PHYSICAL REVIEW VOLUME 150, NUMBER 2 14 OCTOBER 1966

Determination of the Effective Force Constants between a Substitutional Impurity and Its Nearest Neighbors in an Alkali Halide Crystal

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(Received 5 April 1966)

The forces between a substitutional impurity and its nearest neighbors in an alkali halide crystal with rocksalt structure are determined in the harmonic approximation. The deformation dipole model is used for the lattice dynamics of the perfect crystal. Two independent force constants are involved in the problem which is treated in two ways. First, the two force constants are obtained from the equation of motion for the local mode of vibration using experimental values of the local-mode frequencies due to H^- and D^- impurities in NaCl and KCl, and assuming that the force constants are the same for different isotopes of the impurity. This method yields no real solutions for the force constants for U centers in KCl. The second method assumes that the force constants for the impurity (say H^-) are the same as those in an alkali hydride crystal having the same lattice spacing as the alkali halide crystal. A Born-Mayer interatomic potential is used for this calculation. The first method gives 45% softening of the force constants for U centers in NaCl; the second method gives 70% softening. The results are compared with those of previous theories and with experimental results on the KBr:Li^+ system.

I. INTRODUCTION

In studying the dynamical properties of a substitutional impurity introduced into a crystal, one must consider not only the difference in mass between the impurity and the atom which it replaces but also the fact that the forces between the impurity atom and its neighbors will differ from those in the perfect crystal. These factors were taken into account in a calculation of the impurity-induced first-order Raman scattering of light by alkali halide crystals,[1] and the difficulty of determining the changes in force constants between the impurity and its nearest neighbors was briefly described therein. In this paper, a more detailed discussion of this problem will be given. In Sec. II, we give the theory from which the force constant changes due to the impurity can be determined if the frequencies of the impurity modes of vibration are known. The results of this treatment are given and the problems which arise are discussed. In Sec. III, another method is considered which uses data for the perfect crystal constituents only (say NaCl and NaH for the case of U centers in NaCl) to calculate the changes in force constants, using the Born-Mayer form for the interatomic potential. In Sec. IV, the second method is applied to the KBr:Li^+ system. In Sec. V, the limitations of the present theoretical and experimental situation are discussed.

II. THEORY

We assume that substituting an impurity in an ionic crystal affects the impurity-nearest-neighbor interaction only. This assumption is not unreasonable as a first approximation because we shall consider only those cases where the charge on the impurity ion is the same as that on the host ion which it replaces. In such cases, the long-range Coulomb forces are unchanged and only the short-range forces are altered. We also assume that the impurity concentration is sufficiently low that there is no interaction between impurities.

We have shown in Paper I, Appendix B, that when a substitutional impurity in a crystal with rocksalt structure interacts with its nearest neighbors only, the time-independent equations of motion for the modes of vibration of the perturbed crystal which are affected by the impurity can be reduced by group-theoretic methods to a set of equations characterized by eigenvectors which transform according to the irreducible representations A_{1g}, E_g, F_{1g}, F_{2g}, F_{1u}, and F_{2u} of the group 0_h. In Paper I we were concerned with the vibrational modes belonging to A_{1g}, E_g, and F_{2g} which are first-order Raman active. The F_{1g} and F_{2u} modes are neither Raman active nor infrared active in first order. The modes transforming according to F_{1u} are infrared active in first order and they give rise to the localized modes of vibration whose frequencies lie outside the bands of the host crystal. They are the only modes in which the impurity itself moves. For light impurities, the local-mode frequencies are well separated from the continuum of lattice frequencies. We turned our attention to these frequencies because they can be assigned unambiguously to the F_{1u} modes of vibration.

