Elastic Moduli and Ultrasonic Attenuation of Praseodymium, Neodymium, and Samarium from 4.2 to 300°K

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The LA and TA wave velocities and the ultrasonic attenuations of high-purity polycrystalline Pr, Nd, and Sm have been measured by a pulse technique at a frequency of 10 MHz between 4.2 and 300°K. The temperature variation of the Young moduli E, shear moduli G, adiabatic compressibilities K_s, Debye temperatures Θ_D, and ultrasonic attenuations have been determined. The anomalies in the elastic and anelastic properties, observed at temperatures below 25°K, were correlated with the antiferromagnetic transitions known to occur in these metals. The elastic moduli of Nd behave in a normal manner between room temperature and its Néel point (18°K). In contrast, Pr and Sm display maxima at 78 and 109°K, respectively, followed by a sharp decrease in the elastic moduli with decreasing temperature, i.e., the appearance of a lattice-softening phenomenon. Noteworthy is the similarity in the temperature variation of the elastic moduli and ultrasonic attenuations between Pr and Sm. The anomalies at 78 and 109°K, in these metals, are believed to be due to an electron-type transition or to a crystallographic phase change rather than to an antiferromagnetic ordering.

INTRODUCTION

THE low-temperature behavior of the rare-earth elements, from both theoretical[1] and experimental[2] standpoints, has most extensively been investigated in the "heavy" metals from gadolinium to lutetium. The availability of heavy rare-earth single crystals, the great variety of magnetic-ordering transitions and the potential application of ferromagnetic rare-earth alloys and compounds has stimulated active interest in their physical properties. However, relatively little work has been carried out on the "light" rare-earth metals, from lanthanum to europium. Magnetic-susceptibility measurements[3] suggested that these metals, with the exception of lanthanum, might be antiferromagnetic at low temperatures. The exact magnetic structure has been established for neodymium only by means of neutron diffraction.[4]

The present work is concerned with the temperature dependence of the elastic moduli, adiabatic compressibility, Debye temperature, and ultrasonic attenuations of polycrystalline praseodymium, neodymium, and samarium 4.2 and 300°K. The objective of the investigation was to observe the variation of these properties in the vicinity of the magnetic-ordering points, where the criteria of the theories of Landau and co-workers[5,6] require the appearance of anomalies in the elastic moduli and ultrasonic attenuations in a certain fashion. Such anomalies were observed in another of the light rare-earth series, in europium,[7] and in several heavy rare-earth metals.[8]

EXPERIMENTAL DETAILS

The high-purity (99.9%) polycrystalline specimens, supplied by Leytess Metal and Chemical Corp., New York, were in the form of flat disks, 12 mm in diam by about 5 mm thick. The specimens were hand-lapped to a parallelism of faces of better than two parts in 10^4. Thickness was measured by means of a calibrated indicator stand to within 5×10^{-4} mm. Since samarium metal oxidizes rather rapidly in moist air, the specimen preparation including lapping was carried out in an inert-atmosphere (dry argon gas) glovebox in which the pressure was slightly above atmospheric. Room-temperature densities (Table I) were determined to within ±0.005 g/cm^3 by a fluid-displacement method with the specimens immersed in a bath of monobromobenzene. The temperature variation of the acoustical path lengths of the specimens was calculated by using the average coefficients of thermal expansion given by Gschneidner,[9] and listed in Table I.

The elastic moduli, adiabatic compressibilities, and Debye temperatures were determined from the experimentally measured longitudinal and transverse sound-wave velocities. An ultrasonic pulse technique was employed at a frequency of 10 MHz. Experimental

TABLE I. Average densities and thermal expansion coefficients of the specimens.

