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Three-body-exchange interaction in dense rare gases

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Self-consistent phonon calculations are employed to demonstrate the importance of the three-body-exchange interaction in dense rare-gas solids. A Slater-Kirkwood form is adopted, the parameters of which are adjusted on *ab initio* calculations for helium and argon and calculated by a scaling law for krypton and xenon. When used in conjunction with realistic (Aziz) pair potentials and the Axilrod-Teller terms, the exchange interaction brings the calculated equation of state for each rare gas into excellent accord with experiment. This type of interaction should stabilize the hcp structure for all rare gases below 90 GPa.

I. INTRODUCTION

Recently there has been renewed interest in the importance of three-body interactions to model dense rare gases, mostly motivated by the emphasis on the contribution of three-body-exchange interaction. The different papers found in the literature can roughly be divided into two opposing views.

(a) Those that tend to confirm that a good pair potential together with the three-body dispersion interaction, represented by the Axilrod-Teller (AT) term, lead to an accurate description of experiments on dense rare gases in liquid or solid phases. In this spirit, Meath and Aziz[1] have redone the calculation of the zero-pressure zero-temperature cohesive energy of rare-gas crystals with the best available potentials and found good agreement with experimental data when taking into account the AT three-body interaction. Thus, they confirm many previous calculations reviewed in Ref. 1. Barker also has extended the region of validity of such an analysis in dense liquid krypton and liquid xenon,[2] and even in highly compressed solid argon and solid xenon,[3] but with somewhat less satisfactory agreement.

(b) Those that give evidence of the importance of three-body-exchange interactions in the analysis of the properties of dense rare gases. Recent quantum theoretical calculations have indicated that the three-body-exchange interaction is greater in magnitude than the AT term for small interatomic distances but of opposite sign, and consequently cannot be neglected in the analysis of the properties of dense rare gases at high densities.[4–6] Grimsditch *et al.*,[7] analyzing the properties of highly compressed solid argon, have shown that it was impossible to simultaneously reproduce both the equation of state and the elastic constants, using an effective pair potential approach. This demonstrates that noncentral interactions, suspected to be the three-body-exchange ones, are necessary. Ross *et al.*[8] arrived at the same conclusion in analyzing shock-wave data and x-ray measurements on dense argon.

In order to understand the reasons behind these conflicting views, it should be stressed that the conclusions of the calculations are strongly dependent on the reference pair potential used. Although the three-body dispersion interactions are well known, at present there are only fragmentary calculations of the three-body-exchange one for some selected geometries of a triplet.

In this context, helium appeared to be the best candidate for a first quantitative investigation on this problem since its electronic simplicity makes the calculation of its pair potential and its three-body interactions the most reliable. In a recent article,[9] the author of this paper has calculated the equations of state of dense liquid and solid helium using pair and three-body interactions, and has shown that three-body-exchange interaction is necessary to bring the calculation into agreement with experiment. This conclusion was then generalized to the heavier dense rare gases which are known to have greater many-body interactions.

The aim of this article is to quantitatively check this statement by comparing, for each rare-gas solid, the equation of state calculated with and without the three-body-exchange interaction, with recent experimental x-ray data.

In Sec. II we will briefly present our self-consistent phonon calculation and show that for each rare gas the calculations based only on the best pair potential do not agree with experiment and, hence, that many-body interactions must be taken into account. In Sec. III we will probe the influence of three-body-exchange and AT interactions. It will be shown in Sec. IV that three-body-exchange interactions induce an fcc-hcp phase transition in rare-gas solids below 90 GPa.

II. SELF-CONSISTENT PHONON CALCULATION AND PAIR POTENTIAL

In a recent work on the high-pressure phase diagram of ^{4}He (Ref. 10), the self-consistent harmonic (SCH) theory corrected for the cubic anharmonic term calculated on an Einstein phonon distribution [SCH-cubic Einstein (CE) term] was shown to be an accurate statistical model for analyzing properties of dense insulators even near melting; it was tested on Monte Carlo free energy and molecular dynamic structure factor calculations. This model was then used to calculate the properties of dense solid argon.[7]