The local-mode frequencies are obtained from the following determinantal equation,

$$\begin{vmatrix} (g_0/m)\delta l_0+2g_1\beta+4g_2\gamma-1 & 2\beta(g_0/m-g_1) & 4\gamma(g_0/m-g_2) \\ g_1\delta l_0+m[\beta(g_3+g_6)+4\gamma g_4] & \beta[2g_1-m(g_3+g_6)]-1 & 4\gamma(g_1-mg_4) \\ g_2\delta l_0+m[2\beta g_4+\gamma(g_3+g_7+2g_5)] & 2\beta(g_2-mg_4) & \gamma[4g_2-m(g_3+g_7+2g_5)]-1 \end{vmatrix}=0. \tag{1}$$

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[1] X. X. Nguyen, A. A. Maradudin, and R. A. Coldwell-Horsfall, J. Phys. (Paris) **26**, 717 (1965); hereafter referred to as I.

The Green's functions,

$$g_{\alpha\beta}(l\kappa,l'\kappa';x^2)=\frac{1}{N}\sum_{\mathbf{k},j}\frac{w_\alpha(\kappa|\mathbf{k}j)w_\beta(\kappa'|\mathbf{k}j)}{x^2-x_j^2(\mathbf{k})}\times e^{2\pi i\mathbf{k}\cdot[\mathbf{r}(l\kappa)-\mathbf{r}(l'\kappa')]} \quad (2)$$

for convenience have been abbreviated as follows:

$$\begin{aligned} g_0&=g_{xx}(0,0;x), & g_4&=g_{xx}(\bar{1},2;x),\\ g_1&=g_{xx}(0,1;x), & g_5&=g_{zz}(\bar{1},2;x),\\ g_2&=g_{yy}(0,1;x), & g_6&=g_{xx}(\bar{1},1;x),\\ g_3&=g_{xx}(1,1;x), & g_7&=g_{yy}(\bar{1},1;x), \end{aligned} \quad (3)$$

where $x=\omega/\omega_L$ and ω_L is the maximum frequency of the host crystal. The changes in force constants are given, in reduced units, by the relations

$$\begin{aligned} \alpha&=\frac{1}{\omega_L^2(M_0M_n)^{1/2}}\Delta\Phi_{xx}(0,0),\\ \beta&=\frac{1}{\omega_L^2(M_0M_n)^{1/2}}\Delta\Phi_{xx}(0,1),\\ \gamma&=\frac{1}{\omega_L^2(M_0M_n)^{1/2}}\Delta\Phi_{yy}(0,1), \end{aligned} \quad (4)$$

and they satisfy the condition

$$\alpha+2\beta+4\gamma=0, \quad (5)$$

which follows from the requirement that the net force on an atom vanishes under a rigid-body displacement of the crystal. δl_0 is defined by

$$\delta l_0=\epsilon m x^2+\alpha, \quad (6)$$

where $\epsilon=1-M_0'/M_0$ and $m=(M_0/M_n)^{1/2}$. M_0' is the mass of the impurity ion and M_0 is the mass of the ion it replaces. In this paper we use the same notation as in I, where the impurity atom is set at the origin and labeled by $(l\kappa)=(0)$ and its nearest neighbors are along the coordinate axes, labeled by $(l\kappa)=(n)$ with n taking the values 1, 2, 3, $\bar{1}$, $\bar{2}$, $\bar{3}$.

At first sight, it appears to be a simple problem to determine the two independent force constant changes β and γ from the four equations which contain them. Three of these correspond to the first-order Raman-active modes A_{1g}, E_g, and F_{2g} discussed in I, and they are linear in β (A_{1g},E_g) and $\gamma(F_{2g})$. However, difficulties arise in making use of these Raman-active modes. First of all, there is the uncertainty as to whether a particular peak in the observed spectrum is due to a one-phonon or two-phonon process: knowledge of the temperature dependence of the spectrum is required to decide this. Secondly, Raman-active modes may not give rise to resonance modes and hence to well-defined peaks whose frequencies can be determined. Thirdly, the only experimental information available on impurity-induced first-order Raman scattering is for Li^+, I^-, Br^- impurities in KCl,[2] and here the results cannot be attributed to particular modes of vibration since the polarization of light and orientation of the crystals is not stated. We are left with one equation, that for the F_{1u} vibrational mode, from which to determine the two unknown force constant changes, β and γ.