Element	Density (g cm^{-3})	Av. linear coeff. of thermal expansion (°K^{-1})
Pr	6.754	6.79×10^{-6}
Nd	7.011	9.98×10^{-6}
Sm	7.483	10.40×10^{-6}

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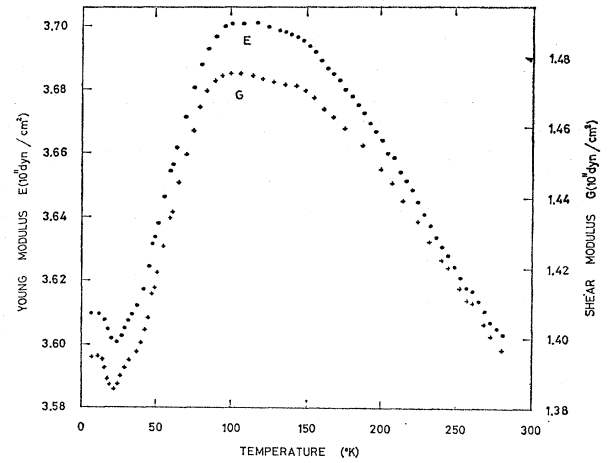

FIG. 1. Temperature dependence of the E and G moduli of polycrystalline praseodymium.

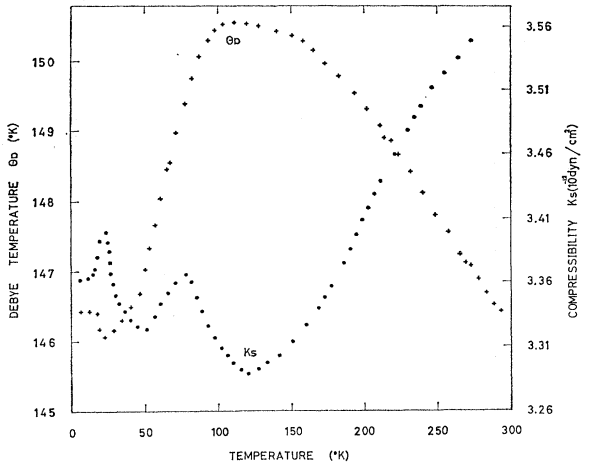

FIG. 2. Temperature dependence of the K_s and Θ_D of polycrystalline praseodymium.

details and method of data analysis are described elsewhere.[8] The estimated error in the absolute values of the elastic moduli is 0.4%. The relative, point to point, precision is better by a factor of 4. The ultrasonic attenuation was determined to within 1% and the temperature to 0.5°K.

RESULTS AND DISCUSSION

A. Praseodymium

Investigation of various physical properties of polycrystalline Pr produced conflicting evidence with regard to the behavior of this metal at low temperatures. Neutron-diffraction measurements[10] suggested that Pr may become antiferromagnetic below 25°K with a sinusoidal arrangement similar to the magnetic structure of the adjacent element in the periodic table, Nd.[4] In contrast, magnetic-susceptibility data[3] gave no indication of a magnetic transition in Pr. Furthermore, theoretical analyses[11,12] were able to account for the behavior of the specific heat[13] and magnetic susceptibility[3] without assuming spin ordering. Electrical-resistivity measurements[14–16] do not reveal any anomalies in the vicinity of 25°K. Nevertheless, the data of Alstad *et al.*[15] exhibit an abrupt increase in the slope of the electrical resistivity at 61°K with a subsequent decrease at 95°K. In this temperature region, the specific heat of Pr shows a broad peak.[13]

The temperature dependence of the Young (E) and shear (G) moduli of Pr is shown in Fig. 1. With decreasing temperature, the elastic moduli increase in a normal manner followed by formation of a flat maximum at about 120°K. The elastic moduli, below 80°K, decrease drastically to their minimum values at 23°K. With further decrease in temperature the moduli increase, finally approaching absolute zero with zero slope as required by the third law of thermodynamics.

