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Thermodynamic properties and superconducting transition temperature of vanadium doped with heavy impurities

M. D. Tiwari
University Grants Commission, Bahadur Shah Zafar Marg, New Delhi 110 002, India

R. Kassing
Institut für Technische Physik, Universität Kassel, 3500 Kassel, Federal Republic of Germany

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The low-temperature phonon specific heat of vanadium-based alloys V:Hf, V:Ta, and V:W has been studied theoretically on the basis of a Green's-function technique. A nearest-neighbor impurity model with radial and angular force-constant changes has been employed. The force-constant changes have been evaluated by fitting the measured lattice specific heat of these systems. The effect of volume change has been taken into account. The theory has been modified for comparatively higher concentrations of impurities. The resonances have been found in F_{1u}-irreducible representations only. The local strength constants were found to be quite important in determining the increase or decrease of the transition temperature T_c. It has been observed that T_c increases slightly if the force constants for a heavy impurity (Hf) change weakly, and T_c shifts to lower temperatures (V:Ta,W) if the changes are strong. The electron-phonon as well as electron-impurity interactions are discussed in detail. The calculated results for both properties are in good agreement with the experimental measurements.

I. INTRODUCTION

The study of the nature of the variation of the temperature T_c, characterizing the transition of metals into the superconducting state, as the number of nonmagnetic impurity atoms is varied, forms the content of a number of papers.[1–25] The question of the influence exerted on T_c of a metal by atoms of non-magnetic impurity with mass M, which differs greatly from the mass M_0 of the atoms of the host metal, when local ($M \ll M_0$) or resonance ($M \gg M_0$) phonon states appear in the phonon spectrum, is one of the interesting but little investigated problems of superconductivity physics. Since, in general, introduction of impurity atoms with $M \neq M_0$ into a metal alters not only the phonon spectrum but also the density of the electron states on the Fermi surface and the Coulomb-repulsion potential, an experimental study of the influence of heavy or light impurity atoms on T_c calls for the use of methods that make it possible to determine the variation of both the phonon and the electron spectra. Such methods have been made possible by the development of tunnel spectroscopy with superconductors as well as of inelastic scattering of neutrons in conjunction with measurements of the temperature dependence of the specific heat, and the electrical conductivity.

The influence of localized and resonance modes in the phonon spectrum on T_c of metals with impurities was considered theoretically by a number of authors.[5–7,10,23–25] In practice, however, the analysis of the connection between the properties of metal in a normal state and T_c is based, both for pure metals and for metals with impurities or alloys, on the McMillan equation[8] or its modification.[25] Most of the theoretical papers, based on the approximate solutions of the integral equations obtained by Eliashberg[1] for the energy-gap function are rigorously valid for regular crystals. In crystals containing many impurities and in disordered compounds, the phonon and electron systems can undergo appreciable changes in comparison with a regular crystal. Obviously, the theoretical concepts applied to such disordered systems should take into account these changes, and take into consideration the dynamic character of the defects. Markowitz and Kadanoff[2] as well as others[25] have considered only static defects in the theory of superconductivity. They[2] have taken the isotropization, caused by the elastic scattering of electrons by defects, of an anisotropic energy-gap in a real regular crystal. According to the usual estimates, isotropization gives rise to a very significant reduction of T_c. Moskalenko and Palistrant[26] had set themselves the aim of determining the role played by impurities in superconductors by assuming the existence of several energy gaps. However, the model with several energy gaps is, generally speaking, inapplicable to nontransition metals where, in accordance with the experimental data,[27] the anisotropy of the gap does not exceed 30–40 %, and it is also inapplicable to transition metals even with a very small content of impurity atoms.[27] Bar'yakhtar *et al.*[28] have investigated the effect on T_c of the modifications of the electron spectrum near singularities due to the presence of impurities. Maksimov[29] has calculated the renormalization due to impurities of the effective interaction parameter, which gives rise to the pairing of electrons. The difference was taken into account in the scattering amplitudes between the atoms of the basis lattice and the impurity atoms, and also, to some extent, the special nature of the oscillations of the group of atoms singled out near the impurity.

An approach to the determination of the critical temperature, applicable for nonideal crystals, can be developed by using Green's-function technique. It is quite clear that such an approach is fruitful in the investigation of the thermodynamic and kinetic properties of impure crystals. In the present work we have considered the effect of changed-lattice dynamics due to impurities on the electron-phonon spectral function $\alpha^2(\omega)f(\omega)$ by using this formalism. Recently, Taylor[21] has calculated the lattice dynamics of isolated H and D interstitials in Al, and studied the superconducting T_c for dilute H and D in Al. We will take some pertinent equations from his work, and use our earlier results to study the effect of impurities on the phonon heat capacity, and transition temperature of V doped with Hf, Ta, and W. The model will include the mass changes at the impurity site as well as changes in the radial (Γ) and angular (Γ') force constants. The changes in volume due to substitution of impurities in V will also be taken into account. We have already used Green's-function formalism for studying various impurity-induced lattice dynamical properties of solids.[23,30–38] In these studies either the volume change effect has been ignored completely[30–32] or no proper account of this effect was made.[33–35,37] One important property of point defects is the static displacement field due to the forces exerted by the defect on its neighbors. A static displacement field also leads to changes of the force constants. Here one has to distinguish between two different kinds of displacement: (i) the displacement d^{∞}, which would occur in an infinite crystal; (ii) in addition to d^{∞} a very small image field, $d(r)^{\text{image}}$, exists, which allows the surface of the finite crystal to be force free. The total image field practically represents a uniform expansion. The total volume change ΔV is the sum of the corresponding volume change ΔV^{∞}, and ΔV^{image}. Near the defect, due to appreciable changes in the nearest-neighbor distance [displacements are larger given by $d^{\infty}(r)$], we have local force-constant changes. However, in the defect-free region the lattice is only dilated due to d^{image}, ΔV^{image}, and, in addition to local force-constant changes, we have a homogeneous softening of the force constants due to the image expansion. Erroneously, it has been assumed in the past[33–35,37] that the change in force constants due to lattice expansion is proportional to ΔV instead of being proportional to ΔV^{image}. Whereas the theory, taking local force-constant changes into account, has been worked out in considerable detail, there are still very few correct treatments of the lattice expansion effect.[39] In the present paper we will emphasize the correct treatment of the volume expansion.

