Lattice Vibrational Spectra of Beryllium, Magnesium, and Zinc

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The lattice vibrational spectra of Be, Mg, and Zn have been obtained using the root sampling method. The force constants used in the calculations were those determined from measurements of the dispersion relations by slow neutron-scattering techniques. Calculations of the specific heat of each metal show good agreement with measured values.

I. INTRODUCTION

IN recent years the scattering of slow neutrons in solids has proved valuable as a tool for investigating the dispersion relations of lattice waves in crystals. In particular, measurements have been made on beryllium, magnesium, and zinc, all having the hexagonal close-packed lattice structure. In the first case (Be), Schmunk et al.[1] have determined the force constants for a central force model with interactions out to fifth nearest neighbors. For Mg, Collins[2] determined the force constants for both a tensor force model and a central force model with interactions out to fourth nearest neighbors. A similar experiment by Borgonovi et al.[3] has given the force constants of zinc for the tensor force model used for Mg.[2] Using these experimentally determined force constants, we have computed the lattice vibrational spectra and specific heat for each of the above metals.

II. RESULTS

The vibrational spectrum of a crystal $\rho(\omega)$ is defined such that $\rho(\omega)d\omega$ is the fraction of frequencies ω between ω and $\omega+d\omega$. The method used here to approximate $\rho(\omega)$ is to sample the frequencies $\omega(\mathbf{k})$ for a large number of values of the wave vector $\mathbf{k}$ in the first Brillouin zone of the crystal. The frequencies obtained must be weighted according to their degeneracy in the zone, and a histogram constructed of the number of frequencies falling in a given frequency interval.

In the Born-von Kármán[4] theory of lattice dynamics the frequencies ω are determined by the following secular equation:

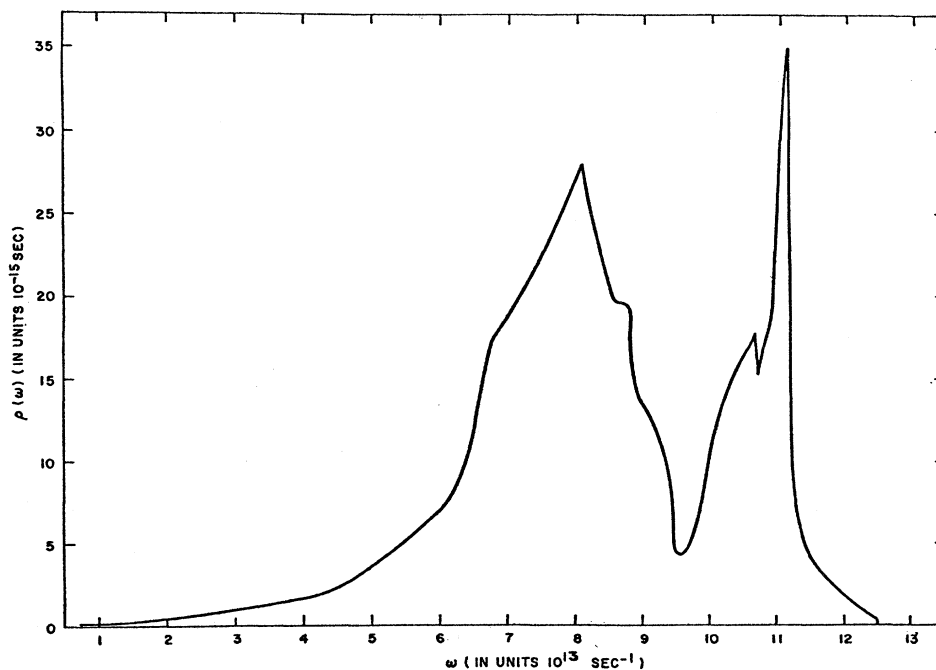$$|D(\mathbf{k})-M\omega^2 I|=0, \tag{1}$$

FIG. 1. Lattice vibrational spectrum of beryllium for a sampling of 10 261 points in the reduced Brillouin zone.

[1] R. E. Schmunk, R. M. Brugger, P. D. Randolph, and K. A. Strong, Phys. Rev. **128**, 562 (1962).
[2] M. F. Collins, Proc. Phys. Soc. (London) **80**, 362 (1962).
[3] G. Borgonovi, G. Caglioti, and J. J. Antal, Phys. Rev. **132**, 683 (1963).
[4] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954).

