

Consequently, we conceive the center frequency as the optical (infrared) value of the characteristic frequency.

As we know, the spectrum of lattice vibrations as a whole contributes to the specific heat of a solid. In order to represent the entire spectrum in this case unambiguously and effectively by one single frequency, we may imagine the spectrum to be concentrated in its center of gravity and thus the accordant frequency to be identical with the characteristic frequency from specific heat.

IV. CENTER LAW OF THE LATTICE VIBRATION SPECTRA

As we conclude from Fig. 6, the center frequencies of the lattice vibration spectra of nonconducting solids can be determined simply by their characteristic temperatures. Introducing this fact into Eq. (2), we obtain

$$\nu_{ctr} = k/h\theta. \quad (3)$$

This relation expresses the equality of the characteristic temperatures with the center of gravity of the lattice vibration spectra in absorption as well as in reflectance. It states:

The higher the characteristic temperature of a solid, the higher also the frequency region of the vibrational spectrum.

Applying Eq. (3), we may now determine the centers of the vibrational spectra in absorption and reflectance for nonconducting solids from characteristic temperature data, or vice versa. The reciprocal case applies to a number of solids whose vibrational spectra we know but incompletely. Among these substances are, e.g., BN,

BeO, Al₂O₃, etc., with structures different in some cases from those of Table I. Other and more important applications of the center law, concerning the study of the solid state in general, will be treated in successive papers.

V. CONCLUSION

The accepted percentage of impurities in the investigated nonconducting solids (averaging close to 1%) may cause small deviations in some of the experimental data. However, no changes, beyond the over-all inaccuracies of the experimental data, are to be expected, either in the center frequency or in the characteristic frequency, provided the small impurities do not influence the electrical conductivity of the materials to any substantial degree.¹⁴

In the past, for various reasons, many experimental data in the far infrared have not met the standards that would be desirable. Hence comparisons made in our study are hampered in many respects by this fact. It is exactly the purpose of this paper to stimulate extensive and more accurate work within the experimental aspect of this field, in order to provide confirmation or modification of our results.

ACKNOWLEDGMENTS

The author wishes to express appreciation to Dr. E. W. Samson and C. E. Ryan of the Air Force Cambridge Research Center, for their study and discussion of this paper, as well as for the helpful suggestions given.

¹⁴ The influence of electrical conductivity on the data, in semiconductors and metals, will be considered separately in a subsequent paper.

Optical Mode Scattering Contribution to Electrical Resistivity in Zirconium Hydride*

PAUL W. BICKEL AND TED G. BERLINCOURT
Atoms International, Canoga Park, California

(Received March 21, 1960)

Electrical resistivity measurements on fcc ZrH_{1.54} and fct ZrH_{1.96} between 1.2°K and 400°K have revealed a sizeable optical mode scattering contribution. Excellent fits to the data are obtained using a simple additive combination of Grüneisen and Howarth-Sondheimer functions for the respective acoustical and optical mode scattering contributions. The corresponding acoustical and optical mode characteristic temperatures are in good accord with values derived from earlier inelastic neutron scattering experiments.

RECENT neutron scattering experiments¹⁻⁵ have shown that hydrogen atoms occupy tetrahedral lattice sites in fcc and fct zirconium hydride (approx-

mately ZrH_{1.5} to ZrH₂), and further that these hydrogen atoms behave much like independent simple harmonic or "Einstein" oscillators. A value of 0.133 eV (average of two neutron scattering determinations) was obtained for the level spacing of these Einstein or optical modes, and a value of approximately 0.02 eV was obtained for the high-frequency cutoff of the acoustical modes. These energies correspond to an Einstein characteristic temperature $\theta_E = 1550^\circ\text{K}$ for the optical branch and a characteristic temperature of approximately 230°K for the acoustical branch. The purpose of this note is to describe electrical resistivity measurements on zirconium

* This research was supported by the U. S. Atomic Energy Commission.

¹ R. E. Rundle, C. G. Shull, and E. O. Woolan, *Acta Cryst.* **5**, 22 (1952).

² I. Pelah, C. M. Eisenhauer, D. J. Hughes, and H. Palevsky, *Phys. Rev.* **108**, 1091 (1957).

³ A. Andresen, A. W. McReynolds, M. Nelkin, M. Rosenbluth, and W. Whittemore, *Phys. Rev.* **108**, 1092 (1957).

⁴ W. L. Whittemore and A. W. McReynolds, *Phys. Rev.* **113**, 806 (1959).

⁵ S. S. Sidhu, L. Heaton, and M. H. Mueller, *J. Appl. Phys.* **30**, 1323 (1959).