The changes in the transition temperature due to impurities will be studied by using the relation given by Bergmann and Rainer:[15]

$$\Delta T_c = \int_0^{\infty} d\omega \frac{\partial T_c}{\partial \alpha^2(\omega)f(\omega)} \Delta \alpha^2(\omega)f(\omega) \ . \tag{1}$$

The functional derivative $\partial T_c/\partial \alpha^2(\omega)f(\omega)$ has the important property that T_c is changed by an amount ΔT_c given by the above equation, when $\alpha^2(\omega)f(\omega)$ is changed by a small amount $\Delta \alpha^2(\omega)f(\omega)$. Bergmann ad Rainer[15] have used the Eliashberg theory in its imaginary-axis form to provide an elegant and definite answer to the question of which phonon frequencies are most influential in determining the magnitude of the superconducting transition temperature T_c. Recently, Mitrović and Carbotte[22] have presented approximate analytic calculations of the functional derivative within the square-well model.[25] But we have followed Bergmann and Rainer's method in our calculations. Changes in $\alpha^2(\omega)f(\omega)$ are considered by taking the effect of the modification of the V dynamics, correlation between V and impurity motion, and the direct contribution due to impurity. The force-constant changes evaluated in the study of phonon specific heat are used to see their effects on T_c. The evaluation of the phonon Green's functions required the vanadium phonon dispersion curves, and the same information will also be used to determine the parameters in the V pseudopotential.

We have undertaken a systematic study of the connection between the restructuring of the phonon spectrum, and the temperature of the transition T_c to the superconducting state. The anomalous behavior of the phonon specific heat in the range of low temperature of alloys of V with Hf, Ta, and W indicates a restructuring of the phonon spectrum in the region of low frequencies. The present systems have been chosen because of many reasons. It is a widely accepted point of view that softening of the phonon spectrum should give an increase in T_c. Thus, the possibility of raising T_c should be expected by introduction of heavy impurities. It is also known that introduction of group-IV elements into vanadium increases T_c, while introduction of group-VI elements decreases it. It is therefore interesting to study the alloys of V with Hf and W, which are the neighbors of Ta in the Periodic Table, which differ only in the number of electrons, having practically equal atomic masses. The experimental results of Shikov *et al.*[24] on the specific heat of these systems point out an impurity resonance, and to an appreciable change in the local strength constants.

The structure of the paper is as follows. Section II A deals briefly with the low-concentration Green's-function theory. In Sec. II B we have given very briefly the theory to see changes in $\alpha^2(\omega)f(\omega)$ due to introduction of impurities, and Sec. II C describes the changes in phonon specific heat. Section II D gives the volume-expansion effect on the specific heat. Section III shows the numerical computations and discussions, and main conclusions are drawn in Sec. IV.

II. THEORY

A. Low-concentration Green's-function technique

The detailed procedure that describes the motion of the host and impurity atoms has been long established.[30–41] Here we will reproduce just the pertinent results. The displacement-displacement correlation $\langle U_\alpha(l)U_\beta(l')\rangle$ is written in terms of the displacement-displacement Green's function $G_{\alpha\beta}(ll';\omega)$:

$$\langle U_\alpha(l)U_\beta(l')\rangle=\frac{\hbar}{2M}\int_0^\infty \omega^{-1}N(\omega)\coth(\hbar\omega/2k_BT)d\omega \ , \tag{2a}$$

where $N(\omega)$ is the dynamic response function, and is given by

$$N(\omega)=(2M\omega/\pi)\mathrm{Im}G(\omega) \ . \tag{2b}$$

Here $\hbar$ is the Planck constant and k_B is the Boltzmann constant. As we are only interested in the correlation function at very low temperatures the coth function can be replaced by unity as $\beta=\hbar/k_BT\rightarrow\infty$.

The Green's function $\mathcal{G}$ for the real system of the impurity ions coupled to the host ions, is related to that for the so-called unperturbed system of the impurity ions uncoupled from the host ions $\mathcal{G}_0$ via the equation

$$\mathcal{G}=\mathcal{G}_0+\mathcal{G}_0\mathcal{P}\mathcal{G} \ , \tag{3a}$$

where $\mathcal{P}$ is the perturbation matrix containing the changes in mass as well as force constants, and is given by

$$\mathcal{P}(\omega^2)=-\omega^2\mathcal{M}_0^{-1/2}\Delta\mathcal{M}\mathcal{M}_0^{-1/2}+\mathcal{M}_0^{-1/2}\Delta\phi\mathcal{M}_0^{-1/2} \ . \tag{3b}$$

Here the new mass and force constant matrices for the imperfect crystal have been denoted by $M_0+\Delta M$, and $\phi_0+\Delta\phi$, respectively.

The Green's function of the host lattice, which has N ions of mass M_0 at site $R_0(l)$, is given by

$$G_{0\alpha\beta}(l,l';\omega)=\frac{1}{NM_0}\sum_{j,\mathbf{q}}\sigma_\alpha^j(\mathbf{q})\sigma_\beta^j(\mathbf{q})ei^{\mathbf{q}\cdot\mathbf{R}_0(l,l')}G_{j0}(\mathbf{q},\omega) \ , \tag{4a}$$

and

$$G_{0j}(\mathbf{q},\omega)=[\omega^2-\omega_{0j}^2(\mathbf{q})]^{-1} \ . \tag{4b}$$

$\omega_j(\mathbf{q})$, and $\sigma_j(\mathbf{q})$ are the eigenvalue and eigenvector of the phonon mode j of wave vector $\mathbf{q}$. The unperturbed Green's function for an impurity ion of mass M at site $\mathbf{R}_i$ will be of the same nature as in Eq. (4)