FIG. 2. Lattice vibrational spectrum of beryllium for a sampling of 2413 points in the reduced Brillouin zone.
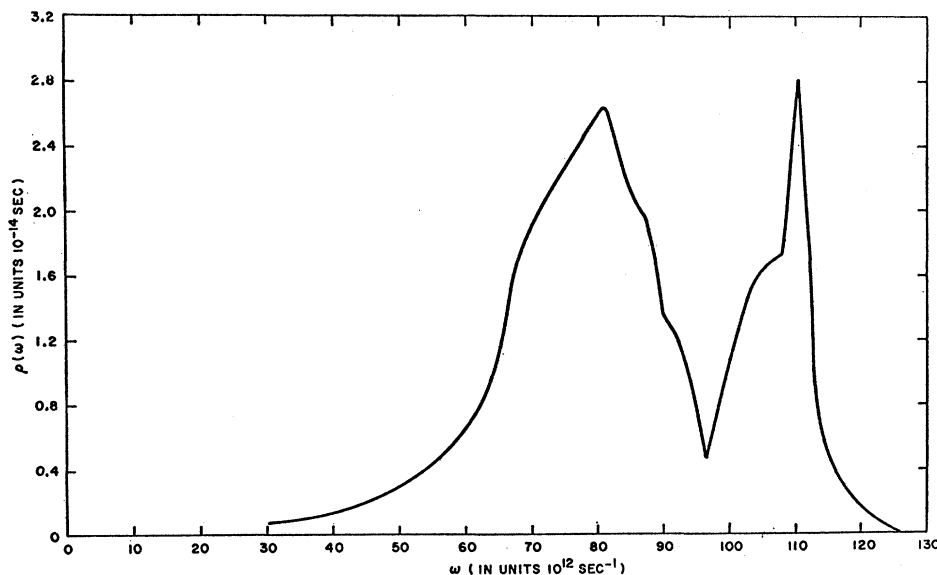
where M is the atomic mass and I the unit matrix. The matrix $D(\mathbf{k})$ is 6×6 for hexagonal close-packed crystals and depends upon the force constants of the lattice. Equation (1) has been solved for equally spaced points in that region which is one twenty-fourth of the first Brillouin zone, and irreducible under the symmetry operations that leave the roots of the secular equation invariant. The points are then weighted as to whether or not they are on the faces, edges, etc., of this reduced zone. For beryllium, the calculation was performed for 10 261 equally spaced points ($\mathbf{k}$ values) in the reduced

zone, and the spectrum shown in Fig. 1. Figure 2 shows, for comparison, the same calculation for 2413 equally spaced points. We see that greatly increasing the number of points does not significantly change the vibrational spectrum.

In the case of magnesium, the calculation was performed for a sampling of 2413 equally spaced points in the reduced zone, for both the central and tensor force models. Figures 3 and 4 show the vibrational spectra for central and tensor forces, respectively.