The departure at about 120°K, from an almost linear dependence of the elastic moduli with decreasing temperature, is marked by a minimum in the adiabatic compressibility (K_s) (Fig. 2). The maximum rate in the degree of the lattice softening, as manifested by the sharp decrease in the elastic moduli, is displayed by a peak in K_s at 78°K. The additional peak in the compressibility, at 23°K, corresponds to the observed minima in the moduli E and G (Fig. 1) at this temperature.

The anomalies in the elastic moduli and adiabatic compressibility at 23°K are similar in character to

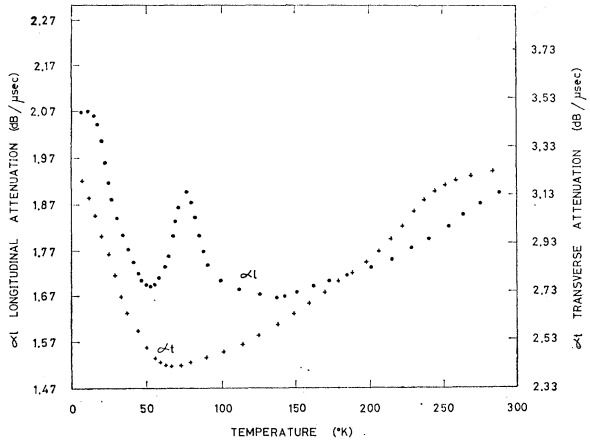

FIG. 3. Temperature dependence of the α_l and α_t ultrasonic attenuations of polycrystalline praseodymium.

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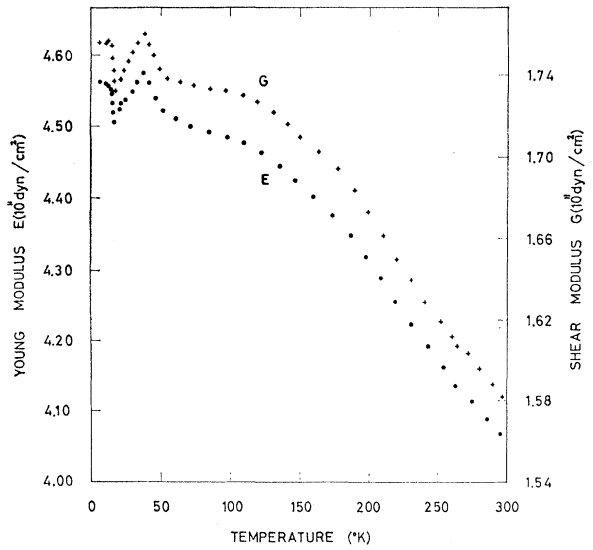

FIG. 4. Temperature dependence of the E and G moduli of polycrystalline neodymium.

those observed in other rare-earth metals at their magnetic transition points.[7,8] The ultrasonic attenuations (Fig. 3), however, do not exhibit the typical peaks expected at temperatures below magnetic transitions.[7] Both longitudinal (α_l) and transverse (α_t) wave attenuations begin increasing at about 50°K, and not at 23°K as would be required by the Landau-Khalatnikov theory.[6]

The α_l (Fig. 3) displays a sharp peak at 78°K, which is the temperature of occurrence of the maximum rate in the lattice softening and the corresponding peak in the adiabatic compressibility. Noteworthy is the fact that the α_t does not exhibit any anomalies in this temperature range. It should be remembered that transverse waves, propagating through the crystal lattice, do not generate localized variations in density and do not distort the Fermi surface. This is in contrast to the behavior of longitudinal waves. The presence of the peak in α_l at 78°K and the absence of any anomaly in α_t in this temperature region seem to indicate that the lattice softening in Pr below 78°K is somehow related to an electron-type transition. Another possibility is a temperature-dependent crystallographic change of the crystal lattice. However, such a change is generally accompanied by anomalies in both α_l and α_t. Mössbauer-effect measurements and accurate lattice-parameter data should be helpful in elucidating this point. Apparently, the anomalies in the elastic moduli and compressibility at 23°K are connected with the lattice-softening mechanism mentioned before, rather than with an antiferromagnetic ordering.