When concentration of the impurity is of the lowest order Eq. (3) can be simplified to[42]

$$\mathcal{G}=\mathcal{G}_0+\mathcal{G}_0\sum_i\mathcal{T}_i\,\mathcal{G}_0 \ , \tag{5}$$

where the T matrix for the ith impurity is

$$\mathcal{T}_i=\mathcal{P}_i(1-\mathcal{G}_0\mathcal{P}_i)^{-1} \ . \tag{6}$$

It is assumed that the impurities are widely spaced so that one may safely ignore the possibility of interaction of neighboring defects. Using the group-theoretical arguments the matrix in Eq. (6) can be inverted. For that we have to transform to the irreducible representations of the symmetry group of the impurity spaces. This has been done by using the transformation matrices[41] Ψ via

$$\sum_{\alpha,\beta,l_i,l_i'}\Psi^{\nu a\xi}(l_i)P_{i\alpha\beta}(l_i,l_i')\Psi_\beta^{\nu b\xi}(l_i')=P_{ab}^\nu \ . \tag{7}$$

Here ξ labels the row of the νth irreducible representation which may appear more than once (label a). Using the tables of Maradudin,[43] and the corrections given by Agrawal,[42] the matrice Ψ can be readily formed in the present case. For the impurity at the substitutional site the point group symmetry is O_h. If we consider only the nearest neighbor of the impurity, the matrices in the defect space reduce according to

$$A_{1g}+A_{2u}+2E_g+2E_u+3F_{1u}+3F_{2u}+3F_{1g}+3F_{2g} \ .$$

For a monoatomic bcc lattice the various resonance denominators for the different irreducible representations are given elsewhere.[31]

In our model we take the Green's function and perturbation matrices, which lie in the subspace of a defect $3b\times 3b$ (where b is the total number of atoms directly disturbed by the presence of a single defect, including the defect itself). The resonant frequencies are found by looking for zeros in the denominators of the T matrices of the different irreducible representations on a solution of the equation

$$\mathrm{Re}D_\nu(Z)=0 \ , \tag{8}$$

where $D_\nu(Z)$ is the determinant

$$D_\nu(Z)=|\,\mathcal{I}+\mathcal{G}_{0\nu}(Z)\mathcal{P}_\nu(\omega^2)\,| \ , \tag{9a}$$

for the irreducible representation ν.

In case of V:W alloy the concentration of the impurity is comparatively high, and as such the expression for the lowest concentration of impurities do not remain valid. The next simplest approximation is that of Elliott and Taylor,[44] which modifies the resonance denominator as

$$D_\nu(Z)=|\,\mathcal{I}+(1-c)\mathcal{G}_{0\nu}(Z)\mathcal{P}_{0\nu}(\omega^2)\,| \ , \tag{9b}$$

where c is the fractional impurity concentration. The approximation has taken into account exactly the scattering of phonons on single impurity, and neglected scattering of clusters of impurities; i.e., we have neglected the possibility of neighboring defects interfering with the scattering on a particular defect. Although the results can be taken in a better approximation, e.g., in the coherent potential approximation[45–47] where essentially single-site self-consistent scatterings are considered after taking into account proper multiple occupancy corrections, the expressions are more involved, and are intractable to computation for the case of a more complex defect.

The expressions for the resonance denominators for a monoatomic bcc lattice in the approximation of Elliott and Taylor can be obtained from the earlier expressions[31] if radial (central) and angular (noncentral) force-constant changes are replaced by $(1-c)\Gamma$ and $(1-c)\Gamma'$, respectively. We get resonance in F_{1u}-symmetry mode only; hence we give the expression for the resonance denominator in this particular mode:

$$\begin{aligned}D_{F_{1u}}(Z)=&D_1(D_5D_9-D_6D_8)-D_2(D_4D_9-D_8D_7)\\&+D_3(D_4D_8-D_5D_7) \ ,\end{aligned} \tag{10}$$

where

$$D_1=1-\epsilon\omega^2 g_1+8A'(g_1-g_2)-16B'g_3 \ ,$$

$$D_2=(\sqrt{2})[-\epsilon\omega^2 g_2+A'(8g_2-x_1)-(\sqrt{2})x_3B'] \ ,$$

$$D_3=4[-\epsilon\omega^2 g_2+A'(8g_3-x_3/\sqrt{2})-B'x_2] \ ,$$

$$D_4=-(\sqrt{8})[A'(g_1-g_2)-2B'g_3] \ ,$$

$$D_5=1+A'(x_1-8g_2)+\sqrt{2}B'x_3 \ ,$$

$$D_6=A'[x_3-8(\sqrt{2})g_3]+2B'x_2 \ ,$$

$$D_7=4[B'(g_2-g_1)+C'g_3] \ ,$$

$$D_8=(\sqrt{2})B'(x_1-8g_2)+C'x_3 \ ,$$

$$D_9=1+(\sqrt{2})B'[x_3-8(\sqrt{2})g_3]+C'x_2 \ ,$$

with

$$x_1=g_1+2g_4+g_5+g_7+g_9+g_{10} \ ,$$

$$x_2=g_1-g_5+g_6+g_7+g_8-g_9 \ ,$$

$$x_3=-(\sqrt{2})(g_6-g_8) \ ,$$

$$A'=\tfrac{1}{3}(1-c)(\Gamma+2\Gamma') \ ;$$

$$B'=\tfrac{1}{3}(1-c)(\Gamma-\Gamma') \ ;$$

$$C'=\tfrac{1}{3}(1-c)(2\Gamma+\Gamma') \ .$$

Here $\epsilon=(M-M_0)/M$ is the change in mass at the impurity site; $\Gamma=\Delta f/M_0$ denotes the change in the nearest-neighbor radial force constant in the units of squared frequency and $\Delta f=f-f_0$, where f_0 and f represent radial force constant of pure and impure crystals. Similarly $\Gamma'=\Delta f'/M_0$ is the change in the nearest-neighbor angular force constant, where $\Delta f'=f'-f'_0$; f'_0 and f' give the angular force constant of pure and impure crystal. The various Green's functions $g_\mu(\mu=1,10)$ are given in earlier work.[31,42]

