4. SUMMARY

The main conclusions of the present research can be summarized as follows:

(a) Vibrationally induced electric-dipole lines associated with the transition to the tetragonally split $^4\Gamma_3$ level are observed at ~3939 and ~3896 Å.

(b) Fine structure associated with exchange-coupled pairs of ions is observed on electric dipole transitions associated with the $^4\Gamma_1$ level. The fine structure involves pairs of ions in a $S=\frac{5}{2}$ ground state, both being excited into a $S=\frac{3}{2}$ upper state. The selection rule for the transitions is that the spin of the pairs is conserved.

(c) The fine structure due to exchange coupled pairs of ions seems to be associated only with the $^4\Gamma_1$ levels.

(d) The $^4\Gamma_1$ level is not vibrationally induced. Some other mechanism is operative, which is tentatively associated with the excitation of an exciton causing a sharp magnetic dipole line and the consequent excitation of a magnon which causes an electric-dipole satellite line.

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Experimental Study of the Lattice Dynamics of Disordered Vanadium Alloys*

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We report on the investigation of the vibrational frequency spectrum of disordered alloys of vanadium consisting of $Be_{0.033}V_{0.967}$ $Ni_{0.05}V_{0.95}$, and $Pt_{0.05}V_{0.95}$. Inelastic-neutron-scattering techniques were used to obtain information about the frequency spectrum of these alloys. The alloys were chosen because they scatter neutrons incoherently, and yet the solute atoms can differ widely from vanadium with respect to atomic mass and electron configuration. The disordered vibrational spectra show high-frequency impurity bands upon alloying with light-mass beryllium impurity atoms, large changes in the whole vibrational pattern caused by long-range interatomic potential differences arising from changes in the electronic properties of the nickel and platinum alloys, and most surprisingly, very small changes in the vibrational spectra upon alloying with heavy-mass platinum impurities.

INTRODUCTION

IN a communication published several years ago, we reported inelastic-neutron-scattering measurements of localized modes of vibration associated with light-mass nickel atoms in nickel-palladium alloys containing 5 and 10 at. % nickel.[1] The data indicated a broad impurity band of vibrations whose peak height increased with concentration. The position of the energy of the peak coincided with the estimate of the localized-mode frequency as determined from theory for a single substitutional impurity differing only in mass from the host atoms.

Recently, neutron scattering measurements have also been performed on other random binary alloys in a search for resonant modes of vibration[2] associated with heavy-mass solute atoms in dilute binary alloys. Svensson, Brockhouse, and Rowe[3] reported measurements on single crystals of gold in copper where the dispersion curves of frequency versus wave vector of the vibrations were determined. Evidence for resonant modes of vibration can be indirectly obtained from the data using a recent theory of Elliott and Maradudin.[4] The theory is based upon assumptions of a dilute random binary alloy in which the solute atoms differ only in mass from the solvent atoms. Their theory shows that the phonons in the alloy should be shifted to lower frequencies and broadened in comparison to the phonons of pure copper. The shift and broadening of the phonons can be predicted from this theory where only a knowledge of the frequency distribution of the perfect crystal is required. The frequency of the resonant modes of vibration, according to the calculation should occur at the first zero in the frequency shift of the perturbed phonons. This resonant frequency obtained from the first zero in the frequency shift is also the resonant frequency predicted from theory for a single heavy-mass impurity. In the measurements on

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[1] B. Mozer, V. W. Myers, and K. Otnes, Phys. Rev. Letters **8**, 278 (1962).

[2] R. Brout and W. M. Visscher, Phys. Rev. Letters **9**, 45 (1962); Yu Kagen and Ya. Iosilevkii, Zh. Eksperim. i Teor. Fiz. **44**, 1375 (1963) [English transl.: Soviet Phys.—JETP **17**, 925 (1963)].

[3] E. C. Svensson, B. N. Brockhouse, and J. M. Rowe, Solid State Commun. **3**, 245 (1965).