The vibrational spectrum of zinc was also obtained

FIG. 3. Lattice vibrational spectrum of magnesium using the central force model.
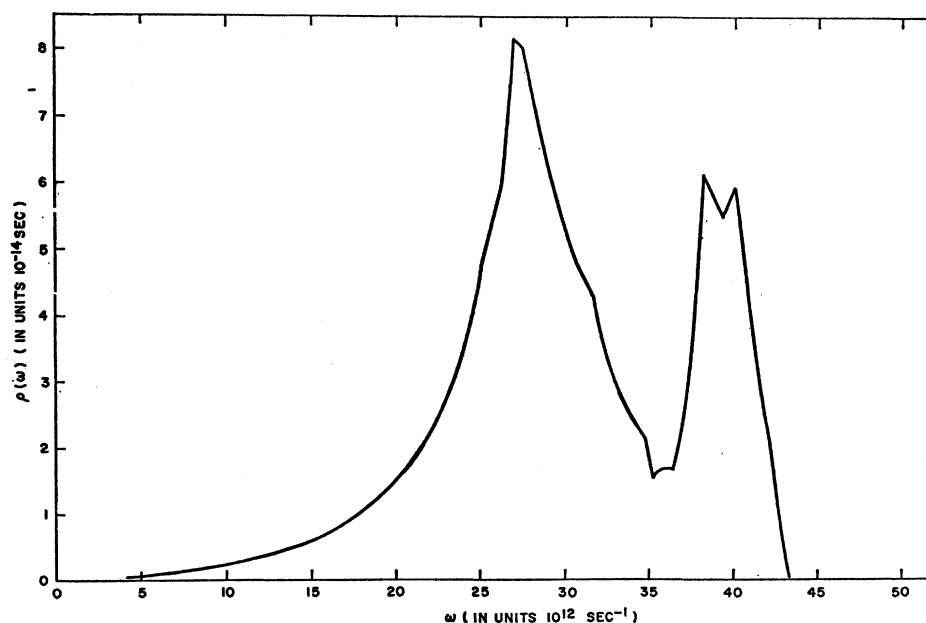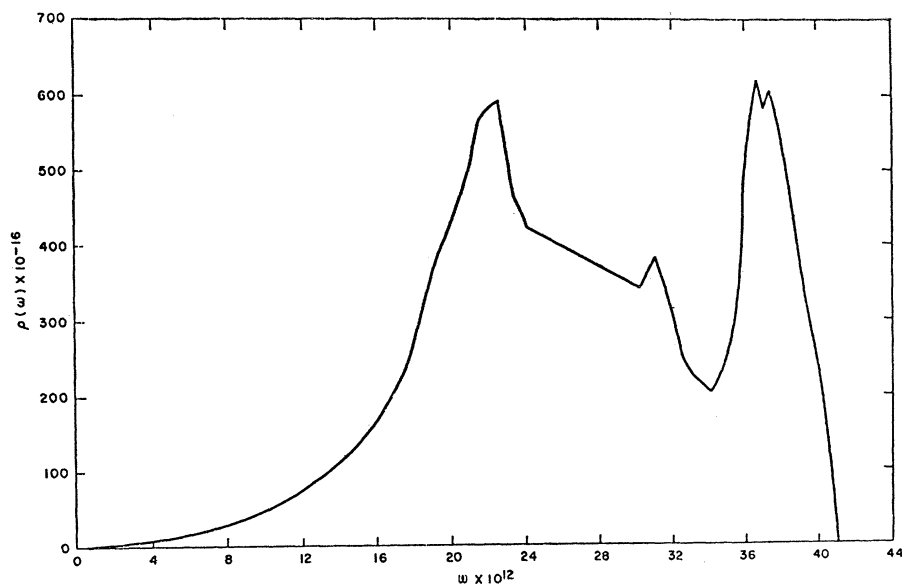
FIG. 4. Lattice vibrational spectrum for magnesium using the tensor force model.
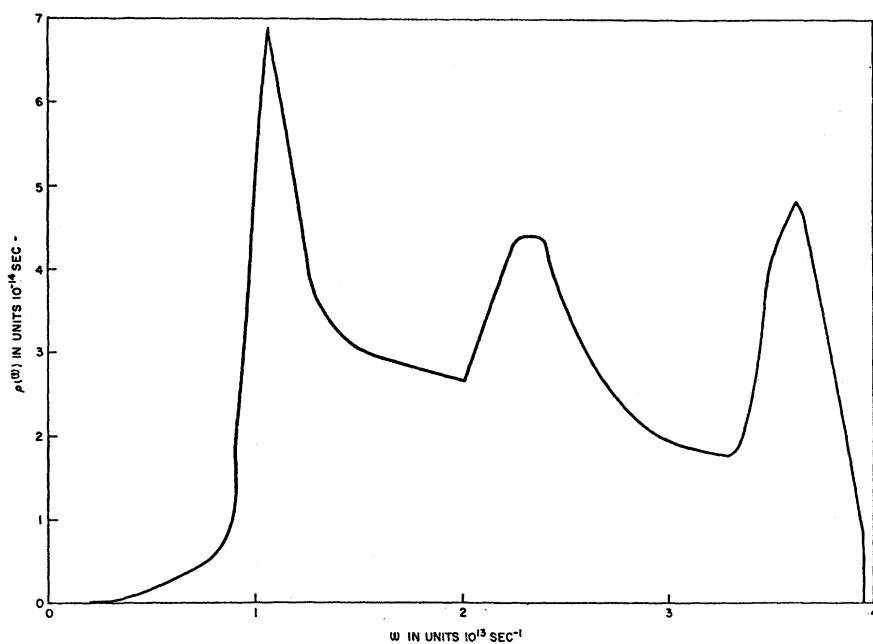

FIG. 5. Lattice vibrational spectrum of zinc using a tensor force model.

from a sampling of 2413 equally spaced points in the reduced zone with the tensor force model, and is shown in Fig. 5.

In order to make some comparison with experiment, the specific heat at constant volume C_V, which is given in terms of the frequency spectrum by

TABLE I. C_V for beryllium (cal/g).