B. Changes in the superconducting transition temperature

The changes in T_c due to small change in $\alpha^2(\omega)f(\omega)$ is already given by Eq. (1). On alloying, T_c is changed by both the electron-impurity scattering, and by any modifications to the electron-phonon interaction. The electron-phonon interaction enters superconductivity calculations via a function $\alpha^2(\omega)f(\omega)$.[48] This has the form of a phonon density of states weighted by the electron-phonon interaction. For an alloy $\alpha^2(\omega)f(\omega)$ is given by[16,21,40]

$$\alpha^2(\omega)f(\omega)=\frac{N(0)S(\omega)}{8\pi^2 q_F^2 N^2}\int_{q<2q_F}\frac{d^3q}{q}\sum_{ll',\alpha\beta}W_l^*(q)q_\alpha \mathrm{Im}G_{\alpha\beta}(ll',\omega)q_\beta W_{l'}(q)\exp[-i\mathbf{q}\cdot(\mathbf{R}_l-\mathbf{R}_{l'}] \ , \tag{11}$$

where $N(0)$ is the single spin density of states for the alloy, and $W_l(q)$ is the pseudopotential form factor appropriate to the kind of ion at the site R_l. The factor

$$S(\omega)=\begin{cases}5\omega/\omega_m, & \omega\le\frac{1}{5}\omega_m\\ 1, & \omega\ge\frac{1}{5}\omega_m\end{cases} \tag{12}$$

has been introduced to compensate for the fact that the form of Eq. (11) is based on a single rather than a multiple orthogonalized plane wave (OPW) calculation of the electron-phonon interaction.[49-51] Using the simplified form of the Green's function given by Eq. (5), we can split Eq. (11) into four terms

$$\alpha^2(\omega)f(\omega)=[\alpha^2(\omega)f(\omega)]_{\mathrm{host}}+[\Delta\alpha^2(\omega)f(\omega)]_{\mathrm{host}}+[\Delta\alpha^2(\omega)f(\omega)]_{\mathrm{host-imp}}+[\Delta\alpha^2(\omega)f(\omega)]_{\mathrm{imp}} \ . \tag{13}$$

The first term at the right-hand side of this equation is not affected by the changed lattice dynamics. The second term describes the changes in $\alpha^2(\omega)f(\omega)$ due to the modification of the host (vanadium) dynamics. It can be written as

$$[\Delta\alpha^2(\omega)f(\omega)]_{\mathrm{V}}=\frac{cN(0)}{8\pi^2 q_F^2}\int\frac{d^3q}{q}\frac{1}{N^2}\sum_{ll',\alpha\beta}W_{\mathrm{V}}(q)q_\alpha \mathrm{Im}\sum_{l_il_i',\Gamma\delta}G_{0\alpha\Gamma}(l_i,l_i',\omega)T_{\Gamma\delta}(l_i;l_i',\omega)$$
$$\times G_{0\delta\beta}(l_i';l';\omega)q_\beta W_{\mathrm{V}}(q)\exp[i\mathbf{q}\cdot(\mathbf{R}_l-\mathbf{R}_{l'})] \ , \tag{14}$$

where l and l' refer to vanadium lattice sites; l_i and l_i' refer to the nearest neighbor of an impurity. For the vanadium pseudopotential $W_{\mathrm{V}}(r)$ we have used a local form of the Heine-Abarenkov type:[51-54]

$$W_V(r)=\begin{cases}-ZA/r_m, & r<r_m\\ -Z/r_m, & r>r_m \ .\end{cases} \tag{15}$$

Here Z is the charge on the vanadium ion, and A is the parameter representing the depth of a potential well for a given model radius r_m, being screened according to Animalu.[53-54] We have used the phonon dispersion curves of vanadium calculated according to the model of Oli and Animalu.[54]

Eq. (14) can be further simplified to

$$[\Delta\alpha^2(\omega)f(\omega)]_{\mathrm{V}}=\frac{cN(0)}{8\pi^2 q_F^2 M_0^2 N}\int\frac{d^3q}{q}W_{\mathrm{V}}(q)^2\sum_{j_1j_2}\mathbf{q}\cdot\sigma^{j_1}(\mathbf{q})\mathrm{Im}G_{0j_1}(\mathbf{q},\omega)T_{j_1j_2}(\mathbf{q},\omega)G_{0j_2}(\mathbf{q},\omega)\mathbf{q}\cdot\sigma^{j_2}(\mathbf{q})\;, \tag{16}$$

where

$$T_{j_1j_2}(\mathbf{q},\omega)=\sum_{\nu,ab,\xi}S(\mathbf{q},j_1;\nu,a,\xi)T_{ab}(\nu,\omega)S^*(\mathbf{q},j_2;\nu,b,\xi) \tag{17}$$

with

$$S(\mathbf{q},j;\nu a\xi)=\sum_{l_i,\alpha}\sigma_\alpha^j(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{R}_0(l_i)}\Psi_\alpha^{(\nu a\xi)}(l_i)\;. \tag{18}$$

The transformation matrices Ψ and other phonon quantities are described previously in Sec. II A. Although $N(0)$ and q_F should have values appropriate to the alloy electron density we used the pure V values in this and the next two terms. This should be an error of order c on a term that is already of order c.

The third term in Eq. (13) is due to a correlation between vanadium and the impurity motion. It can be reduced to the form

$$[\Delta\alpha^2(\omega)f(\omega)]_{\mathrm{V}-I}=\frac{cN(0)}{8\pi^2 q_F^2 M_0^2 MN}\int\frac{d^3q}{q}W_{\mathrm{V}}(q)W_I(q)\sum_{j,\beta,b}\mathbf{q}\cdot\sigma^j(\mathbf{q})\mathrm{Im}G_{0j}(\mathbf{q},\omega)T_{1b}(\nu,\omega)G_j'(\mathbf{q},\omega)q_\beta[2\mathrm{Re}S(\mathbf{q},j;\nu b\beta)]\;, \tag{19}$$

where G_j' represents the Green's function of the impurity, and $W_I(q)$ is the screened pseudopotential of the impurity. We have used the same form for $W_I(q)$ as for vanadium [Eq. (15)]. The parameters of the host as well as of the impurity pseudopotential were chosen as described by Animalu.[53] In our calculations we have taken the numerical values of the pseudopotentials as computed by him. The final term in Eq. (13) is the direct contribution from the impurity to $\alpha^2(\omega)f(\omega)$, and can be represented as

$$[\Delta\alpha^2(\omega)f(\omega)]_I=\frac{cN(0)}{8\pi^2 q_F^2 M^2 N}\mathrm{Im}G'T_{ll'}(\nu,\omega)\times\int_{q<2q_F}\frac{d^3q}{q}W_I^2(q)\;. \tag{20}$$

