fig. 3(a), which is in good agreement with experiment.

In the case of Ar-Ne, the results of the calculations are in qualitative agreement with experiment, yielding a resonant band. However the calculated peak is at 18 cm^{-1}, whereas the experimental one is at 28 cm^{-1}. Increasing the LJ parameter σ by about 5% gives a re-
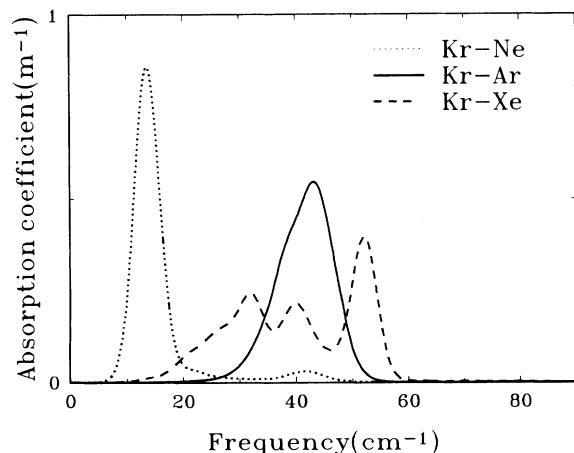
TABLE III. Frequencies of the peaks (in cm^{-1}) and integrated absorptions (in cm^{-2}) of the calculated infrared absorption spectra of the twelve systems and experimental values from Ref. 9. In parentheses values calculated with modified mixed LJ σ parameters (see Fig. 3).

	ν_p	α_{int}	ν_p[a]	α_{int}[a]
Ne-Ar	68.6	0.15		
Ne-Kr	66.8	0.54		
Ne-Xe	69.8	1.46		
Ar-Ne	18.8(27.9)	0.086(0.064)	28.0	0.24[b]
Ar-Kr	40.8(67.9)	0.01(0.116)	63.0	0.9
Ar-Xe	70.0	0.46		
Kr-Ne	13.7	0.054		
Kr-Ar	43.1	0.066		
Kr-Xe	52.0	0.068		
Xe-Ne	5.9	0.086		
Xe-Ar	28.0	0.162		
Xe-Kr	36.8	0.106		

[a]From Ref. 9.
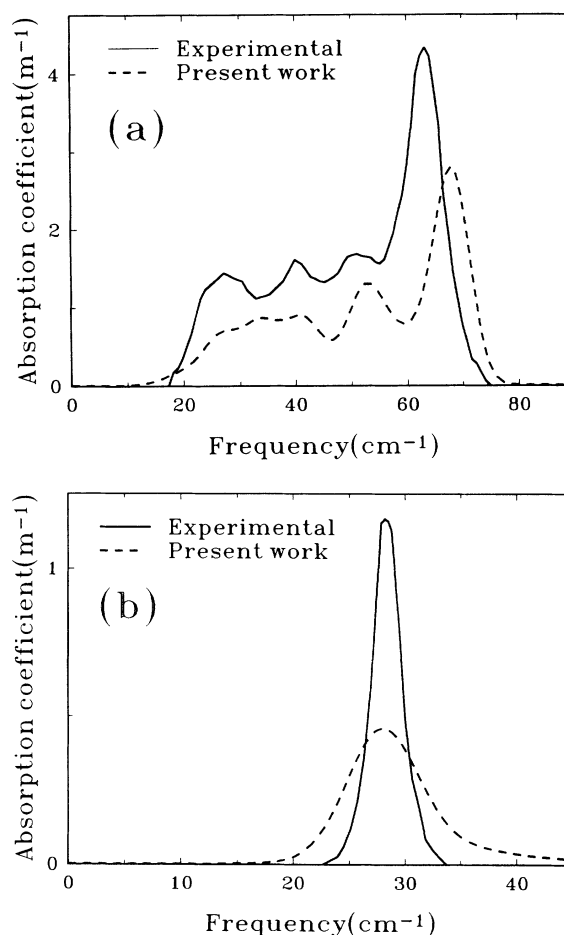[b]Normalized for a concentration of 1%.

FIG. 3. Calculated infrared absorption spectra with modified σ parameters of the LJ mixed-atom potentials compared with experimental data from Keeler and Batchelder (Ref. 9): (a) Ar with 1% of Kr at 2 K and (b) Ar with 0.15% of Ne at 2 K. The calculated intensities of the spectra are multiplied by 5.

FIG. 2. Calculated infrared absorption spectra for the Kr-impurity systems at 0 K and with 1% impurity concentration.

sult that exactly reproduces the position of the observed peak [Fig. 3(b)]. The calculated absolute intensities are about one order of magnitude smaller than observed ones, although the relative intensities of the two systems are qualitatively correct. It should be taken into account that the induced dipole model used here has been fitted to experiments involving interatomic distances between 0.6 and 0.85 of the potential minimum, and extrapolated to the distances used here; furthermore, these are very rapidly varying functions.

VI. CONCLUSIONS

It can be seen from the examples that comparison of the present calculations with available experiments may provide valuable information on the mixed rare-gas interactions. It certainly does not make too much sense to try a detailed refinement of parameters with the few existing experimental data. Furthermore, the two-body interactions between unlike rare-gas atoms seem to be well established, and three-body forces are known to be relevant in the rare-gas crystals. Since almost nothing is known about the three-body mixed-atom interactions, experiments—and the corresponding calculations—on complementary systems, i.e., A in B and B in A, which depend on the same two-body, but different three-body, terms (A-B-B and B-A-A, respectively), and the study of systems with larger impurity concentrations are sure to produce relevant on this very interesting problem. The present work is intended to be a step in that direction.

ACKNOWLEDGMENT

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