[4] R. J. Elliott and A. A. Maradudin, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. I, p. 231.

the Au-Cu system the resonant frequency is difficult to determine from the behavior of the frequency shifts, but appears to occur at a much higher frequency than expected for a single impurity. Measurements similar to those of Svensson, Brockhouse, and Rowe were obtained by Møller and Mackintosh[5] on a single crystal of chronium containing 3% tungsten. In the latter experiment the frequency shift and width of the perturbed phonons was in closer agreement with theory, but the frequency of the resonant mode was again found to be high at one-half the maximum frequency for pure chromium. The frequency of the resonant mode for a single heavy-mass impurity in chromium can be estimated if the frequency distribution for pure chromium were known. Since the frequency distribution of pure chromium is not available, one can use Fine's[6] distribution for a bcc lattice, and one finds the resonant frequency for the single impurity of mass ratio 3.54 occurs at $\frac{1}{3}$ the maximum frequency. A similar calculation for a gold impurity in copper[3] shows the resonant frequency for mass ratio 3.1 to occur at 0.35 times the maximum frequency of copper which is much lower than the experiment indicates. Thus, there is quite a discrepancy in the frequency of the resonant mode derived from single-crystal measurements using the present Elliott and Maradudin theory and the frequency expected for a single impurity. There is no doubt that some of this discrepancy between theory and experiment could be removed if the calculations included changes in the interatomic potential upon alloying. Such potential differences are certainly expected for those alloys studied in the single-crystal experiments. One way of seeing this is to compare the frequency spectrum of the pure components, e.g., chromium or tungsten. Phonon dispersion curves of tungsten[7] and chromium[8] show that the frequency spectrum of one metal relative to the other metal does not scale as the square root of the mass ratio as expected from the Born–von Karman theory of lattice dynamics for materials with identical interatomic potentials. In the case of tungsten and chromium there is a 20 to 30% discrepancy in this method of scaling frequencies. Since the phonon dispersion relations have not been measured for gold, we can compare the ratio of Debye temperatures of gold and copper to see if it equals the square root of the mass ratio. Here again there is a 10 to 20% discrepancy in the ratios which suggests different interatomic potentials. Thus, it appears that additional calculations are necessary to take into consideration the shift and width of the perturbed phonons under combined mass and interatomic potential differences in these alloy systems in order to determine resonant-mode frequencies.

In another measurement, Tchernoplekov and Zemlyanov[9] investigated the inelastic neutron scattering of a powder specimen of a dilute alloy of magnesium containing 2.8 at. % lead and observed a spectrum that would correspond to the resonant mode of vibration associated with the heavy-mass lead atoms. Objections raised to the earlier work of Mozer, Myers, and Otnes in their investigations of Ni–Pd alloys could be raised here in that the Mg–Pb alloy is a coherent neutron scatterer and the peak showing the resonant modes could conceivably arise from coherent scattering effects in the alloy. We do not believe the coherence effects are that important and neglecting the possible uncertainty in determining precisely the frequency of the resonant mode and its absolute intensity in this alloy because of coherence effects, we also conclude that the measurements of Tchernoplekov and Zemlyanov do demonstrate the occurrence of resonant modes of vibration. It is interesting to note that the electronic structure in the Mg–Pb alloy is probably much simpler than the electronic structure in either the Au–Cu or Cr–W alloys where the *d* bands are so important and therefore the resonant modes in Mg–Pb seem to be predicted accurately taking into account only the mass difference.

In the present paper we wish to report additional attempts at investigating defect modes of vibration in dilute binary alloys. Because of objections raised about coherent scattering effects on powder specimens of the Ni–Pd alloys previously reported, it was decided to concentrate on alloys of vanadium where one can obtain samples which scatter neutrons incoherently. Such alloys could be checked for coherent scattering by taking neutron powder diffraction patterns; such patterns were taken on the alloys reported here to determine the coherent elastic scattering of the alloys. From the residual coherent scattering of the alloy, one can determine the amount of solute atoms that are in solid solution in the vanadium matrix by observing the change in the strongest peak associated with the very small coherent cross section of pure vanadium. It was noted for all the alloys discussed here that the solute atoms were in solid solution to within the error of the diffraction measurements except for the Be–V alloy where only 85% of the beryllium was in solid solution. In the latter alloy, no new coherent peaks were observed in the diffraction pattern.

EXPERIMENTAL PROCEDURES AND RESULTS

Neutron scattering data were obtained on the following metals and alloys, vanadium, $Be_{0.033}$-$V_{0.967}$, $Pt_{0.05}$-$V_{0.95}$, and $Ni_{0.05}$-$V_{0.95}$. All concentrations are in atomic

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[5] H. B. Møller and A. R. Mackintosh, Phys. Rev. Letters **15**, 623 (1965).

[6] P. C. Fine, Phys. Rev. **56**, 355 (1939).