The reader is referred to the comprehensive reviews of Ref. 11 and to Ref. 12 for a detailed presentation of the method. Since we have used the same program as previously, the basic equations and numerical implementation of the method can be found in these two previous papers.[7,10] Here we will simply survey the basic ideas of the method. In the SCH model the force constants, used to calculate the dynamical matrix, are self-consistently averaged over the positions of the atoms undergoing thermal motion. These vibrational consistency conditions are the variationally best choice of a harmonic reference system and that mostly takes into account even anharmonic terms. The first odd anharmonic term of the perturbation correction to the SCH free energy, F_{33}, has to be taken into account for better accuracy[10] only near the melting region. Since it involves a lengthy procedure with a double sum on the Brillouin zone, an estimate of it was obtained within the framework of an Einstein approximation; a multiplicative constant was added in order to compensate for the fact that by replacing the frequency spectrum by its Einstein approximation, F_{33} would be underestimated. This multiplicative constant was determined against Monte Carlo free energy calculations for the fcc and bcc structures;[13] we took the same value of this corrective constant for the hcp structure as for the fcc one since the dispersion curves of the hcp structure can be obtained in a first approximation by folding the fcc Brillouin zone.

Having a reliable model to describe the solid phase, we need to select the best available pair potential for each rare gas considered in this work: As pointed out in the Introduction, this is mostly important for not biasing the conclusions on the importance of three-body-exchange interaction. It should reproduce, at best, the purely pair potential properties like virial coefficients, viscosity, dimer spectroscopy, and collision cross sections. In this field, Aziz and co-workers have brought outstanding contributions over the past ten years; they continuously improved pair potentials for rare gases with new experimental data. Furthermore, their analytical form is simple and has the correct *ab initio* dependence on small and large interatomic separations; this gives us confidence in the second- and third-order derivatives of the potential with respect to the interatomic distance, needed for the SCH-CE calculations and also in the extrapolation of the potential in the intermediate repulsive wall region between the potential well and the repulsive region probed by beam scattering measurements. The forms proposed by Aziz are slightly different variants of the Hartree-Fock-dispersion (HFD) initial one. Their expressions are

$$\begin{aligned} &V(x)=e(V_1^*(x)+V_2^*(x)) \ , \\ &V_2^*(x)=-F(x)\sum_{j=0}^{2} C_{2j+6}/x^{2j+6} \ , \\ &F(x)=\begin{cases} \exp\{-[D/(x-1)]^2\}, & x<D \ , \\ 1, & x>1 \ , \end{cases} \\ &V_1^*(x)=A\exp(-ax) \end{aligned} \tag{1}$$

(HFD form) or

$$=Ax^G\exp(-ax)$$

(HFD-C form) or

$$=A\exp(-ax+bx^2)$$

(HFD-B form).

In a recent review by Aziz[14] on the pair interaction of rare gases, it was shown that the best potential was of HFD form for helium, of HFD-C form for argon and krypton, and of Barker-Fisher-Watts (BFW) form for xenon. Since that time there have been improvements: An HFD-B form is now proposed for argon[15] and for krypton[15] which slightly differ from the HFD-C previous determinations, and an HFD-B form is also proposed for xenon[16] which greatly differs from the one of Barker.

In Figs. 2–4 we compare the SCH + CE calculations of the equations of state with their recent x-ray diamond anvil cell measurements, respectively, for argon by Ross *et al.*,[8] for krypton by Polian *et al.*,[17] and for xenon by Asaumi[18] and by Zisman *et al.*[19] The error bars are mostly the ones of the ruby pressure scale, going from 2% around 1 GPa to 9% around 60 GPa,[8] but systematic errors exist on the volume which will be discussed herein. For helium such x-ray measurements have not been completed at the present time, and so in Fig. 1 the comparison is made against the accurate 4 K solid isotherm of Stewart measured with a piston cylinder device up to 2 Gpa.[20] It is easily seen that for all these comparisons, at a given pressure, the calculated SCH + CE volume is greater than the experimental one. It equivalently indicates that the pair potential of each of them is too stiff to agree with experiment and using softer effective pair interactions, as Ross has done in analyzing dense argon,[8] could bring agreement with experiment. Our aim in this paper is not to force agreement with experiment on a set of data which was shown to be unsatisfactory for a complete description of argon,[7] but to probe quantitatively the importance of three-body interactions.

III. THREE-BODY INTERACTIONS

The potential energy of a system of N closed-shell entities can be developed in a cluster series:

$$V(1,2,\ldots,N)=\sum_{(i,j)} V_2(i,j)+\sum_{(i,j,k)} V_3(i,j,k)+\cdots \ . \tag{2}$$

Generally only the first term of the right-hand side (rhs) is kept in assuming pairwise additivity of the interaction, and this assumption has been essential for the practical success in statistical treatments of many physical phenomena. The second term V_3 is the three-body correction to the interaction of a triplet of atoms by its representation in a sum of pair interactions. Higher-order many-body interactions known to be much smaller are neglected here. At large interatomic separation the main contribution to V_3 comes from the triple dipole interaction, the AT term, and, at smaller internuclear separations, the three-body-exchange overlap interaction is the dominant term.

