

Vibrational Spectrum of Gold

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 (Received November 28, 1960)

A theoretical lattice vibration spectrum is calculated for gold on the basis of a three-force-constant model as elaborated by Bhatia. The lattice specific heat is calculated and compared with the experimental data.

IN 1955 Bhatia¹ proposed a model for the monovalent cubic metals for obtaining the secular equation for determining the normal modes of vibration and applied it to the calculation of the frequency spectra and specific heats of sodium¹ and silver.² The main purpose of the model was to take into account the volume-dependent forces due to the electron gas in the metal in some approximate way. The present calculation for gold follows exactly the method used by Bhatia and Horton² in the case of silver.

The values of the elastic constants used in the calculation as well as the other constants needed are listed below:

$$c_{11} = 20.163 \times 10^{11} \text{ dynes/cm}^2,$$

$$c_{12} = 16.967 \times 10^{11} \text{ dynes/cm}^2,$$

$$c_{44} = 4.544 \times 10^{11} \text{ dynes/cm}^2,$$

the nearest neighbor distance $a = 2.881 \text{ \AA}$ and the density $\rho = 19.32 \text{ g/cm}^3$. These values of the elastic constants are taken from the low-temperature measurements of Neighbours and Alers³ and refer to the temperature 0°K .

The frequency distribution function $G(\omega)$ is plotted against ω in Fig. 1, where the singularities of $G(\omega)$, characteristic of Houston's approximation, have been replaced by finite peaks of equal area.¹ Using the

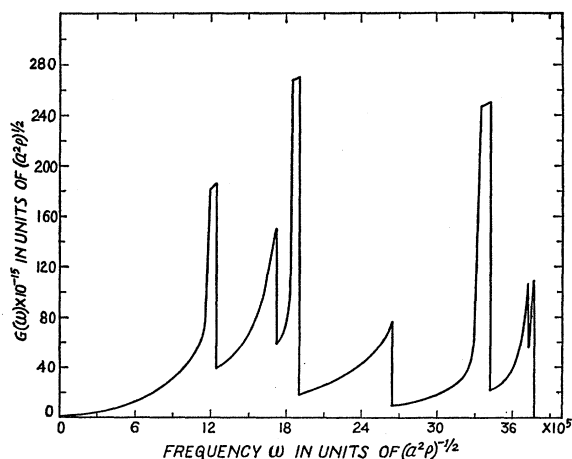


FIG. 1. The lattice vibrational spectrum of gold.

¹ A. B. Bhatia, Phys. Rev. **97**, 363 (1955).

² A. B. Bhatia and G. K. Horton, Phys. Rev. **98**, 1715 (1955).

³ J. R. Neighbours and G. A. Alers, Phys. Rev. **111**, 707 (1958).

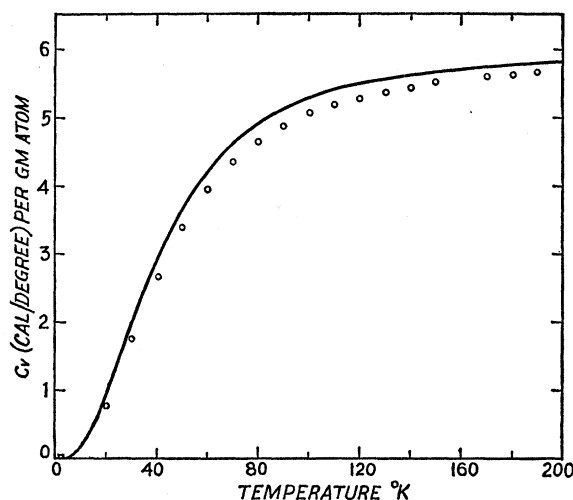


FIG. 2. The specific heat of gold at different temperatures. The solid line depicts the calculated values from the frequency spectrum. The circles \circ represent experimental values due to the measurements of Geballe and Giauque. The squares \square show the measured values due to Corak *et al.*

approximate spectrum of Fig. 1, the lattice heat capacity was obtained in the usual manner by numerical integration. The calculated and the experimental specific heats are plotted against T in Fig. 2. The experimental values of C_v above 16°K are due to Geballe

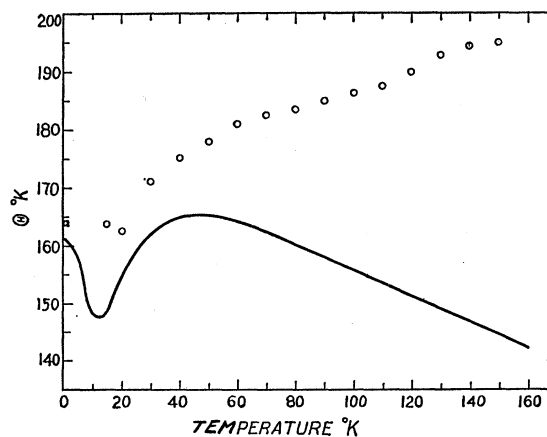


FIG. 3. Debye characteristic temperature Θ as a function of temperature. The circles \circ and the squares \square correspond to the experimental measurements of Geballe and Giauque, and Corak *et al.*, respectively. The solid curve is obtained from the calculated specific heat curve of Fig. 2.