The determinantal equation for the local-mode frequencies [Eq. (1)] was expanded, and using the condition given in Eq. (5), may be written as

$$l_i\beta\gamma+m_i\beta+n_i\gamma+p_i=0, \quad (7)$$

where the coefficients l_i, m_i, n_i, and p_i are functions of the local-mode frequency x_i, viz.,

$$\begin{aligned} l_i=&(\epsilon x_i^2g_0-1)[(2g_1-m(g_3+g_6))(4g_2-m(g_3+g_7+2g_5))-8(g_1-mg_4)(g_2-mg_4)]\\ &-2(\epsilon m x_i^2g_1-1)[(g_0/m-g_1)(4g_2-m(g_3+g_7+2g_5))-4(g_0/m-g_2)(g_2-mg_4)]\\ &-4(\epsilon m x_i^2g_2-1)[(g_0/m-g_2)(2g_1-m(g_3+g_6))-2(g_0/m-g_1)(g_1-mg_4)],\\ m_i=&4g_1-2g_0/m-m(g_3+g_6)-\epsilon m x_i^2[2g_1^2-g_0(g_3+g_6)],\\ n_i=&8g_2-4g_0/m-m(g_3+g_7+2g_5)-\epsilon m x_i^2[4g_2^2-g_0(g_3+g_7+2g_5)],\\ p_i=&\epsilon x_i^2g_0-1. \end{aligned} \quad (8)$$

The local-mode frequencies due to both hydride and deuteride impurities in KCl and in NaCl have been measured.[3–5] We can therefore calculate two sets of coefficients, $l_H\cdots$, $l_D\cdots$ for Eq. (7) using the experimental values of ω_H and ω_D together with numerical values for the Green's functions g_s [Eq. (3)]. If we now assume that it is a reasonable approximation put β_H equal to β_D and γ_H equal to γ_D, then the two Eqs. (7) yield quadratic equations in β and γ, respectively. In general, two solutions for the pair (β,γ) will be obtained.

We have carried out this calculation using the data[3,4] for NaCl and KCl. The Green's functions g_s have been calculated[6] using the normal-mode eigenfrequencies $\omega_j(\mathbf{k})$ and eigenfunctions $\mathbf{w}(\kappa/\mathbf{k}j)$ of the perfect alkali

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TABLE I. Calculated values of β, γ for U centers in NaCl by method of Sec. II.

x_H	x_D	β	γ
2.197[a]	1.584[a]	0.10609[b] 0.02187	−0.01414[b] 0.02804

[a] Reference 3.
[b] Dimensionless units [see Eq. (4)].

TABLE II. Interatomic potential and force constants in NaCl and in NaCl containing U centers [Φ_i, β_i, and γ_i in reduced units defined by Eq. (4)].

	r_0(Å)	ρ_0(Å)	$\Phi_0(r_0)$ (cm^2)	$-\beta_0$	γ_0
NaCl[a] (0°K)	2.7935	0.3163	0.02444×10^{-16}	0.24427	0.02766
		ρ_1(Å)	$\Phi_1(r_0)$ (cm^2)	$-\beta_1$	γ_1
NaCl+U centers		0.2733 0.69963	0.01032×10^{-16} 0.10886×10^{-16}	0.13817 0.22240	0.01352 0.05570

[a] Reference 9.

halide crystal calculated at 0°K by Jaswal[7] on the basis of the deformation dipole model of Hardy.[8] The results obtained for U centers in NaCl are shown in Table I.

One possible way of differentiating between the two solutions for the pair (β,γ) is to look at the interatomic potential which results from the change in force constants. The force constants β_1, γ_1, between the impurity and its nearest neighbors are given, according to the definition of the force constant changes, by the relations

$$\begin{aligned}\beta_1&=\beta_0+\beta\,,\\ \gamma_1&=\gamma_0+\gamma\,,\end{aligned}\tag{9}$$

where β_0, γ_0 are the nearest-neighbor force constants in the perfect crystal. For an interatomic potential of the form

$$\Phi(r)=\lambda e^{-r/\rho}\,,\tag{10}$$

the force constants are given by

$$\begin{aligned}-\beta_i&=(1/\rho_i^2)\Phi_i(r_0)\,,\\ \gamma_i&=(1/\rho_i r_0)\Phi_i(r_0)\,,\end{aligned}\tag{11}$$

where r_0 is the nearest-neighbor spacing of the host crystal and the index i takes the values 0 and 1 for the perfect host crystal and the crystal with impurity, respectively. We used the 0°K parameters of Karo and Hardy[9] to calculate β_0 and γ_0, and obtained β_1, γ_1 and thence ρ_1 and Φ_1 from Eqs. (9) and (11) using the solutions for β and γ given in Table I. These results are shown in Table II and we see that neither solution for the pair (β,γ) yields an obviously unphysical interatomic potential.