TABLE I. Parameters of the Slater-Kirkwood form of the three-body interaction given in Eq. (7); e is the well-depth parameter of the Aziz pair potential.

Rare gas	A/e	a (Å^{-1})	C/e	e (K)
Helium	892 377.9	1.936	140.9	10.8
Argon	2 929 433.3	1.650	3770	143.224
Krypton	2 695 078.6	1.546	8113	201.2
Xenon	2 197 074.9	1.422	19319	282.29

A. Triple dipole interaction, AT

This term, abbreviated AT because it was first introduced by Axilrod and Teller,[21] can be straightforwardly derived by applying third-order Rayleigh Schrödinger perturbation theory to a triplet i,j,k of rare-gas atoms, i.e., neglecting exchange effects. It is of simple analytical form:

$$V_{\mathrm{AT}}=C(1+3\cos t_1 \cos t_2 \cos t_3)/(r_1 r_2 r_3)^3 \; , \tag{3}$$

where r_1,r_2,r_3 and t_1,t_2,t_3 are the sides and internal angles of the triangular configuration of the interacting atoms. The values of the coefficient C are taken from Doran and Zucker[22] and reported in Table I. Its contribution to the free energy is taken into account by its static lattice energy given by

$$E_{\mathrm{AT}}=\frac{1}{6}\sum_{i,j,k} V_{\mathrm{AT}}(i,j,k) \; . \tag{4}$$

Adding this term to the SCH + CE free energy calculated with the pair potential interaction gives the SCH + CE + AT free energy. By its volume differentiation we obtain a new equation of state which is compared with the experimental one in Fig. 1 for helium, Fig. 2 for argon, Fig. 3 for krypton, and Fig. 4 for xenon. The common feature of all these comparisons is that taking into account the AT term increases the discrepancy with experiment; except in the near melting region where the experimental points reported are those of Anderson and Swenson.[23]

The conclusion of this subsection is that above a certain density, many-body interactions other than the AT interaction and of negative contribution play an important role. The purpose of the following subsection is to prove that this three-body-exchange interaction is the dominant contribution which has to be considered.

B. Three-body-exchange interactions

At small interatomic distances, three-body-exchange interaction quantifies the effect that the charge clouds of two interacting molecules are altered by the presence of a third one. In the past ten years, many *ab initio* works on this exchange repulsion nonadditivity for rare gases and H_2 have been completed based on different methods of calculation such as self-consistent field[24] (SCF), configuration interaction[25] (CI), perturbational,[4] and variational approaches.[6,26] The large scattering of the results of the various methods illustrates that this interaction is vastly more difficult to calculate accurately than the dispersion nonadditive interactions, especially for large interatomic distances. Furthermore, there is no intrinsic simple geometrical form to represent this six-dimensional energy surface as for the AT one. Except for Jansen and Bruch, who have given analytical fits of their calculations, generally only few selected configurations of the atomic triplets have been considered, and that prevents even a coarse tabulation of the energy surface needed in calculations. The contribution of this nonadditive ex-

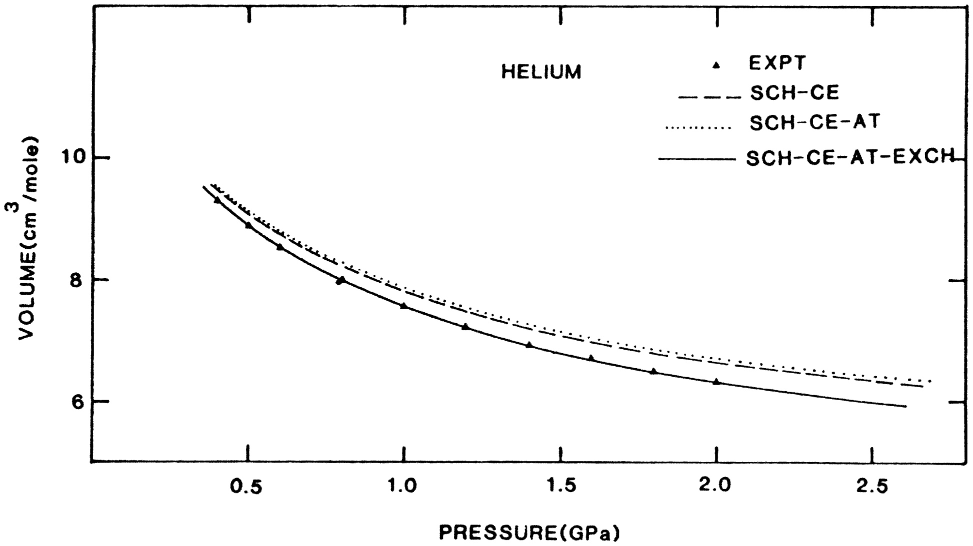

FIG. 1. Comparison between various equations of state of solid ^{4}He at $T=4$ K: triangles, measurements of Stewart (Ref. 20); dashed line, SCH + CE model with Aziz pair potential; dotted line, AT interaction is added to the pair one; full line, exchange three-body and AT interactions are added to the pair one.