C. Changes in lattice specific heat

The lattice specific heat of the ideal lattice in the harmonic approximation is given by

$$C_L(T)=k_B\int_0^\infty d\omega\,N(\omega)(\hbar\omega/2k_BT)^2\csc^2(\hbar\omega/2k_BT)\;, \tag{21}$$

where $N(\omega)$ is the number of normal modes in the interval ω, and $\omega+d\omega$ in the limit $d\omega\to0$. $N(\omega)$ is related to a similarly defined function $N(\omega^2)$ which is a more common function in the theory of crystal dynamics, as

$$N(\omega)=2\omega N(\omega^2)\;.$$

The change in the lattice specific heat due to impurities is[31,37,38]

$$\Delta C_L(T)=Nck_B\int_0^\infty d\omega\,\Delta N(\omega)\times(\hbar\omega/2k_BT)^2\csc^2(\hbar\omega/2k_BT)\;. \tag{22}$$

Here $\Delta N(\omega)$ is the change in density of states due to a single impurity, and cN is the total number of impurities in the lattice, since in the low concentration limit of impurities the change in specific heat is equal to the change due to a single impurity multiplied by the total number of impurities. The change in the density of states due to a single defect can be written as

$$\Delta N(\omega^2)=\sum_\nu\Delta N_\nu\omega^2\;, \tag{23}$$

where $\Delta N_\nu(\omega^2)$ is the contribution made by the symmetric motion ν, and is given by

$$\Delta N_\nu(\omega^2)=-\frac{1_\nu}{\pi}\mathrm{Im}\frac{d}{d\omega}\ln[D_\nu(Z)]\;. \tag{24}$$

By introducing the phase shift

$$\theta(\omega)=\arctan\left[-\frac{\mathrm{Im}D_\nu(Z)}{\mathrm{Re}D_\nu(Z)}\right] \tag{25}$$

the contribution of the symmetry modes ν towards the change in the density of states can be written as

$$\Delta N_\nu(\omega^2)=\frac{1_\nu}{\pi}\frac{d\theta_\nu}{d\omega^2}\;. \tag{26}$$

Substitution of (26) in Eq. (22), and integrating once by parts, the change in specific heat due to a single defect can be given as

$$\Delta C_L(T)=\sum_\nu cN\Delta C_L^\nu(T)\;, \tag{27}$$

where the contribution of each irreducible representation is

$$\Delta C_L^{\nu}(T) = -\frac{2k_B E'}{3N\pi}\int_0^{\infty} \theta_{\nu}\omega \csc^2(E'\omega) \times [1 - E'\omega \coth(E'\omega)]d\omega \ , \quad (28)$$

where $E' = \hbar/2k_B T$.

D. Effect of volume expansion

It is well known that presence of an impurity causes local changes in the force constants but the volume-dependent force-constant changes are less understood. With the introduction of impurities in the lattice, apart from thermal vibrations, the atoms are permanently displaced from their equilibrium position, and one gets static displacements leading to volume changes in the lattice. The static displacements, and consequently the volume changes, also induce changes in the force constants. Here we distinguish two different types of displacements: (a) the displacement d^{∞}, which would occur in an infinite crystal, and (b) a very small image field d^{image}, which allows the surface of the finite crystal to be force free. The image field is slowly varying over the crystal dimension, and practically represents a uniform expansion. As the force constants are determined by the change of the distance between the nearest neighbors (near the impurity), we have a local force-constant change due to considerable change in the nearest-neighbor distance. Such changes in the nearest-neighbor distances are caused by the total displacements, which are large (given by $\sim d^{\infty}$). However, away from the impurity, we have homogeneous softening of force constants due to image expansion. Thus the change in force constant, and, in turn, any dynamical property due to volume expansion, is proportional to ΔV^{image}, and not to $\Delta V (\Delta V^{\infty} + V^{\text{image}})$.

Erroneously, in the past[33–34,37] it has been assumed that the change in force constants due to lattice expansion (or contraction) is proportional to a total volume change ΔV instead of being proportional to ΔV^{image}.[39] The total change in the density of states may be expressed as

$$\Delta N^{\text{total}}(\omega) = \Delta N(\omega) + \Delta N^{\text{image}}(\omega) \ . \quad (29)$$

The change in density of states due to volume expansion can be calculated from the volume or pressure derivative of the ideal phonons

$$\Delta N^{\text{image}}(\omega) = \frac{\partial N}{\partial V}\Delta V^{\text{image}} = -\frac{\partial N(\omega)}{\partial P}\frac{K}{V}\Delta V^{\text{image}} \ , \quad (30)$$

where K is the bulk modulus. Thus, to find out the total change in density of states we need the perfect lattice phonons as well as their pressure derivatives. This practically doubles the numerical computations. In the low temperature limit, therefore, we estimate the contribution of the image expansion to the lattice specific heat by evaluating the change in Debye temperature of the lattice. We note that for understanding the dynamics of an imperfect lattice the dynamical structure of the impurity is important, while the image expansion gives only a general softening of force constants throughout the crystal. Also, the contribution to any dynamical property due to volume changes is, in general, small compared to the contribution due to local perturbation.