Another way of differentiating between the two solutions (β,γ) would be to look at the A_{1g}, E_g, and F_{2g} modes for each pair (β,γ) and see whether a resonance mode occurs which could be observed in Raman scattering or thermal conductivity. At present there are no experimental results on Raman scattering by alkali halide crystals containing U centers but the thermal conductivity of KCl with U centers has been measured by Walker [10,11] and a dip in the curve is attributed to an impurity-resonance mode. Until such experiments are carried out for other alkali halides containing impurities, in particular for NaCl with U centers, we cannot choose fairly between the two solutions (β,γ). However, we can state a preference for the solution with a larger value of β, since we have shown in I that resonance modes are most likely to occur for large values of β.

In the case of U centers in KCl, we do not have the problem of trying to decide between the two solutions for (β,γ) because we obtain no real solutions when the data for KCl are used to evaluate the coefficients in Eq. (7). When plotted as a function of β and γ, the equation for KCl with D$^-$ impurity gave a curve almost identical and parallel to that for KCl with H$^-$ impurity. Further study showed that the existence of real solutions is extremely sensitive to the values of the local-mode frequencies used to evaluate the coefficients in Eq. (7): varying either ω_H or ω_D by 1% is sufficient to yield real solutions for (β,γ). However, the local-mode frequencies are measured with an error of about 0.1% and although some uncertainty arises because the measurements were made at 100°K whereas the Green's functions and maximum frequency of the lattice, ω_L, were all calculated for 0°K, we do not feel justified in making such adjustments to the values of x_H and x_D as are necessary to yield real solutions for (β,γ). Furthermore, the model used for the perfect alkali halide crystals is approximate and cannot give sufficiently accurate values of the Green's functions for a physical significance to be attributed to difference between (β_H,γ_H) and (β_D,γ_D), the equality of these quantities being the basic assumption of our method of solving Eq. (7). If the difference is real, it could be due to a larger mean-square amplitude of vibration of the H$^-$ ion relative to that of the D$^-$ ion with correspondingly greater local distortion of the surrounding lattice which, in the harmonic approximation, is absorbed into the force constants. For these reasons, in the calculations for the first-order Raman spectra of KCl described in I, we made a different approximation, namely, we put γ equal to zero, since this force constant is an order of magnitude smaller than β, and determined β_H and β_D from Eq. (7). The values of β obtained in this approximation for both NaCl and KCl are shown in Table III. The difference between β_H and β_D is

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[10] C. T. Walker (to be published); see Ref. 11.
[11] J. A. Krumhansl, in *Proceedings of the Conference on Lattice Dynamics, Copenhagen, 1963* (Pergamon Press, Inc., New York, 1965), p. 533.

TABLE III. Values of β calculated from Eq. (7) in approximation $\gamma=0$: comparison with results of Jaswal[a] and Fieschi *et al.*[b]

	ω_L	X_H	X_D	β_H	β_D	$\frac{\beta_1}{\beta_0}$	$\left(\frac{\beta_1}{\beta_0}\right)^a$	$-\alpha_H$	$-\alpha_S{}^b$
NaCl	257.2 cm^{-1}	2.197^c	1.584^c	0.07718	0.07641	0.68	0.56	0.1544	0.1627
KCl	210.1 cm^{-1}	2.398^c	1.716^c	0.08276	0.08412	0.63^e	0.55	0.1655	0.1930
		2.384^d	1.707^d	0.08383	0.08524			0.1677	

[a] Reference 12.
[b] Reference 13.
[c] Reference 3.
[d] Reference 4.
[e] Value of β_0 obtained from 0°K data of Ref. 9.