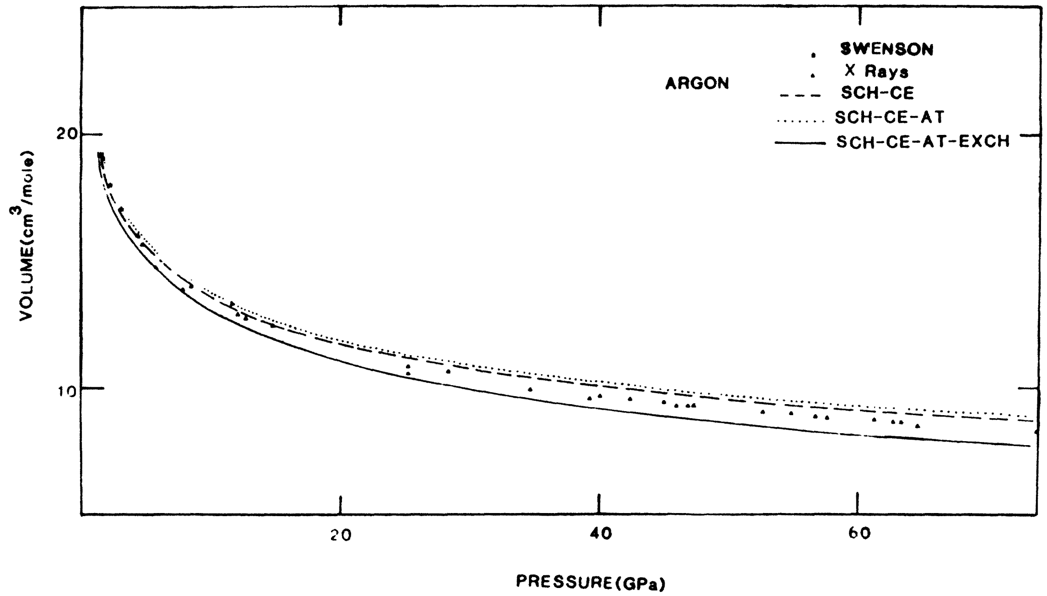

FIG. 2. Comparison between various equations of state of dense solid argon at $T=300$ K: stars, piston-cylinder measurements (Ref. 23); triangles, x-ray measurements of Ref. 8; dashed line, SCH + CE calculation with Aziz pair potential; dotted line, AT interaction is added to the pair one; full line, exchange three-body and AT interactions are added to the pair one.

change effect to the free energy is mainly due to its static lattice energy, particularly at high density. The dynamical contribution is much smaller and will be neglected here as it was previously for the AT term. Knowing that the three-atoms-exchange interaction affects only the immediate neighborhood of an atom, this energy is calculated by summing over all the different triplets composed of two nearest neighbors surrounding a central atom (66 for an fcc or hcp structure) and with a $\frac{1}{3}$ multiplicative constant for equilateral triangles to prevent double counting. For an fcc or hcp lattice with nearest-neighbor distance $R_1(=2^{1/6}v^{1/3})$ it gives

$$f_{\text{exch}}=8V_3(R_1,R_1,R_1)+12V_3(R_1,R_1,\sqrt{2}R_1)+24V_3(R_1,R_1,\sqrt{3}R_1)+6V_3(R_1,R_1,2R_1)\ . \quad (5)$$