As a result of image expansion the change in Debye temperature can be calculated by employing Grüneisen's constant γ which is given as

$$-\frac{\partial \ln\theta_D}{\partial \ln V} = \gamma$$

or (31)

$$-\frac{\Delta\theta_D}{\theta_D} = \frac{\Delta V^{\text{image}}}{V} \ .$$

In earlier papers,[33–34,37] in a similar expression, ΔV has been used instead of ΔV^{image}. If we use the continuum model the total volume change is given by[55]

$$\Delta V = 3\frac{1-p}{1+p}\Delta V^{\infty} (= \Delta V^{\infty} + \Delta V^{\text{image}}) \ , \quad (32)$$

where p is the Poisson ratio. Hence the change in volume due to image expansion is

$$\Delta V^{\text{image}} = \frac{2}{3}\frac{1-2p}{1+p}\Delta V \ . \quad (33)$$

Thus, by knowing the Debye temperature of the perfect lattice and defect lattice, and the change in θ_D due to volume change, the change in lattice specific heat due to

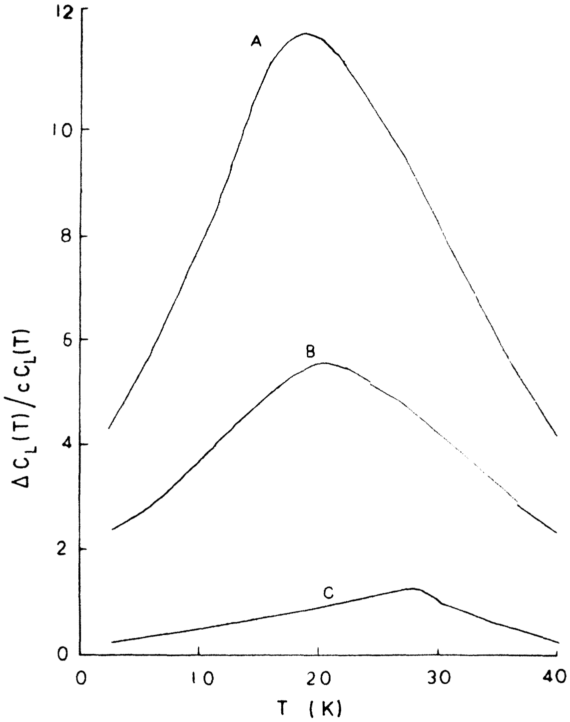

FIG. 1. Temperature dependence of the relative change of the lattice specific heat of three vanadium alloys: A, $V_{99.1}Hf_{0.9}$; B, $V_{96.4}Ta_{3.6}$; C, $V_{94.8}W_{5.2}$.

TABLE I. Values of ΔT_c, Γ and Γ', ω_r, and the Debye temperatures of expanded lattices and alloys. The Debye temperature for pure vanadium is 373 K.

Systems	ΔT_c Expt.	Theory	Γ (10^{26} sec^{-2})	Γ' (10^{26} sec^{-2})	ω_n (cm^{-1})	Expanded θ_D (K)	Alloys θ_D (K)
$V_{99.1}Hf_{0.9}$	0.10	0.10	0.935	−0.362	29	371.13	368
$V_{96.4}Ta_{3.6}$	−0.69	−0.68	1.638	−0.401	38	366.68	359
$V_{94.8}W_{5.2}$	−1.16	−1.12	2.271	−0.432	47	369.54	364

volume expansion $\Delta C_L^{\text{image}}$ (volume effect), and due to local perturbation ΔC_L (impurity effect), can be easily calculated. Hence, the total changed-lattice specific heat is

$$\Delta C_L^{\text{total}} = \Delta C_L^{\text{image}} + \Delta C_L(T) \ . \tag{34}$$

III. NUMERICAL RESULTS AND DISCUSSION

Colella and Battermann[56] have measured the phonon spectrum of vanadium by using thermal diffuse scattering in the three principal symmetry directions. Oli and Animalu[54] have fitted the experimental results in the framework of the resonance model, and a nearly free-electron approximation of pseudopotential theory. This required reformulation of the local transition-metal model-potential approach,[57] so as to incorporate the strong nonlocality of the resonance term. For calculating Green's functions we have used the eigenfrequencies, and eigenvectors computed under this approach. The integrals over **q** were calculated by the procedure of Carbotte and Dynes.[58] We have used a coarse mesh of 112**q** points in the reduced $\frac{1}{48}$th of the first Brillouin zone. In order to find out the imaginary parts of the Green's functions we have evaluated them at a finite distance δ off the real axis. This has the advantage of eliminating some of the noise due to the coarse **q** mesh. A somewhat larger value of $\delta = 0.05\omega_m$ has been chosen, which removes most of the noise without producing tails of too great an extent.

We have calculated the lattice part of the specific heat of $V_{94.8}W_{5.2}$, $V_{96.4}Ta_{3.6}$, and $V_{99.1}Hf_{0.09}$ alloys by using Eqs. (27), (28), and (34) by treating the radial and angular force-constant changes Γ and Γ' as parameters. The measurements of the specific heat of these alloys have been made by Shikov *et al.*[24] The relative change in the lattice specific heat of all three systems are shown in Fig. 1.

The introduction of the impurity atoms Hf, Ta, and W in V, which have practically equal masses, deforms the phonon spectrum differently, as shown in this figure. A small maximum at about 29 K is observed in V:W alloy in the curve of $\Delta C_L(T)/cC_L(T)$ versus temperature. In the case of V:Ta and V:Hf alloys the maximum shifts toward lower temperatures (at about ~20 K). The maxima for V:Ta, and V:Hf alloys are five to ten times larger, respectively, than the maximum observed for V:W alloy. These curves show the presence of resonance modes in the phonon spectrum of the alloy, and appreciable changes in the effective local force constants. In the beginning an attempt was made to fit the experimental results by taking mass defects into consideration; then we included the radial force-constant changes. It was ob-

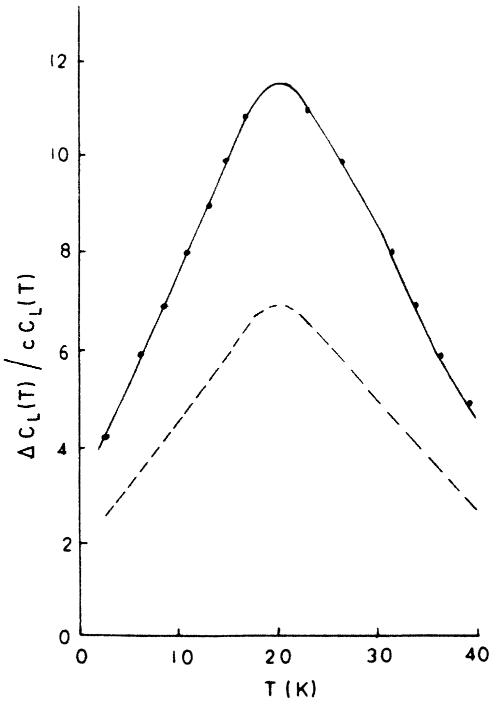

FIG. 2. Temperature dependence of the relative change of the lattice specific heat of $V_{99.1}Hf_{0.9}$ alloy. The points are the experimental results, and the solid curve shows the theoretical calculations for $\Gamma = 0.935 \times 10^{26}$ sec^{-2} and $\Gamma' = -0.362 \times 10^{26}$ sec^{-2}. The dotted curve represents mass-defect calculations.