[7] S. H. Chen and B. N. Brockhouse, Solid State Commun. **2**, 73 (1964).

[8] H. B. Møller and A. R. Mackintosh, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. I, p. 95.

[9] N. A. Tchernoplekov and M. G. Zemlyanov, Zh. Eksperim. i Teor. Fiz. **49**, 449 (1965) [English transl.: Soviet Phys.—JETP **22**, 315 (1966)].

percent. The pure material was in pellet or powder form, whereas the alloys consisted of arc-melted buttons.[10] Samples were mounted in a 0.001-in.-vanadium foil holder whose dimensions are 4 in. by 2 in., by $\frac{1}{4}$ mean free path for elastic scattering. Since the inelastic cross section is at least one order of magnitude smaller than the elastic scattering cross section, the samples are *very* thin and multiple inelastic scattering can be neglected. Vanadium and its alloys were mounted in the same holder in order to have comparable conditions. The measurements were performed at room temperature on the BNL cold-neutron facility which was described elsewhere.[11] The essential features of the apparatus are that a refrigerated beryllium filter is used to provide an incoming beam of neutrons having wavelengths greater than 4 Å (the energy of these neutrons goes from zero to 5×10^{-3} eV and the spectrum is practically triangular with a width of 2 to 3×10^{-3} eV.

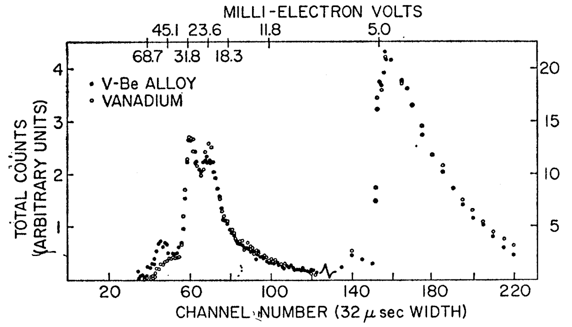

FIG. 1. Time-of-flight data for neutron scattering from vanadium and Be$_{0.033}$-V$_{0.967}$ alloy. The scattering angle was 90° and the sample was at room temperature. A constant background was subtracted from the raw data. Each channel corresponds to 32 μsec and the conversion to neutron wavelength in Å is given by $\lambda=0.02563\,(N+2)$, where N is the channel number. The incoming neutron spectrum begins at channel 125 and goes to channel 256.

The scattering sample used in transmission is placed in an evacuated chamber to eliminate gas scattering and neutrons scattered from the sample pass through a Fermi chopper and are detected by BF$_3$ counters after having traversed a 5-m flight path filled with helium. The resolution of the system excluding the incoming beam is $1\frac{1}{4}\%$ for 4-Å neutrons or a resolution in time corresponding to 64 μsec (two channels exhibited in the following spectra). Figure 1 shows a set of raw data with constant background subtracted for vanadium and the Be–V alloy at 90° scattering angle. The vanadium data are essentially the same as the BeV data except that in the alloy there are two small peaks corresponding to large energy gain, at channels 46 and 49. The raw data for the Pt–V and Ni–V alloys are similar in shape to the pure vanadium data except that the major peaks in the inelastic spectrum are shifted to lower channel numbers corresponding to shorter wavelength neutrons which have gained more energy in the scattering process as observed in Figs. 2 and 3.

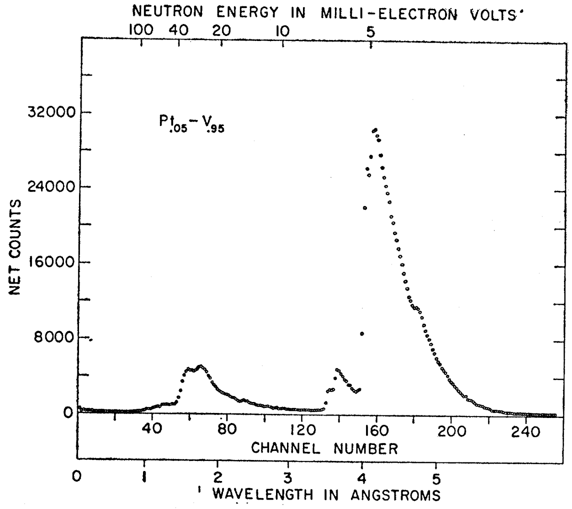

FIG. 2. Time-of-flight data for neutron scattering from Pt$_{0.05}$-V$_{0.95}$ alloy. The scattering angle was 90° and the sample was at room temperature. A constant background was subtracted from the raw data. Each channel corresponds to 32 μsec and the conversion to neutron wavelength in Å is given by $\lambda=0.02563\,(N+2)$ where N is the channel number. The incoming neutron spectrum begins at channel 125 and goes to channel 256.