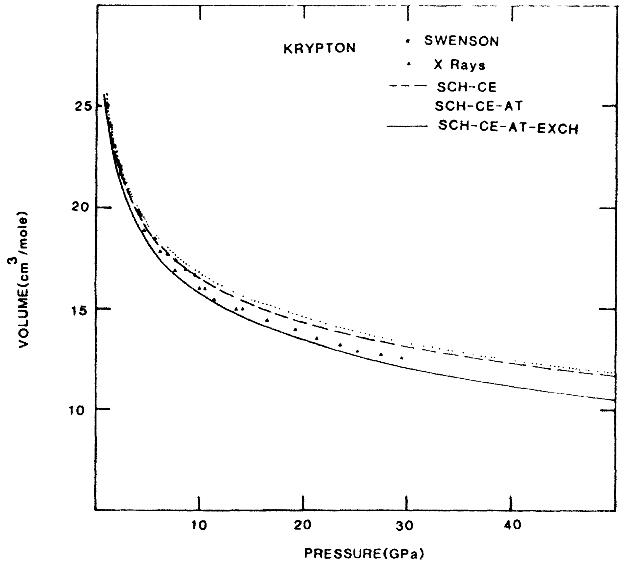

FIG. 3. Comparison between various equations of state of dense solid krypton at $T=300$ K: The symbols are the same as in Fig. 2 except for the triangles which represent x-ray measurements of Ref. 17.

This three-body-exchange free energy is added to the SCH + CE + AT terms to make up the total free energy of the system. The equation of state is then obtained by differentiation with the volume. Such a calculation can only be done if the different triplet configurations which come in the sum can be taken into account. As pointed out above, few calculations give data for three atoms in an isosceles configuration as the apex angle and the triplet length are varied.

Because of its electronic simplicity, calculations on helium are less time consuming and more accurate; Bruch and McGee[26] have derived a simple analytical fit of their calculations which agree with the recent ones of Jeziorski *et al.*,[27] given by

$$V_{\text{exch}}=-A\exp[-a(r_1+r_2+r_3)]\times(1+3\cos t_1\cos t_2\cos t_3)\ , \quad (6)$$

where A and a are constants and r_1, r_2, r_3, t_1, t_2, and t_3 have the same meanings as in Eq. (3).

That makes a Slater-Kirkwood form of the three-body interaction V_3:

$$V_3=\{-A\exp[-a(r_1+r_2+r_3)]+C(r_1r_2r_3)^{-3}\}\times(1+3\cos t_1\cos t_2\cos t_3)\ . \quad (7)$$

It has the same geometrical dependence as the AT term,

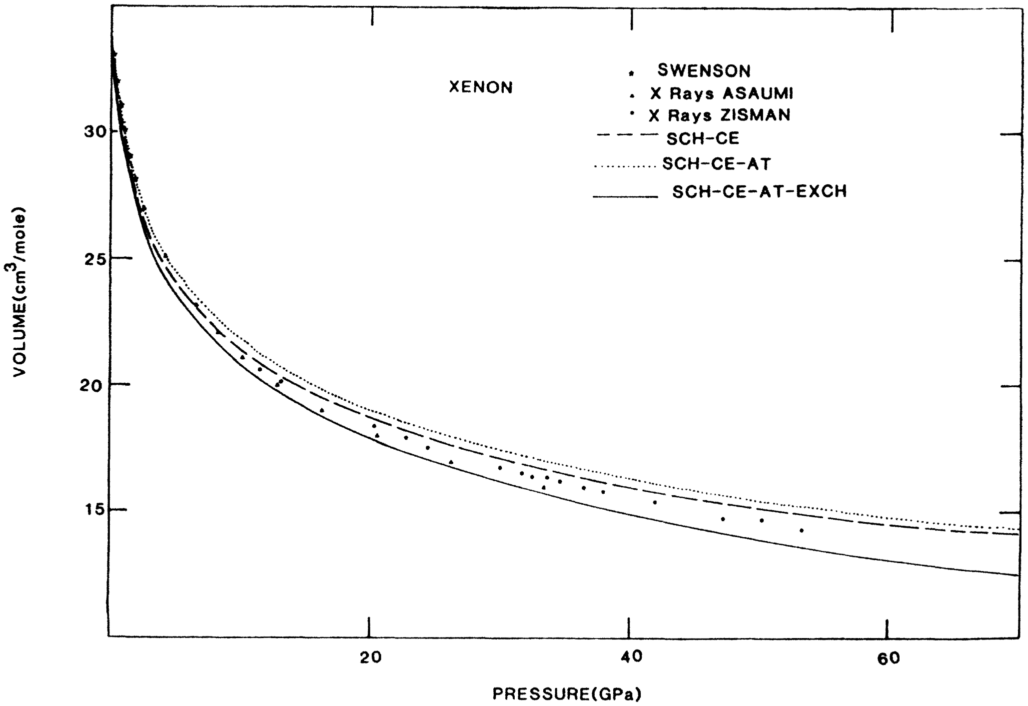

FIG. 4. Comparison between various equations of state of dense solid xenon at $T=4$ K: The symbols are the same as in Fig. 2 except for the triangles which represent x-ray measurements of Ref. 18 and the dots the ones of Ref. 19.