The temperature dependence of the Debye temperature (Θ_D) of Pr is shown in Fig. 2. The general shape of the curve is similar to those of E and G (Fig. 1). This is an expected behavior, since the Debye temperature represents a certain averaging procedure of the elastic moduli of a metal.[17]

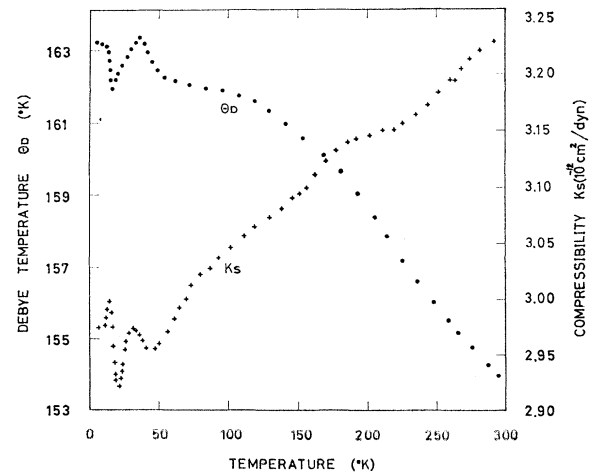

FIG. 5. Temperature dependence of K_s and Θ_D of polycrystalline neodymium.

B. Neodymium

Measurements of specific heat,[13] magnetic susceptibility,[3,18] electrical resistivity,[15] and neutron diffraction[4] showed that Nd orders antiferromagnetically below 19°K. The ordering takes place between layers in which atoms are distributed in an hexagonal environment and longitudinal spin waves are observed. Below 7.5°K, the magnetic structure of Nd changes[4] into one in which the magnetic moments are associated with atoms in an fcc environment.

Figure 4 shows the temperature dependence of the E and G moduli of polycrystalline Nd. Although Nd follows Pr in the periodic table, the behavior of their low-temperature elastic properties are markedly differ-

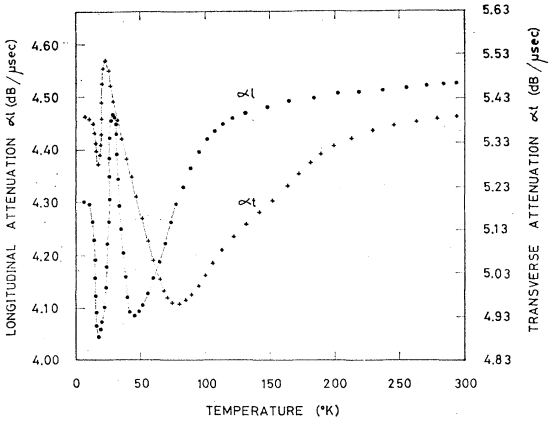

FIG. 6. Temperature dependence of the α_l and α_t ultrasonic attenuations of polycrystalline neodymium.

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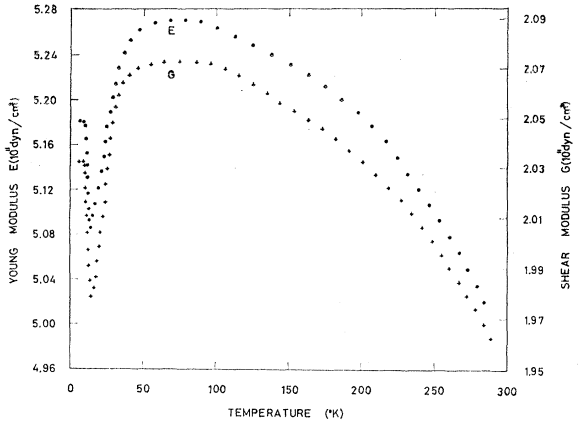

FIG. 7. Temperature dependence of the E and G moduli of polycrystalline samarium.