TABLE IV. Values of β and γ calculated according to method of Sec. III, using room-temperature data.

	r_0(Å)	ρ_{mol}(Å)	$10^{16}\Phi(r_{\mathrm{Cl}})$ (cm^2)	$-\beta_i$	γ_i	$\beta=\beta_1-\beta_0$	$\gamma=\gamma_1-\gamma_0$	$\omega_L{}^2(M_nM_0)^{1/2}$ (10^4 erg cm^{-2})	β_1/β_0
NaCl	2.8138	0.2477	0.01885	0.30740	0.02705			11.144	0.32
NaCl (crystal data[a])	2.8138	0.3280	0.02495	0.23190	0.02703				
NaH	2.44	0.4413	0.01917	0.09844	0.01544	0.2089	0.01161		
NaD	2.44	0.4527	0.02016	0.09838	0.01583	0.2090	0.01122		
KCl	3.139	0.2766	0.01948	0.2546	0.02244			9.6779	0.39
KCl (crystal data[a])	3.139	0.3240	0.02273	0.2177	0.02248				
KH	2.85	0.4724	0.02190	0.09815	0.01477	0.1565	0.00767		
KD	2.85	0.4719	0.02187	0.09817	0.01476	0.1565	0.00768		

[a] Reference 14.

significant. The ratio of β_1 to β_0 is also given in this table and we see that the values are close to those obtained by Jaswal[12] for the molecular model of U centers. This model also assumes that γ is zero.

Fieschi, Nardelli, and Terzi[13] have calculated the local-mode frequency due to U centers in NaCl, KCl, and KI on the basis of the shell model. They are concerned with a single force constant change, namely, α_S, and therefore the condition that no net force acts on the impurity atom under a rigid-body translation of the crystal does not hold. However, as shown in Table III, their values for α are not very different from those which we obtain using Eq. (5) in the approximation $\gamma=0$, i.e.,

$$\alpha=-2\beta.$$

The force-constant change α does not seem to be very sensitive to the differences between the lattice dynamical models used in these two calculations.

III. SECOND METHOD OF ESTIMATING THE CHANGES IN FORCE CONSTANTS

In an attempt to gain some insight into the question of what magnitude to expect for the change in the force constants of the alkali halide crystal due to the presence of U centers, we turned our attention to the alkali hydrides. It seems reasonable that the force constants between the hydride (deuteride) impurity and its nearest neighbors in the alkali halide host crystal should be similar to those for the perfect alkali hydride (deuteride) crystal evaluated at the nearest-neighbor separation in the perfect halide crystal. Unfortunately, there are insufficient data on the solid hydrides to calculate the force constants from Eq. (10) in the same way as for the halides.[14] The best we can do[15] is to combine the value of ρ determined from molecular data,[16] with measured values of the lattice spacing r_0 [17] to determine the parameter λ and then evaluate $\Phi_1(r)$, β_1, and γ_1 at the halide lattice spacing. The parameters ρ and λ, and thence β_0 and γ_0, were determined in the same way, i.e., using both molecular and crystal data, for NaCl and KCl so that the changes in force constants were obtained in a consistent manner. The results of these calculations are shown in Table IV, together with the corresponding quantities calculated from the alkali halide-crystal data.[14] These are all room-temperature values. Note that the values of $\Phi_0(r)$ and β_0 obtained partially from molecular data are, respectively, smaller than and greater than those obtained wholly from crystal data, but the values of γ_0 obtained from the two sets of data are essentially the same. From these results

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TABLE V. Force constants in KBr:Li$^+$ and KCl:Li$^+$ by method of Sec. III using room-temperature[a] and 0°K[b] crystal data.