It is possible to obtain estimates of the frequency distribution for some of the alloys and in the cases where there are large mass differences, more correctly, the frequency spectrum[12] of the average of the Green's

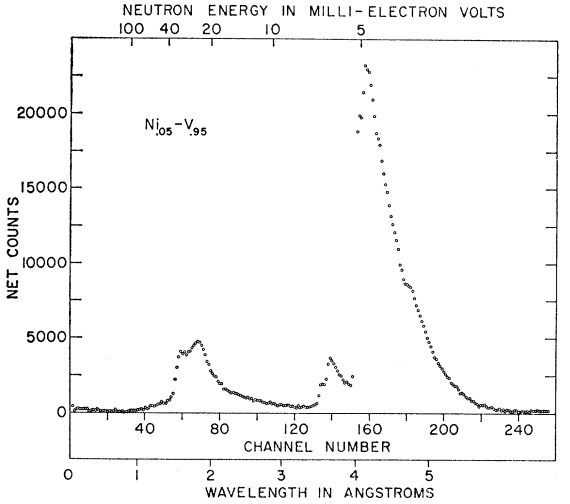

FIG. 3. Time-of-flight data for neutron scattering from Ni$_{0.05}$-V$_{0.95}$ alloy. The scattering angle was 90° and the sample was at room temperature. A constant background was subtracted from the raw data. Each channel corresponds to 32 μsec and the conversion to neutron wavelengths in Å is given by $\lambda=0.02563\,(N+2)$, where N is the channel number. The incoming neutron spectrum begins at channel 125 and goes to channel 256.

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[10] The Be–V alloy was fabricated by Nuclear Metals of West Concord, Massachusetts.

[11] B. Mozer, K. Otnes, and H. Palevsky, *Lattice Dynamics* (Pergamon Press, Inc., Oxford, 1965), p. 63.

[12] We shall use frequency and energy interchangably.

function of the quadratic displacements for the alloy:

$$\varphi(\omega)=2\omega\langle\sum_{i,\alpha}\operatorname{Im}G_{ii}{}^{\alpha\alpha}(\omega^2)\rangle$$
$$=2\omega\langle\sum_{i,\alpha}\sum_{s}\psi_\alpha(i,\omega_s{}^2)\psi_\alpha(i,\omega_s{}^2)\delta(\omega^2-\omega_s{}^2)\rangle,$$

where Im means imaginary part, $\psi(i,\omega_s{}^2)$ is the vector amplitude of vibration of the ith atom at normal-mode frequency ω_s, and $\langle\,\rangle$ refers to an average over the random distribution of solute atoms. An estimate of the frequency distribution or Green's function can be determined from the measured cross section as follows[11]:

$$\varphi(\omega)\propto\frac{d^2\sigma}{d\Omega dE}\frac{k_0}{k}\frac{(E-E_0)}{\kappa^2N(E-E_0)},$$

where k_0/k refers to the ratio of the incoming wave vector of the neutron to the outgoing wave vector of the neutron, $\kappa^2=|\mathbf{k}-\mathbf{k}_0|^2$, and $N(E)$ is the Bose-Einstein distribution function, $N(E)=(e^{E/kT}-1)^{-1}$. Figure 4 exhibits the frequency distribution, or the Green's function as a function of energy for vanadium and two alloys.