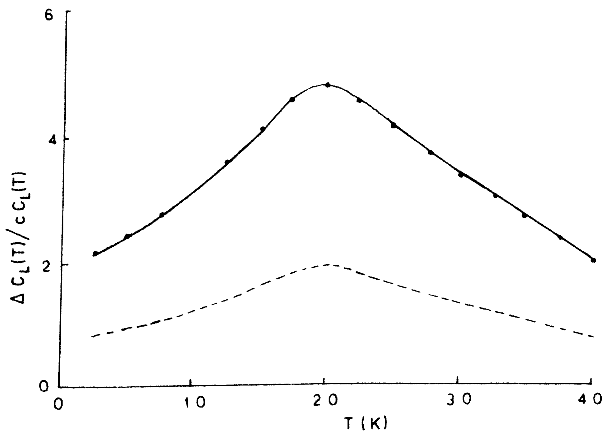

FIG. 3. Temperature dependence of the relative change of the lattice specific heat of $V_{96.4}Ta_{3.6}$ alloy. The points are the experimental results, and the solid curve shows the theoretical calculations for $\Gamma = 1.638 \times 10^{26}$ sec^{-2} and $\Gamma' = -0.401 \times 10^{26}$ sec^{-2}. The dotted curve represents mass-defect calculations.

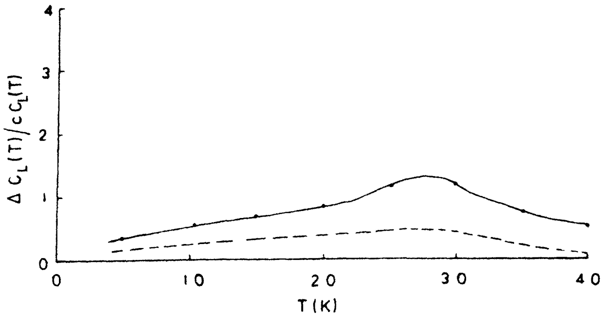

FIG. 4. Temperature dependence of the relative change of the lattice specific heat of $V_{94.8}W_{5.2}$ alloy. The points are the experimental results, and the solid curve shows the theoretical calculations for $\Gamma=2.271\times10^{26}$ sec^{-2} and $\Gamma'=-0.432\times10^{26}$ sec^{-2}. The dotted curve represents mass-defect calculations.

served that the radial force-constant model is unable to explain the experimental data, and inclusion of angular force-constant changes is not only necessary but instrumental for obtaining a good fit. The experimental results have been fitted very well with the unique values of Γ and Γ' in different systems. The enhancement of the lattice specific heat has been observed in all three systems. In the case of V:W alloy we have used Elliott and Taylor's approximation[44] for calculating the changes in specific heat. The obtained values of the force-constant changes in the different impurity-host systems are given in Table I. The percentage impurity contribution due to force-constant changes is on an average above 60% in V:Ta and V:Hf alloys, and above 40% in V:W alloy. The change in Debye temperatures in different systems has been calculated utilizing Eq. (31), and is given in Table I along with measured values of Debye temperatures of the pure lattice and alloys. In all three systems a volume expansion has been observed due to introduction of impurity atoms. The difference between the Debye temperature of the alloy and the expanded lattice is accounted for by the local perturbation. Before considering the impurity contribution to the lattice specific heat, only the effect of volume expansion was taken into account by us. Shikov *et al.*[24] also analyzed their experimental data by using a different model in which radial and angular forces were assumed to be equal, but their theoretical results are quite different from the experimental ones. Our theoretical calculations along with the experimental data are shown in Figs. 2–4, which show good agreement with the experiment.

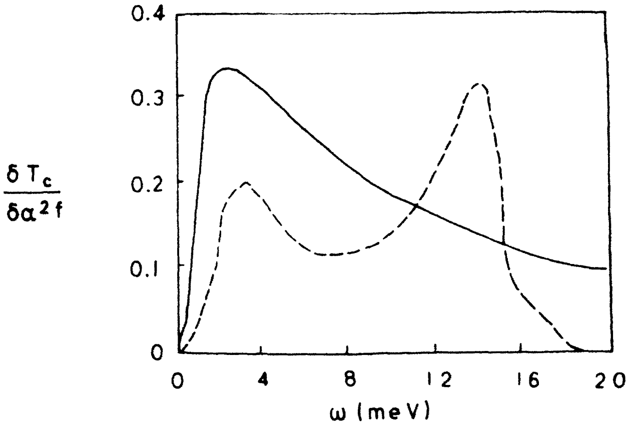

FIG. 5. Solid and dashed curves represent the plot of $\delta T_c/\delta\alpha^2(\omega)f(\omega)$ and $\alpha^2(\omega)f(\omega)$, respectively, with respect to frequency for V:Hf alloy.

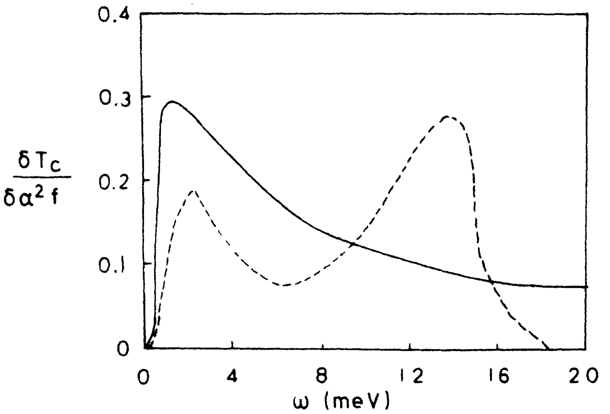

FIG. 6. Solid and dashed curves represent the plot of $\delta T_c/\delta\alpha^2(\omega)f(\omega)$ and $\alpha^2(\omega)f(\omega)$, respectively, with respect to frequency for V:Ta alloy.