	r_0(Å)	ρ(Å)	$\Phi(r_K)$ (10^{-13} erg)	$-\beta_i$ (10^4 erg cm^{-2})	γ_i (10^4 erg cm^{-2})	β (10^4 erg cm^{-2})	γ (10^4 erg cm^{-2})	$\beta_{\mathrm{Li}^+}/\beta_{K^+}$
KBr[a]	3.293	0.334	2.07	1.856	0.188			
LiBr[a]	2.745	0.348	0.64	0.5288	0.0559	1.327	0.1323	0.2850
KCl[a]	3.139	0.3236	2.196	2.097	0.2161			
LiCl[a]	2.565	0.3346	0.619	0.553	0.0590	1.544	0.1572	0.2638
KCl[b]	3.117	0.3114	2.134	2.201	0.2199			
LiCl[b]	2.554	0.3218	0.5745	0.5548	0.0573	1.646	0.1626	0.2521
KCl[c]	3.147	0.337	2.520	2.219	0.2376			
LiCl[c]	2.570	0.342	0.3816	0.3262	0.0434	1.892	0.1942	0.1470

[a] Reference 14.
[b] Reference 9.
[c] Reference 20.

we conclude that a decrease of about 70% in the magnitude of both β_0 and γ_0 is to be expected when a hydride (deuteride) impurity ion replaces a halide ion.

IV. THE KBr:Li$^+$ SYSTEM

Resonance modes due to lithium impurities in potassium bromide have recently been studied experimentally by Sievers.[18] In a theoretical study of this system, Sievers and Takeno[19] fitted the experimental data with a single, remarkably soft, force constant between the Li$^+$ impurity and its nearest-neighbor Br$^-$ ions, namely, 0.6% of the force constant in the pure KBr crystal. We were interested to see whether such a softening of the force constant for the KBr:Li$^+$ system would be obtained by the method described in Sec. III above for *U* centers in NaCl and KCl. The two parameters of the interatomic potential [Eq. (10)] for the potassium and lithium halides can be obtained from crystal data. We used the room-temperature values given by Born and Huang[14] to calculate β_i and γ_i for KBr and LiBr, in each case evaluated at the lattice spacing of KBr, and we again found 70% softening of the force constant β_0.

The experiments of Sievers[18] were carried out at 1.5°K, therefore it is of interest to see whether the softening of the force constant β_0 is increased by using low-temperature values of the potential parameters. Unfortunately, we do not have the necessary low-temperature parameters for LiBr. However, we do have values of the potential parameters of KCl and LiCl at both room temperature and 0°K and we expect the effect of temperature to be much the same for the chloride system as for the bromide system, therefore we calculated the force constants for Li$^+$ in KCl at both room temperature and 0°K. The results are shown in Table V. There is a greater softening of the force constant β_0 at 0°K than at room temperature—a 75% reduction in β_0 is obtained at 0°K due to the presence of the Li$^+$ impurity. We obtain a greater reduction in β_0—85% at room temperature, if we use the potential parameters calculated by Tosi and Fumi[20] for the Huggins-Mayer form of the Born repulsive energy to determine the force constants. These results are also shown in Table V. However, it does not seem that we can obtain such a large reduction as 99.4% by the method we have used, unless we evaluate β_1 at an impurity-nearest-neighbor separation r_1 much greater than r_0 of the host crystal, and such a relaxation effect adds yet another unknown to the problem.

Recent calculations of the minimum-energy configuration of Li$^+$ in KCl[21] show that the ideal K$^+$ lattice site is not a stable position for the Li$^+$ ion; instead there are six equivalent symmetrically placed energy minima about the ideal lattice site in which the lithium ion is stable. The asymmetry thus introduced might cause the remarkable softening of the force constant β_0 which is observed[18]; however, to take this asymmetry into account would greatly complicate the theoretical treatment of the problem and also increase the number of unknown force-constant changes.

V. DISCUSSION

This study of the problem of determining the force-constant changes when a substitutional impurity is introduced into a cubic ionic crystal accentuates the need for more experimental work on such crystals which would enable observed peaks in the frequency spectrum to be assigned unambiguously to modes of particular symmetry, together with theoretical Green's functions based on a better model of the perfect crystal. Then, for example, if we knew the frequencies ω_r of the impurity-resonance modes of symmetry A_{1g}, E_g, and F_{2g} due to either positive or negative ion impurities in KCl, we could obtain β and γ directly from the curves in Figs. 1 and 2 of I. These curves show the linear combinations of Green's functions appropriate to the symmetry of the mode under consideration, plotted as a function of the reduced frequency x. The value of the ordinate at $\omega=\omega_r$ is equal to β^{-1} and γ^{-1} for the A_{1g},