For small mass differences between solute and solvent atoms the Green's function is proportional to the frequency distribution. The points representing the Green's function for the Be–V alloy show complete similarity to the curve representing pure vanadium in the region of common frequencies. The positions of the peaks and the over-all spectrum have the same shape. The points for the Be–V alloy appear lower than the curve for vanadium because of the normalization used. One should note the structure at higher energy in the Be–V data which is a striking demonstration of localized modes broadened into an impurity band. The data for many experiments on this alloy indicate a splitting of the band as shown in the figure. Such structure in the impurity band can be explained by the theoretical work of Dean[13] and Langer.[14] In Langer's theory, or an extension of it to three dimensions, the frequency distribution of the disordered alloy reflects to some extent the structure in the frequency distribution of the host lattice; the same effect would be expected for the impurity band observed in the Green's function, i.e., the impurity band should reflect some of the structure in the Green's function for the perfect lattice. This behavior of the impurity band is a result of the linear concentration approximation for the self-energy of the phonon in the Langer theory, and would not be valid at high concentration. Structure in the impurity band has not been observed in the previous experiments on the Ni–Pd alloys,[1] in additional experiments on the Ni–Pd system,[15] or in vanadium hydrides.[16] No structure in impurity bands was observed in electron-tunneling experiments on superconducting alloys reported by Rowell, McMillan, and Anderson,[17] and by Adler, Jackson, and Chandrasekhar.[18] (It should be noted, under the assumption that the electron-phonon coupling constant is independent of frequency, that the tunneling experiments measure the same Green's function as do the neutron experiments and, as mentioned, only under certain conditions of small differences does this Green's function represent the frequency distribution.[19]) A theoretical estimate of the frequency of a localized mode of a beryllium atom in vanadium can be made taking into account only the mass difference and it is found that this frequency coincides with the high-frequency peak in the impurity band. The localized-mode frequency would be expected at the high-frequency peak according to Dean's calculation, but not Langer's original calculation. The measurements on the Be–V alloy seem to indicate that the mass difference are most important in describing this alloy and such conclusions are being verified by additional work on a lower concentration alloy.

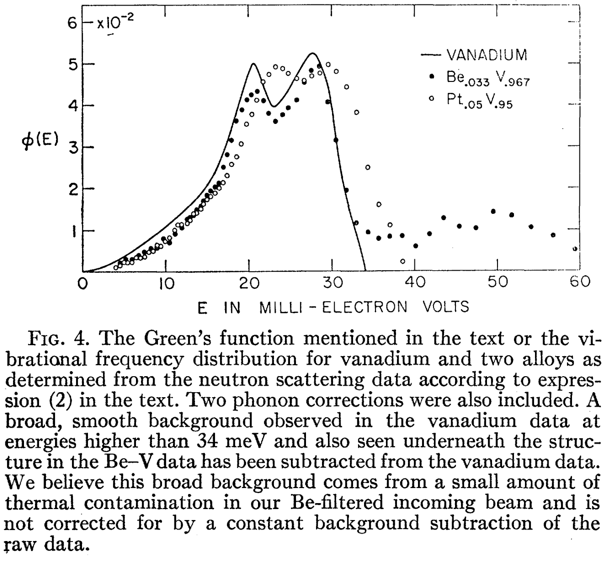

FIG. 4. The Green's function mentioned in the text or the vibrational frequency distribution for vanadium and two alloys as determined from the neutron scattering data according to expression (2) in the text. Two phonon corrections were also included. A broad, smooth background observed in the vanadium data at energies higher than 34 meV and also seen underneath the structure in the Be–V data has been subtracted from the vanadium data. We believe this broad background comes from a small amount of thermal contamination in our Be-filtered incoming beam and is not corrected for by a constant background subtraction of the raw data.

In contrast to the large mass effect in the Be–V alloy, one notes the striking difference in the Pt–V alloy data where large changes occurred in the region of frequencies common to vanadium. The Pt–V data should have ex-

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[13] P. Dean, Proc. Roy. Soc. (London) **A260**, 263 (1961).

[14] J. S. Langer, J. Math. Phys. **2**, 548 (1961). The extension of Langer's method to three-dimensional solids has been considered by A. A. Maradudin and others. See A. A. Maradudin, in *Solid State Physics*, edited by F. Sietz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, pp. 274–392.

[15] B. Mozer and K. Otnes, Bull. Am. Phys. Soc. **8**, 41 (1963) and to be published.

[16] W. Kley, J. Peretti, R. Rubin, and G. Verdan, in Proceedings of the Symposium on Inelastic Scattering of Neutrons by Condensed Systems, 1965 (unpublished).

[17] J. M. Rowell, W. L. McMillan, and P. W. Anderson, Phys. Rev. Letters **14**, 633 (1965).

[18] J. G. Adler, J. E. Jackson, and B. S. Chandrasekhar, Phys. Rev. Letters **16**, 53 (1966).