is of opposite sign, and varies with interatomic distances exponentially as a two-body-exchange overlap interaction. Using this potential for helium with the parameters given in Table I, it is seen in Fig. 1 that it brings good agreement with Stewart's experimental data.[20] Furthermore, it was shown in a previous article that the exchange term also brings agreement with the room-temperature liquid-helium equation of state measured by Brillouin scattering up to 12 GPa (Ref. 28), but that the AT term alone would increase the discrepancy. Another fit of three-body-exchange interaction potential for the heavier rare gases was proposed by Jansen.[29] Using this type of fit of the three-body-exchange energy surface,[30] we have calculated the equation of state of dense solid argon and compared it to experiment in Fig. 5. It is clear that at small densities, the Jansen-type fit overestimates three-body-exchange forces: It confirms what has been pointed out before, i.e., that the Gaussian charge distri-

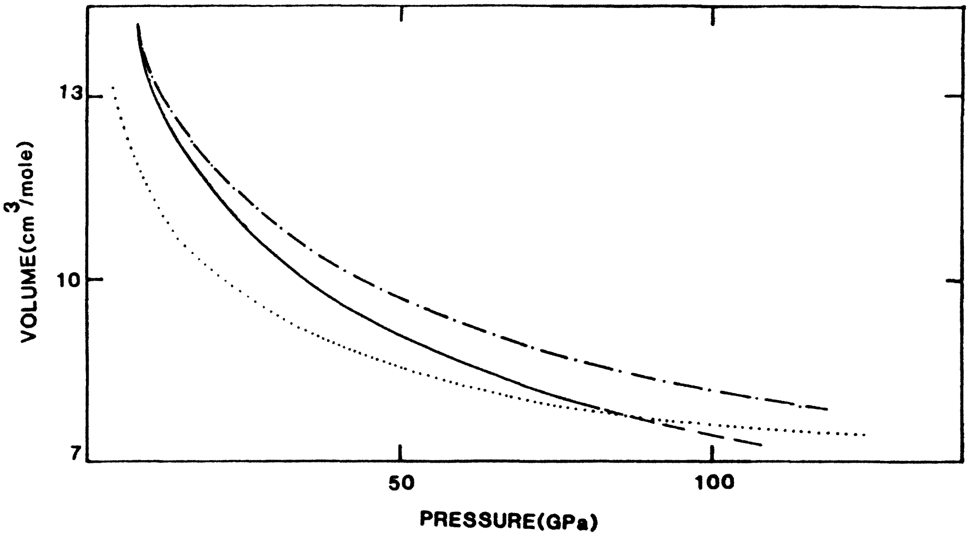

FIG. 5. Comparison between various equations of state of dense solid argon at $T=300$ K: full line, fit of the x-ray measurements (Ref. 8); dashed and dotted line, SCH + CE calculation with the Aziz pair potential; dotted line, three-body interaction of the Jansen type (Ref. 30) are added to the pair interaction.

bution used in his perturbational calculation is much too extended and leads to an unrealistically large overlap between interacting atoms.[1] The discrepancy at higher pressures shows that even its variation with density is not good.

All studies on the geometrical evolution of three-body-exchange interaction indicate clear similarities with the AT one but of opposite trends, i.e., for an equilateral geometry its contribution is negative, and positive for a linear contribution. Bruch *et al.*[31] have studied this evolution more quantitatively by determining the position of the nodal angle (it is the apex angle of an isosceles triangle for which the three-body interaction is zero). For the AT term it is equal to 117.22°. For three-body-exchange energy there is no universal value: For a triangle composed of three helium atoms it is equal to 120°, very near the AT value, and that explains why the simple Slater-Kirkwood form was used by Bruch and McGee[26] to fit He three-body interactions. For neon atoms it is equal to 106° and for argon atoms to 125°.

However, since the position of the nodal angle is quite sensitive to the method of calculation used, we can postulate that the geometrical dependence of three-body-exchange interaction in rare gases is the same as the AT one. Furthermore, its variation with interatomic distances is supposed to be of an exponential type as for two-body-exchange overlap interaction. These two hypotheses are equivalent to assuming a three-body interaction potential of the Slater-Kirkwood form, given in Eq. (7), which is of great computational ease for calculations in dense matter. In the continuation we will use this analytical form to model three-body interactions in argon, krypton, and xenon.