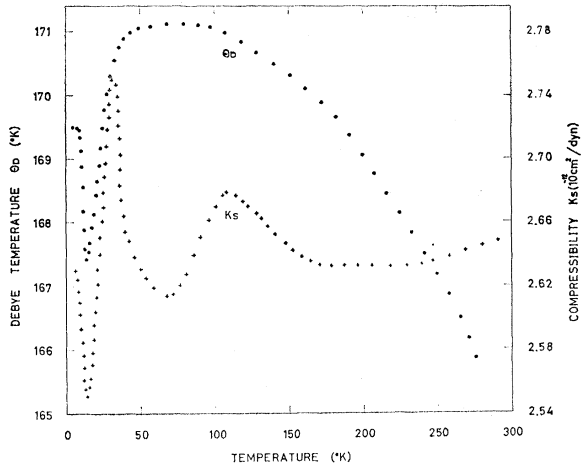

FIG. 8. Temperature dependence of K_s and Θ_D of polycrystalline samarium.

ent. Nd does not display a lattice softening as was observed in Pr, and the temperature variation of the Young and shear moduli (Fig. 4) is normal, i.e., they increase with decreasing temperature. A minimum in the moduli, which is indicative of an antiferromagnetic transition, is developed at 18°K. The change in the magnetic structure at 7.5°K, observed by means of neutron diffraction,[4] is not manifested by a corresponding anomaly in the elastic properties. This is not quite clear in view of the fact that the elastic properties are very sensitive to changes in magnetic structure, e.g., in gadolinium[9] at 224°K.

The adiabatic compressibility of Nd (Fig. 5) behaves normally with decreasing temperature from the ambient. The magnetic transition point at 18°K is represented by an appropriate anomaly in K_s. Similarly, the α_l and α_t attenuations (Fig. 6) display sharp peaks at the magnetic-ordering point. The anomalies do not start at the transition point proper, as required by theory,[6] but at about 50°K, which is significantly higher than the Néel point of Nd. A similar behavior was observed in Pr (Fig. 3). Apparently, the spreading out of the attenuation anomalies to temperatures above the transition point is connected with the presence of short-range order at these temperatures. However, the absence of subsidiary peaks, such as were observed in Eu [7] and in the heavy rare-earth metals,[8] is not quite clear. The temperature dependence of Θ_D of Nd is shown in Fig. 5.

C. Samarium

The physical properties of polycrystalline Sm at low temperatures have been extensively studied. Electrical-resistivity,[15] magnetic-susceptibility,[3,19,20] and heat-capacity[21,22] measurements revealed the occurrence of two anomalies in these properties, at 14 and 106°K. The anomaly at 14°K was attributed to the onset of antiferromagnetism. However, the nature of the anomaly at about 106°K, in the form of small kinks and shallow maxima, remained obscure. From thermal[21] and magnetic[3] data it appears as though this anomaly is also due to antiferromagnetism. The dip, at 113°K, in the temperature dependence of the coefficient of thermal expansion[23] seems to support this hypothesis. However, powder-susceptibility measurements[19] indicate no evidence of a maximum at 106°K. Neither did Mössbauer-effect techniques[24] reveal any ordered spin structure at temperatures above 77°K. The Hall coefficient[25,26] is

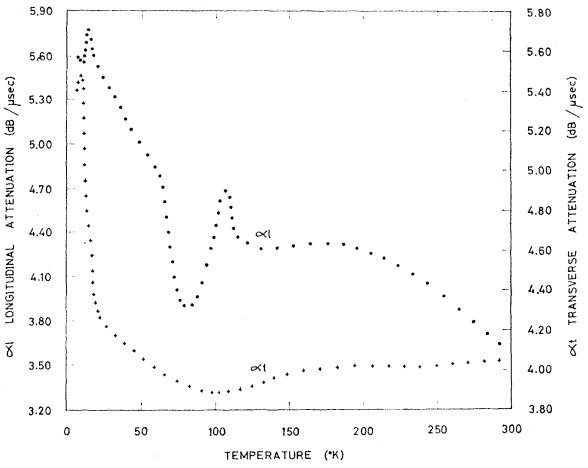

FIG. 9. Temperature dependence of the α_l and α_t ultrasonic attenuations of polycrystalline samarium.