[19] There are additional assumptions involved in the interpretation of the tunneling measurements such as the incoherent approximation in the electron-phonon cross section involving the self-correlation Green's function instead of more complicated Green's functions involving pair displacements of the atoms.

hibited a peak at lower frequencies arising from the resonant behavior associated with the heavy-mass platinum atoms. It would have been expected that all the frequencies should be lowered, whereas the are all raised. One should note however that the addition of 5% platinum atoms will change the average band electrons, and in effect change the interatomic potential. These are long-range effects coming from modifications of the electron gas in a metal in contrast to short-range interatomic potential changes as one usually thinks of them in nonmetallic solids. Such effects in alloys have already been reported by Woods and Powell[20] in their study of the molybdenum and niobium alloys. If one can assume rigid bands for transition-metal alloys widely separated in the periodic table, one expects to find an increase in the vibrational frequencies on adding electrons to the vanadium system since the addition of one more electron to vanadium produces a chromium-like system with very high vibrational frequencies.[21] We are making a stronger assumption of rigid bands for transition-metal alloys than did Woods and Powell[20] for alloy constituents adjacent in the periodic table which differ by only one electron. In addition to simply adding electrons to the vanadium system, the platinum atoms have different ionic cores and both modifications of the electron system alter the interatomic potentials. Figure 5 shows a comparison between the frequency spectrum of the Pt–V alloy and a Ni–V alloy of the same composition. One also sees here that the frequencies of the Ni–V alloy are considerably higher than the frequencies of the pure vanadium, but the frequencies of the Pt–V are higher still. Thus there is some evidence that differences in the ionic cores of nickel and platinum produce additional modification of the interatomic potential in the alloy system.

It seems that one should be able to see some effects of the heavy-mass platinum atoms on the vibrational spectrum of the alloy but *no* large effects are observed. A comparison of the Ni–V data with the Pt–V data as shown in Fig. 5 seems to indicate a rather broad bump in the Pt–V data in the energy range from 10 to 16 meV; the bump is not so striking a demonstration as the peak observed by Tchernoplekov and Zemlyanov.[9] The frequency and width of a resonant mode for a single isotopic impurity in vanadium using the perturbed frequency distribution shown for the Pt–V alloy in Fig. 3 instead of the pure vanadium distribution would be 12 meV and 4 meV, respectively.[22] Thus the position of the bump seems to agree with what would be expected from a simple theory although in an alloy with 5% concentration of heavy atoms one would expect a larger peak perhaps shifted to lower frequencies. It is probable that the force constant differences in the Pt–V alloy can smear out a large peak associated only with heavy-mass effects.

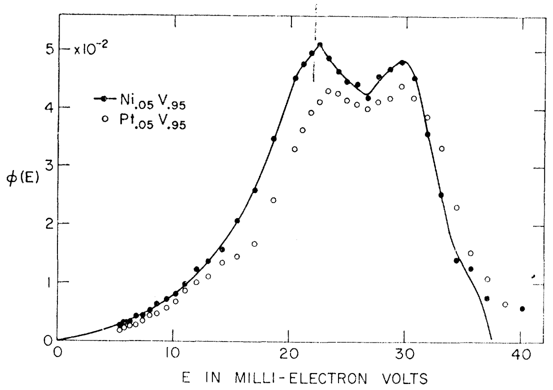

FIG. 5. The Green's function versus energy for the Ni–V and the Pt–V alloy as determined from the inelastic-neutron-scattering data according to expression (2) in the text. Two-phonon corrections were also included in the data reduction. Data were averaged over three channels to improve statistics in the region of frequencies from 7 to 20 meV.

The changes observed here in the vibrational spectrum of disordered alloys should also be seen in specific-heat measurements on the same alloys, especially so in the Pt–V and Ni–V alloys where the total spectrum is so drastically changed. Experiments on the superconducting properties of these same alloys in conjunction with the neutron experiments should help yield information on the electron-phonon coupling constant as a function of the lattice-vibrational frequencies and on such gross effects as the variation in the critical temperature with changes in the vibrational frequencies.

ACKNOWLEDGMENTS

The authors are very grateful to A. Cinquepalma for his assistance with many aspects of the experiments and and to H. Palevsky for making the slow chopper available to them and for his continued interest in the experiments.

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[20] A. D. B. Woods and B. M. Powell, Phys. Rev. Letters **15**, 778 (1965).

[21] In some unpublished work of one of the authors, the time-of-flight spectrum of chromium has been observed; the chromium phonon spectra show structure similar to the phonon spectra of vanadium except that the frequencies are higher in agreement with the work in Ref. 8.

[22] P. L. Leath and B. Mozer (to be published).