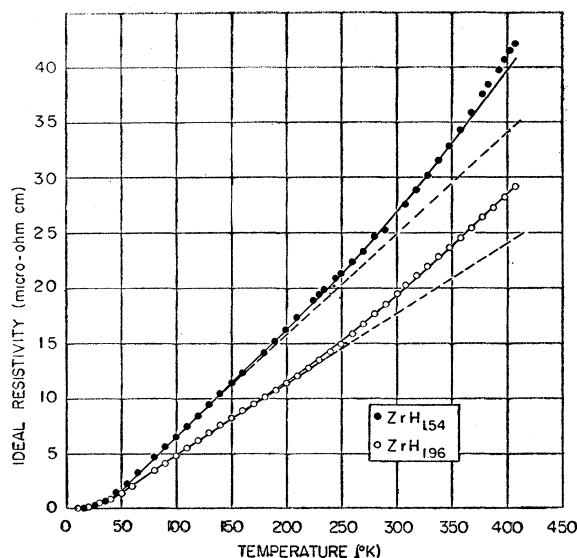


FIG. 1. Ideal electrical resistivity as a function of temperature for $\text{ZrH}_{1.54}$ and $\text{ZrH}_{1.96}$. The solid lines represent fits of Eq. (1) to the experimental data, and the dashed lines represent the Grüneisen contributions.

hydride which also exhibit manifestations of both types of lattice modes.

If scattering by impurities (including hydrogen vacancies) and by the acoustical and optical modes all make independent contributions, the electrical resistivity of zirconium hydride should be approximated by a function of the form

$$\rho = \rho_r + \rho_i = \rho_r + (aT/\theta_p)G(\theta_p/T) + bH(\theta_E/T), \quad (1)$$

where ρ_r is the residual resistivity, ρ_i is the ideal resistivity, a and b are constants involving scattering cross sections and electronic factors, T is the temperature, $G(\theta_p/T)$ is the well-known Grüneisen function⁶ for acoustical mode scattering, θ_p is the resistive characteristic temperature, and $H(\theta_E/T) = [(T/\theta_E)\sinh^2(\theta_E/2T)]^{-1}$ is the first order approximation of the Howarth-Sondheimer function⁷ for optical mode scattering. The function $H(\theta_E/T)$ becomes appreciable only above about $0.1\theta_E$.

In Fig. 1, the ideal resistivities are plotted (experimental points) as functions of temperature for polycrystalline fcc $\text{ZrH}_{1.54}$ and fct $\text{ZrH}_{1.96}$. The solid lines represent fits of Eq. (1) to the data using the parameters listed in Table I, while the dashed line represents only

TABLE I. Parameters used to fit Eq. (1) to experimental electrical resistivity data on polycrystalline zirconium hydride.

	$\text{ZrH}_{1.54}$	$\text{ZrH}_{1.96}$
a (μ ohm-cm)	19.17	11.96
b (μ ohm-cm)	18.35	15.06
θ_p (°K)	225	200
θ_E (°K)	1550	1550
ρ_r (μ ohm-cm)	41.8	4.02

the Grüneisen term. Reasonable fits are obtained using the neutron scattering experiment value for θ_E and values for θ_p which agree to within experimental accuracy with the neutron scattering value for the acoustical mode high-frequency cutoff. The deviations (especially for $\text{ZrH}_{1.54}$) between experiment and Eq. (1) are not unexpected in view of possible lack of independence of terms in Eq. (1), inexactness of G and H , finite rather than infinite number of Einstein levels, lack of complete independence of the hydrogen oscillators, distortions of the potential due to hydrogen vacancies, and the possibility of occupancy of some octahedral sites by hydrogen at higher temperatures. In spite of these complicating factors the resistivity data appear to corroborate the existence of optical and acoustical modes which contribute nearly independently to the physical properties of zirconium hydride. This contention is further supported by preliminary specific heat data obtained by W. J. Tomasch of this laboratory. Still other manifestations of optical mode contributions should be observable in the thermal conductivity, thermal expansion, and elastic properties.

The present investigation has revealed in addition that for compositions approaching ZrH_2 the hydride is a considerably better electrical conductor than is pure zirconium, and the hydrogen vacancy contribution to the resistivity is of the order of 2.2μ ohm-cm per atomic percent vacancies relative to the entire lattice. The room temperature Hall coefficient is large and positive (35 to $40 \times 10^{-5} \text{ cm}^3/\text{coulomb}$) for the fcc phase and large and negative (-20 to $-68 \times 10^{-5} \text{ cm}^3/\text{coulomb}$) for the fct phase.

We plan to extend these measurements to higher temperatures, to deuterides (in which θ_E should be smaller by the factor $1/\sqrt{2}$) and to other hydrides which have been shown by neutron scattering experiments to possess similar lattice mode distributions.

ACKNOWLEDGMENTS

We are indebted to G. W. Lehman and W. J. Tomasch for valuable discussions and to D. L. Henry for supplying the zirconium hydride samples.

⁶ N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1936), Chap. 7, p. 240.

⁷ D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).