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negative at room temperature and changes sign in the vicinity of 170°K, i.e., quite remote from 106°K.

The E and G moduli of polycrystalline Sm are shown in Fig. 7. Their temperature dependence is strikingly similar to that of the elastic moduli and ultrasonic attenuations of Pr (Figs. 1–3). The appearance of a lattice softening in both Pr and Sm is probably due to a common mechanism.

With decreasing temperature, from the ambient, the elastic moduli of Sm (Fig. 7) increase in a normal manner and subsequently form a broad maximum. In this temperature region, K_s (Fig. 8) develops a rather wide hump peaked at 109°K. With further decrease in temperature, K_s exhibits a dip at 70°K. The peak in K_s at 109°K is consistent with the occurrence of anomalies in the vicinity of this temperature in the electrical resistivity,[15] heat capacity,[21] and other physical properties. The nature of these anomalies was not firmly established.[19,24] Additional evidence for the similarity in behavior of the elastic moduli in both Pr and Sm is the temperature variation of the α_l and α_t wave attenuations. In Sm (Fig. 9), as in Pr (Fig. 3), α_l displays a peak, whereas α_t shows a smooth behavior in the temperature region in which the adiabatic compressibilities (Figs. 2 and 8) are anomalous. As was speculated for Pr, these anomalies and the accompanying lattice softening in Sm may be due to an electron-type transition or to temperature-dependent crystallographic change.

The sharp minimum in the elastic moduli of Sm (Fig. 7) at 14°K and the corresponding anomalies observed in the compressibility (Fig. 8) and ultrasonic attenuations (Fig. 9) are characteristic of a magnetic-ordering point. This is in agreement with the behavior of other physical properties of Sm.[3,15,21]

The temperature dependence of Θ_D of Sm is shown in Fig. 8. The limiting Θ_D, at absolute zero, for the antiferromagnetic phase is 169°K.

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Moment-Conserving Decoupling Procedure for Many-Body Problems

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A new, well-defined procedure for linearizing double-time, statistical Green's functions is proposed. The resultant spectral function automatically conserves the first several frequency moments. This compares very favorably with the usual mean-field decoupling results, which conserve only the first (and, rarely, up to three) frequency moments.

THE Green's function method has been widely used in the study of equilibrium as well as nonequilibrium properties of interacting many-body systems.[1] Since exact solutions to these problems (except for a few one- and two-dimensional cases) can in general not be obtained, approximations have to be introduced. The approximation procedures fall into two distinct categories: (i) The first is the diagrammatic expansion,[2] which aims at calculating the spectral function to any desired accuracy whenever a perturbation approximation is meaningful; or which are designed to sum a selected subset of the total set of diagrams to many (and possibly infinite) orders when perturbation approximation itself is not appropriate. (ii) The second category is the Green function or equation of motion decoupling procedure. This consists of self-consistent mean-field approximations, which can often (especially for fermion or boson systems) be interpreted in terms of diagrams but the primary motivation for which is provided by their heuristic simplicity.

The difficulty with the usual decoupling procedures is that they are crude and often they do not lead to a very accurate description of the elementary excitation spectrum of the system. As the structure of the elementary excitation spectrum is embodied in the frequency-wave-vector dependence of the spectral function, the simple decouplings do not lead to accurate representation of the spectral function. Consequently, the frequency moments of the spectral function calculated via the usual mean-field decoupling procedures are not accurately reproduced.

To improve on this situation, we propose a new decoupling scheme which is well defined and which

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[2] See, for example, R. D. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem* (McGraw-Hill Book Co., New York, 1967).