For argon, the parameters A and a of Eq. (7) are adjusted on the best available three-body exchange calculations of Bulski and Chalasinski[5] which were done for equilateral configurations of different side lengths. Their values are reported in Table I.

With this three-body potential we calculate the equation of state of solid argon reported in Fig. 2. We see that three-body-exchange interaction brings reasonable agreement with experiment over a large density domain. For small density, in the near melting region the best agreement is obtained by the AT term only as previously remarked; the three-body-exchange interactions are certainly overestimated in this large interatomic distance region as noted by Wells and Wilson[32] who have recently shown that taking into account basis set superposition errors in the calculation of the three-body energy of three helium atoms in an equilateral configuration of side length $5.6a_0$ gives a value 4.7 times smaller than the Bertran-Lopez[33] one which ignored this source of error.

For a better comparison between theory and experiment, we have to report what seems to be an inherent drawback of diamond-anvil-cell (DAC) x-ray measurements of the equation of state of rare-gas solids; i.e., the lattice constant obtained from the (200) line is always greater than those obtained from other diffraction lines. As pointed out in Refs. 17 and 18, this discrepancy increased as the pressure was increased, and amounted to 1.3% around 30 GPa. So, the more lines that are considered for averaging the volume, the less is the systematic discrepancy induced by the (200) line. Knowing that, it thus seems to us that: The volumes of xenon measured by Asaumi[18] [averaged over eight diffraction lines including the (200) one] are 0.6% too large; the volumes of xenon measured by Zisman *et al.*[19] [averaged over three lines including the (200) one] are 2% too large; the volume of krypton measured by Polian *et al.*[17] [averaged over six lines including the (200) one] are 0.8% too large; finally the volume of argon measured by Ross *et al.*[8] [averaged over the (111) and (200) lines] are 2% too large.

So, lowering the experimental x-ray equation of state of argon by 2% brings good agreement with the SCH + CE calculation corrected for three-body exchange and AT interactions.

For krypton and xenon there is unfortunately no accurate calculation, like the one of Bulski and Chalasinski for argon, on which to fit the A and a parameters of their Slater-Kirkwood three-body interaction potentials [Eq. (7)]; the c parameter is given from Ref. 22 as noted above. We will make the intuitive hypotheses, verified *a posteriori* by the good agreement with experiment over a large density region: In reduced atomic distance units, i.e., $x = r/s_i$, where s_i is the hard-core diameter of atom i, the ratio of three-body-exchange interaction of argon (denoted 1 in the following two equations) over the one of xenon or krypton (denoted 2) is equal to the ratio of their two-body-exchange interactions as formulated in Eq. (8a); and their variations with interatomic distances are equal in reduced distance units as formulated in Eq. (8b)

$$A_1\exp(-3a_1s_1x)/A_2\exp(-3a_2s_2x) = V_1(xs_1)/V_2(xs_2)\ , \quad (8a)$$

$$a_1s_1 = a_2s_2\ . \quad (8b)$$

The V_i are the Aziz pair potentials of the rare gases considered; the ratio of the two-body-exchange interaction potentials is averaged over different repulsive interatomic distances. The values of A and a so calculated for krypton and xenon are reported in Table I.

The equation of state of krypton and xenon, calculated with these three-body interactions, are compared in Figs. 3 and 4 to their experimental x-ray measurements. The agreement is much improved over the calculations considering only the pair potential or adding the AT term. Furthermore, if we consider, as analyzed above, a systematic positive deviation of roughly + 1% for the measured volume of krypton by Polian *et al.*[17] and for xenon by Asaumi,[18] the agreement becomes quite good. As for argon, the agreement gets worse in the near melting region where the AT term by itself well represents three-body interactions. Three-body-exchange interactions are overestimated in this density region, as pointed out recently.[32]

It could be argued about the need of such a description of three-body interaction since an effective pair potential which includes their isotropic average can well reproduce the experimental equation of state. First, it was shown for argon at high densities that the potential that best reproduces the equation of state worst reproduces the equation of state worst reproduces the elastic constants, which are direction-dependent quantities.[7] In the next section, we will show that an fcc-hcp phase transition is induced by three-body exchange forces; if that were experimentally confirmed in the future, it would certainly illustrate the improvement gained by explicitly taking into account three-body-exchange interaction.