T (°K)	Computed value	Measured value
100	0.070	
150	0.195	
200	0.311	
293	0.455	0.466
400	0.535	

TABLE II. C_V for magnesium (cal/g).

T (°K)	Computed value	Measured value
123	0.1839	0.1767
153	0.2023	0.2025
223	0.2236	0.2228
300	0.2329	

$$\frac{C_V}{3R}=\int_0^{\omega_{max}} d\omega\left(\frac{\omega}{T}\right)^2\frac{e^{\omega/T}}{(e^{\omega/T}-1)^2}\rho(\omega),\qquad(2)$$

where R is the gas constant, ω_{max} the maximum frequency of the crystal, and T the temperature measured

TABLE III. C_V for zinc (cal/g).

T (°K)	Computed value	Measured value
72	0.0538	0.0573
173	0.0826	0.0814
300	0.0882	

in energy units, has been computed for all three metals. Tables I–III compare the calculated specific heat with measured values,[5] for the vibrational spectra of Be, Mg, and Zn, respectively. The agreement is quite good in all cases, although specific heat comparisons do not provide a good test.

ACKNOWLEDGMENTS

Electron Spin Resonance Studies with Superconducting Magnets: The Spectrum of Dy³⁺ and Sm³⁺ in CaF₂

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An electron spin resonance spectrometer has been constructed using strong magnetic fields up to 46 000 G generated by a superconducting magnet. It is being used for the measurement of the magnetic properties of transition elements in ionic crystals such as (a) small g factors, (b) energy level separations up to 20 cm⁻¹, (c) isotropic and anisotropic exchange terms in spectra of pairs of paramagnetic ions, (d) spin-lattice relaxation times at high magnetic fields. The method is illustrated in the measurements of (1) the energy level separation of $\Gamma_8-\Gamma_7$ levels of Dy³⁺ in CaF₂ which is found to be $7.3_5\pm0.2$ cm⁻¹; (2) the g factors of the tetragonal spectrum of Sm³⁺ in CaF₂ which are found as $g_{||}=0.907\pm0.01$, $g_{\perp}=0.544\pm0.015$.

INTRODUCTION

ELECTRON spin resonance methods have been widely used in determining the magnetic properties of transition elements in ionic and semiconducting crystals.[1] Most of these experiments have been performed with magnetic fields of less than 20 000 G.[2] The availability of superconducting magnets with fields of the order of 50 000 G permit a number of additional experiments of interest. These experiments are of the kind: (a) Measurements of energy level separations of the order of 3–20 cm⁻¹. (b) Measurement of small g factors, i.e., $g\ll1$. (c) Measurement of some isotropic

or anisotropic exchange splittings of neighboring paramagnetic ions. (d) Spin-lattice relaxation phenomena in high magnetic fields.

Many iron group and rare-earth elements have an energy level scheme in which a few levels are closely bunched together. Examples of such ions are V³⁺, Cr⁴⁺ (d^2) in trigonal fields which have a singlet as a ground state and a doublet at 7–10 cm⁻¹ above the singlet. A similar case is Fe²⁺ (d^6) in noncubic fields. In some crystal hosts, transitions between the two levels of the non-Kramers doublet can be induced. However, transitions between the singlet and the doublet cannot be seen with conventional resonance spectrometers and magnetic fields. With very strong magnetic fields one of the doublet levels can be brought close enough to the singlet so that transitions between these levels can be effected. One usually can find a suitable magnetic-field orientation with respect to the crystal axis which will permit transitions of the type $\Delta S_z=\pm1$ of sufficient intensity. The appropriate spin Hamiltonian is

$$\mathcal{H}=g_{||}\beta HS_z+g_{\perp}\beta(H_xS_x+H_yS_y)$$
$$+D(S_z^2-\tfrac{1}{3}S(S+1))+E(S_x^2-S_y^2),\qquad(1)$$

[1] See, for example, W. Low, Paramagnetic Resonance in Solids (Academic Press Inc., New York, 1960).

[2] S. Foner and W. Low, Phys. Rev. 120, 1585 (1960), have performed ESR experiments using pulsed magnetic fields of the order of 2 000 000 G. However, this method has the disadvantage of poor accuracy in the field measurements. Relaxation effects due to fast variation of the magnetic field as a function of time effect the intensity of the spectrum. It can be used, however, to some advantage in the measurement of relaxation times at high magnetic fields [L. Rimai (private communications)].