and Giauque,⁴ while those below 5°K are due to Corak *et al.*⁵ The experimental C_v at lower temperatures are corrected for the electronic contribution. It is seen that the calculated values are systematically greater than the measurements. In Fig. 3, the more sensitive plot, Θ vs T is given. The discrepancy between the theory

⁴ T. H. Geballe and W. F. Giauque, *J. Am. Chem. Soc.* **74**, 2368 (1952).

⁵ W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite, and A. Wexler, *Phys. Rev.* **98**, 1699 (1955).

and the experiment here can be attributed to the approximate method of calculating the frequency spectrum and the neglect of anharmonic effects.

ACKNOWLEDGMENTS

The authors are grateful to Professor K. Banerjee for his interest in the investigation and Dr. S. S. Mitra of Ontario Research Foundation, Canada, for discussion.

Paramagnetic Behavior of Metallic Cerium and Europium

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(Received November 28, 1960)

The magnetic behavior of metallic polycrystalline cerium and europium has been studied above room temperatures. The measured paramagnetic behavior of cerium can be explained using the interacting Ce^{+++} ion model ($\theta = -50^\circ K$) and the Van Vleck theory of paramagnetism with an additional temperature-independent paramagnetic term $\chi_c = 1.00 \times 10^{-6} \text{ g}^{-1} \text{ cm}^3$ resulting from the conduction electrons. Europium metal has an unusual magnetic behavior. Its paramagnetic properties in the solid state cannot be explained on the basis of the noninteracting Eu^{+++} model. Near the melting point metallic europium behaves as a collection of weakly interacting Eu^+ ions. The Bohr magneton number of liquid europium is very close to that of Eu^{++} ions.

INTRODUCTION

RECENTLY we have been studying the paramagnetic behavior of polycrystalline rare-earth metals in order to enlarge our knowledge about their electronic structures. Our results on neodymium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, and thulium have been reported earlier.¹⁻³ These measurements have clearly indicated that the $4f$ electrons in the rare earth metals are quite localized and that the Van Vleck theory can approximately explain the observed magnetic susceptibilities. In this paper we present further results on this problem by discussing our magnetic measurements on metallic europium and cerium.

EXPERIMENTAL CONSIDERATIONS

Distilled and recast europium used in this investigation was obtained from Lindsay Chemical Division of American Potash and Chemical Corporation. This material contained 0.3% oxygen, less than 0.1% other rare-earth elements, and traces of calcium and tantalum. About 4.5 grams of material was cut from a larger piece in a dry-box containing argon. This sample was weighed,

wrapped in a tantalum foil, and enclosed in a silica capsule filled with argon gas at 20 cm Hg at room temperature. All these operations were performed in argon atmosphere, and during these operations the europium sample maintained a bright surface.

Cast polycrystalline cerium was purchased from the St. Eloi Corporation and according to the manufacturer was at least 99.5% pure. A sample having a mass of about 4.3 grams was sealed in a silica container using the same procedure as for europium.

The magnetic susceptibilities of europium and cerium metals were measured using the Faraday method. The apparatus has been described in detail earlier.⁴

THEORY

The electronic configuration of a Ce^{+++} ion is $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^1, 5s^2 5p^6$. The lowest multiplet consists of two energy levels $^2F_{5/2}$ and $^2F_{7/2}$, the term $^2F_{5/2}$ representing the ground state. The position of the level $^2F_{7/2}$ with respect to the ground state can be approximately calculated using the modified Goudsmit formula^{5,2}:

$$\Delta E = \frac{8\pi^4 m e^2}{c^3 h^5} \frac{2L+1}{n^3 l(l+1)(2l+1)} (Z-\sigma)^4, \quad (1)$$

¹ S. Arajs, *J. Chem. Phys.* **32**, 951 (1960); S. Arajs and D. S. Miller, *Suppl. J. Appl. Phys.* **31**, 325S (1960).

² S. Arajs, *Phys. Rev.* **120**, 756 (1960).

³ S. Arajs and R. V. Colvin, a paper presented at the Sixth Annual Conference on Magnetism and Magnetic Materials in New York, New York, November 16-19, 1960 (unpublished).

⁴ S. Arajs and D. S. Miller, *J. Appl. Phys.* **31**, 986 (1960).

⁵ S. Goudsmit, *Phys. Rev.* **31**, 946 (1928).