IV. fcc-hcp PHASE TRANSITION IN DENSE RARE GASES

The idea that three-body interactions are probably the key to understanding the problematical $P=0$ GPa rare-gas solid stability was first pointed out by Axilrod,[35] who found that the AT term tends to favor fcc over hcp, but not enough to explain the well-known fcc stable structure of rare-gas solids. Then Jansen[36] proposed for the first time to take into account the three-body-exchange interaction, but serious doubts were cast on his calculation, and a review of this problem is fully discussed in Ref. 37. However, this can give us some insights to guess that hcp should be more stable than fcc in dense rare-gas solids from the following considerations: Three-body-exchange interaction as shown above has the same geometrical dependence as the AT one, but is of opposite sign; consequently, as the AT stabilizes the fcc structure, the exchange term would favor the hcp one, and being the dominant term at high density, hcp could be more stable in dense rare-gas solids.

Using the free energy calculation and the potentials presented above, which bring good agreement with the experimental equations of state, we can quantitatively probe this idea. On the 66 triplets, composed of a central atom and two of its nearest neighbors, which constitute the three-body-exchange energy per atom, only nine are different between the fcc and hcp structures. Calling R_1 the nearest neighbor distance, the three-body-exchange energy is given by Eq. (5) for the fcc phase and by the following expression for hcp:

$$\begin{aligned} f_{\mathrm{exch}} = {} & 8V_3(R_1,R_1,R_1)+12V_3(R_1,R_1,\sqrt{2}R_1) \\ & +3V_3(R_1,R_1,\sqrt{8/3}R_1) \\ & +18V_3(R_1,R_1,\sqrt{3}R_1)+6V_3(R_1,R_1,\sqrt{11/3}R_1) \\ & +3V_3(R_1,R_1,2R_1) \; . \end{aligned} \tag{9}$$

The total free energies of the fcc and hcp structures are calculated for different volumes at $T=300$ K. A double Maxwell tangent construction gives the fcc-hcp transition pressures for helium, argon, krypton, and xenon. They are reported in Table II.

It seems that we can have confidence in the prediction of this phase transition since the calculated pressures are in the density regions where there is good agreement between the experimental and theoretical equations of state. But it should be remembered that the free energy difference is very small at the transition (roughly 10^{-4}) and can depend on the fit used to represent exchange three-body interactions. However, the calculated transitions are not incompatible with existing previous experimental data: at the limit of x-ray experimental investigation for argon;[8] for krypton well above any measurements;[17] for xenon above x-ray and absorption measurements.[18]

TABLE II. Pressure of the predicted fcc-hcp phase transition.

Rare gas	Pressure fcc-hcp
Helium	60 GPa
Argon	80 GPa
Krypton	65 GPa
Xenon	64 GPa

More interestingly, such a phase transition is now within experimental reach; its investigation could bring very sensitive information on the geometrical dependence of exchange three-body interaction.

This could also change the predicted pressure of metallization of xenon[38] since the possible stability of the hcp phase was not considered. Finally, it should be recalled that such a sequence of transitions fcc-hcp-bcc was predicted in He (Ref. 39) and argon (Ref. 40) by linear muffin-tin orbital (LMTO) band-structure calculations by Young *et al.* and McMahan. They could only give an upper pressure bound for the fcc-hcp transition, less than 1100 GPa for helium and less than 230 GPa for argon since in the density regions where the atomic electronic shell is not distorted enough, the fcc-hcp free energy difference is less than the numerical uncertainty of the LMTO calculations. That further stresses the utility of such a description in terms of three-body interactions to bridge the gap between two well-known models of solids: at low densities, standard statistical calculations with pair interaction, possibly corrected by the AT term, and in the very high-density region where the solid is a semiconductor approaching metallization, band structure calculations which effectively take into account higher-order many-body interactions.

V. CONCLUSION

This study is the first quantitative analysis showing the importance of three-body-exchange interaction in dense rare-gas solids. It was enabled by the recent developments of high-pressure technology which have produced DAC x-ray measurements of the equations of state of rare-gas solids up to nearly 100 GPa, and by the care paid by Aziz's group to determine more and more accurate pair potentials. We have assumed a Slater-Kirkwood form for the three-body-exchange potential that was somehow verified *a posteriori* by the very good agreement with experiment over a large density domain. It induces an fcc-hcp phase transition below 90 GPa in all the rare-gas solids investigated. In the low-density region we have confirmed that the AT term alone brings good agreement with experiment and that three-body-exchange forces are generally overestimated there.

We hope that this work will stimulate accurate *ab initio* calculations of three-body interactions for various geometry of the triplets of rare-gas atoms which should be presented in a form of simple computational use. Furthermore, the experimental investigations of the possible fcc-hcp phase transition, being a very sensitive test of these interactions, could be of great use for future theoretical analyses on the importance of three-body forces in dense matter. Works proceeding in this direction are in progress in our laboratory.

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