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E_g modes and F_{2g} modes, respectively. The value of β which we obtain for Li^+ in KCl by the method of Sec. IV (see Table V) yields resonance modes of symmetry E_g at the following frequencies: $\omega_1 \sim 47$ cm^{-1}, $\omega_2 \sim 76$ cm^{-1}, $\omega_3 \sim 101$ cm^{-1}, and $\omega_4 \sim 111$ cm^{-1}. Observed spectra[2] of Li^+ in KCl exhibit peaks at 130 cm^{-1} and 200 cm^{-1} which might correspond to the second-order processes $\omega_1+\omega_2$ and $2\omega_3$. However, such comparison with experiment is not very meaningful in the present circumstances due to the approximations made in the theory, viz., the restriction to nearest-neighbor interactions only, the lattice dynamical model used to represent the perfect crystal, and its use of 0°K data. All these factors contribute to a shift in the resonant-mode frequency. Also, no assignment of the peaks in the observed spectra[2] to modes of particular symmetry has been made.

It is to be hoped that there will soon be sufficient experimental data available to obtain a set of values for the parameters which enter a calculation of the impurity induced first-order Raman and infrared spectra of alkali halide crystals. The consistency of these values would provide a test of the lattice dynamical model used in the calculations.

ACKNOWLEDGMENT

It is a pleasure to thank Professor A. A. Maradudin for many helpful discussions during the course of this work.

PHYSICAL REVIEW VOLUME 150, NUMBER 2 14 OCTOBER 1966

Resistance and Magnetoresistance of $Li(NH_3)_4$[†]

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(Received 22 March 1966)

Measurements are reported on the resistivity and magnetoresistance of the bronze-colored compound formed on freezing a saturated solution of lithium in ammonia. The lithium compound freezes at 89°K. The residual resistivity at 4.2°K is 0.30 $\mu\Omega$ cm. The lithium compound shows a nonsaturating magnetoresistance of the form $\Delta\rho/\rho_0=AB^2$ where $A=46$ m^4 volt^{-2} sec^{-2}, at fields up to 43 kG. The large magnetoresistance is assumed to originate from hole and electron bands containing equal numbers of carriers; that is, the material is taken to be completely compensated.

INTRODUCTION

THE increased interest in liquid metals in the last decade has stimulated interest in solutions of alkali metals and alkaline earth metals in ammonia as they exhibit metallic behavior. At least two of the metals in group I and II elements (all of which are soluble in liquid ammonia) form solid compounds with the ammonia; they are lithium and calcium.[1] These compounds have the approximate formulas $Li(NH_3)_4$ and $Ca(NH_3)_6$. We report here measurements on the lithium compound: lithium tetrammine.

As this material has not been extensively studied, a few qualitative observations are in order. The solid is a golden-red color, the same as the liquid. No sign is seen of metal precipitation from the solution on freezing, as with Na–NH_3. There is no large change in volume on freezing, so the density must be close to that of the liquid (0.5 g/cm^3). The crystal structure is not known for $Li(NH_3)_4$: for $Ca(NH_3)_6$ Cagle reports[2] body-centered cubic. The only other previous work is that of Jaffe,[3] Birch and MacDonald,[4] and Morgan *et al.*,[5] all on the lithium compound. They reported, respectively, Hall data and magnetoresistance, freezing points and composition, and resistivity and several phase changes. The freezing point at 89°K has the appearance of a eutectic; it lies at a minimum in a melting point-versus-composition diagram. Hence 89°K may not be the melting point of $Li(NH_3)_4$, as melting points of compounds are usually found to be at maxima. However, the character of the material in the solid does not fit ideas of either a solid solution or a metal precipitated from the solvent. Furthermore, examples can be found wherein "submerged maxima" or peritectics lie beneath, or nearly beneath, eutectics.[6] Hansen[7] reports such struc-

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[†] Research assisted by the U. S. Office of Naval Research and the R. A. Welch Foundation.

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