Out of eight irreducible representations appearing in the problem the main contributions to the specific heat come from F_{1u}, F_{1g}, F_{2g}, E_g, and A_{1g}. This behavior is quite different from the fcc alloys[33–34,37] in which the changed-lattice specific heat is mainly determined by F_{1u} modes only. At very low temperatures (<3 K) the contribution from F_{1g}, F_{2g}, E_g, and A_{1g} symmetry motions dominates over that of F_{1u} modes. The contribution of F_{1u} modes increases with an increase in temperature because of the excitation of the resonance modes, and, in fact, dominates over all other symmetry modes at comparatively higher temperatures. In all three systems the low-frequency resonance occurs in F_{1u}-symmetry modes, only. The resonance frequencies (ω_r) are given in Table I.

For calculating $\delta T_c/\delta\alpha^2(\omega)f(\omega)$ we have used the method of Bergmann and Rainer.[20] The calculated results for the three systems are shown in Figs. 5–7. From the figures it can be concluded that the curve increases from zero at $\omega=0$, being linear at small frequencies, reaches a maximum slightly above $\omega=2\pi T_c$, and then decreases monotonically, remaining positive all the way up to the maximum frequency considered. This is a universal shape, and insensitive to the difference in shape of the corresponding $\alpha^2(\omega)f(\omega)$.

The changes in $\alpha^2(\omega)f(\omega)$ due to different impurities have been calculated by using Eqs. (19) and (20). Equation (16) remains the same for all three impurities since it represents the changes due to the modification of the host lattice dynamics. We have not considered the lattice dynamics of impure crystals. The calculated and experimental results for ΔT_c are given in Table I. We see a good agreement with theory. In calculating the changes in $\alpha^2(\omega)f(\omega)$ we have used force-constant changes evaluated in the case of specific-heat studies.

Experiments[24] (for clarity we have reproduced the experimental results in Table II) show a decrease in T_c, θ_D,

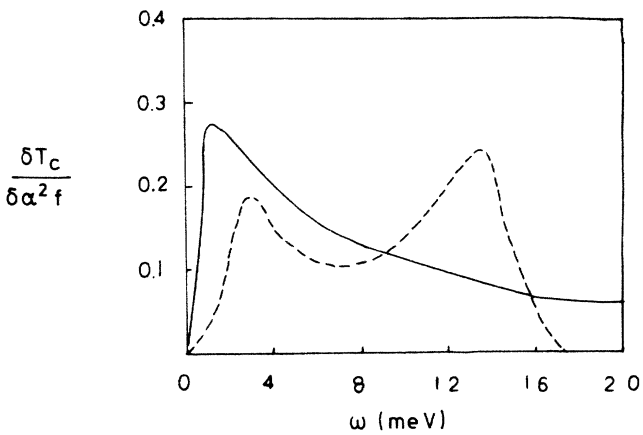

FIG. 7. Solid and dashed curves represent the plot of $\delta T_c/\delta\alpha^2(\omega)f(\omega)$ and $\alpha^2(\omega)f(\omega)$, respectively, with respect to frequency for V:W alloy.

TABLE II. Experimental values (Ref. 24) of T_c, θ_D, and Γ''.

Systems	T_c (K)	θ_D (K)	Γ'' (mJ/mol K)
V	5.24	373	9.80
$V_{99.1}Hf_{0.9}$	5.34	368	9.78
$V_{96.4}Ta_{3.6}$	4.55	359	9.25
$V_{94.8}W_{5.2}$	4.08	364	9.36

and Γ'' (electronic specific-heat coefficient) due to introduction of Ta and W impurity atoms in V, whereas in the case of the V:Hf system we observe a small increase in T_c, while θ_D and Γ'' remain practically constant. This shows that in the case of V:Hf alloy the electronic spectrum is practically unchanged, and therefore the only contribution to changes in T_c is due to deformation in the phonon spectrum, which is very strong. This observation is also confirmed by the fact that there is an anomalous increase of the density of the phonon states at low frequencies, and we get the resonance at a lower frequency than compared to the other two systems. In the case of V:Ta alloy the density of the electronic states on the Fermi surface decreases (Γ'' decreases). The interaction of the electrons with the resonant mode leads to a decrease in T_c. Thus the observed decrease in T_c in the case of the V:Ta system is mainly due to restructuring of the electronic spectrum, and deformation of the phonon spectrum. In V:W alloy the density of the electronic states at the Fermi surfaces again decreases noticeably. The resonant modes lie relatively high on the low-frequency side. Also the force-constant changes are quite high in this system. These reasons lead to a decrease in T_c when W is substituted into V. It is also observed, since the masses of the three impurities are almost equal, that it is the contribution due to force-constant changes of the deformation of the phonon spectrum which matters in the present problem. We see that in V:Hf alloy the changes in force constants are much smaller compared to V:Ta and V:W systems. This may be the important reason for enhancement of the transition temperature due to introduction of Hf impurity atoms in V. Here it is to be pointed out that we have not taken into account the change in $N(0)$ in $\alpha^2(\omega)f(\omega)$, Eqs. (16), (19), and (20), based on the electronic specific heat (Γ''). This will give an error of an order of fractional impurity concentration on a term which is already of the same order.

IV. CONCLUSION

We have used a lattice dynamical model which takes into account the changes in the phonon spectrum due to introduction of impurities. The force-constant changes have been evaluated by fitting the measured phonon specific heat of alloys studied here. Previously it has been observed that these parameters (Γ and Γ') in this frame of model also explain other impurity-induced vibrational properties of the same system.[31,33,38] The effect of volume changes has also been taken into account. It has comparatively small effect but is quite significant. The changes in transition temperatures have been calculated by observing the changes in $\alpha^2(\omega)f(\omega)$. It has been seen that for the impurity atoms of practically equal masses the effect of force-constant changes is quite noticeable. The scale and position of $\Delta C_L(T)/cC_L(T)$ turn out to be significantly different owing to the change of force constants. When the force constant for heavy impurity atoms changes weakly and a low-frequency resonance mode is observed, the transition temperature is slightly increased, and if the changes in the force-constants are strong, T_c changes (lowered) appreciably, and resonances are observed at comparatively higher frequencies.

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