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2006 J. Phys.: Condens. Matter 18 10971

(http://iopscience.iop.org/0953-8984/18/48/024)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **18** (2006) 10971–10976 doi:10.1088/0953-8984/18/48/024

Unusual pressure response of the E_{2g} mode and elastic shear modulus C_{44} in hcp scandium

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Received 13 August 2006, in final form 23 October 2006
Published 17 November 2006
Online at stacks.iop.org/JPhysCM/18/10971

Abstract

Scandium (Sc) was studied by Raman spectroscopy to pressures up to 20 GPa. The E_{2g} mode frequency increases throughout the stability field of the hexagonal-close-packed (hcp) phase, which contrasts the softening of this mode observed in its heavier homologue Y and the related regular lanthanides. The unusually low mode Grüneisen parameter and the small increase of elastic modulus C_{44} are discussed with respect to pressure-induced changes of the electronic structure.

1. Introduction

Lattice vibrations are important excitations in solids: they contribute to many thermodynamic parameters, are related to elasticity and play a crucial role in certain types of phase transitions. Therefore, knowledge of lattice dynamics is essential in understanding many properties of solids. The phonon frequencies are determined by the interatomic forces, which in metals are controlled to a large extent by the electronic structure.

To elucidate correlations between electronic and dynamical properties, investigations of the elements, in particular by pressure tuning of the electronic structure, are of specific interest. Previous high-pressure studies of lattice vibrations in the regular lanthanides have revealed common trends for the transitions from hcp to their high-pressure phases, which are associated with a softening of the E_{2g} mode and of the elastic shear modulus C_{44} [1, 2]. It has been argued that these anomalies might be connected with special aspects of electronic s → d transfer [1], which occurs in the lanthanides both along the series at ambient pressure and under pressure for the individual metals, and which is thought to be responsible for the initial structural sequence hcp → Sm-type → dhcp (double hexagonal) → fcc (face-centred cubic) [3, 4].

Scandium (Sc), the lightest rare earth metal, has an isovalent valence electron configuration. Since its evolution under pressure shows the same general features, one would expect for Sc a high-pressure behaviour closely related to that of Y and the lanthanides [5]. Evidence that this picture might be too simple comes from the observation that Sc does not enter the high-pressure structural sequence of the regular lanthanides [6–8], but rather crystallizes in quite complex structures, e.g. an incommensurate host–guest lattice for Sc-II [9, 10], and a

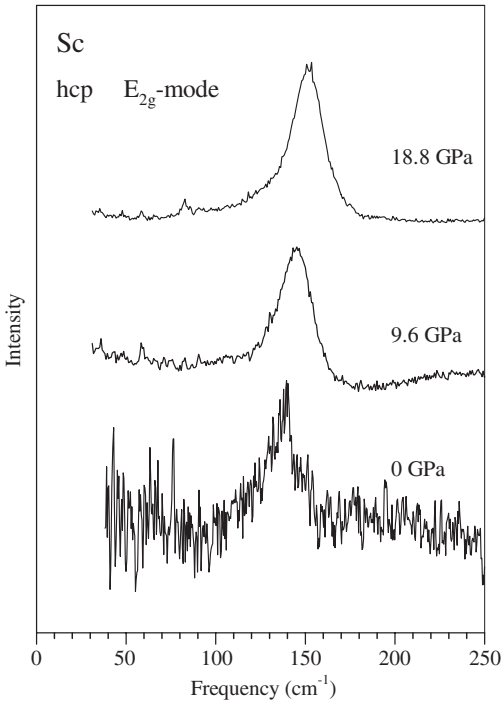

Figure 1. Raman spectra of hcp Sc at various pressures.

hexagonal lattice for Sc-V [11], whereas the structures of Sc-III and Sc-IV have not yet been solved [11]. This points to special differences in the evolution of electronic structure under pressure, and might show up also in a different lattice dynamical behaviour of hcp Sc.

For hcp Sc, lattice vibrations were investigated at normal pressure by inelastic neutron scattering [12], but no high-pressure data are available, and, as in the case of the lanthanides, there are no theoretical investigations, which means that the present understanding of the lattice dynamics of this important group of metals is less advanced. The present paper reports Raman spectroscopic studies as the first contribution to the lattice dynamics of hcp Sc at high pressure.

2. Experimental details

High pressures were generated with diamond-anvil cells. In order to prevent oxidation, polycrystalline Sc samples (Aldrich, No. 45 7930, 99.9%) were loaded under oil and no pressure medium was utilized in order to avoid surface contamination, but since Sc is a relatively soft material, quasihydrostatic conditions are expected to prevail. The 514.5 nm line of an Ar^+ laser and the 647 nm line of a Kr^+ laser were used to excite the Raman spectra. The scattered light was analysed using a triple spectrograph equipped with a liquid-nitrogen-cooled CCD multichannel detector. The pressure was determined in one run by the E_{2g} phonon of Zn [13] and in a second run by the ruby fluorescence method [14, 15].

3. Results

The E_{2g} mode was observed throughout the hcp phase, Raman spectra of which are shown in figure 1 at various pressures. The frequency obtained in the present study for the E_{2g} mode of hcp Sc at normal pressure is 139 cm^{-1} and this compares favourably with the value of 135 cm^{-1} obtained from inelastic neutron scattering [12]. From figure 2 one can notice that the frequency

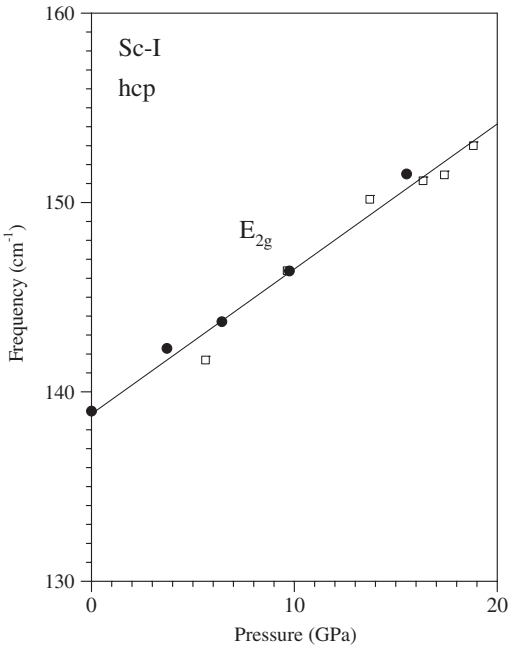

Figure 2. Pressure shift of the E_{2g} mode in Sc. Solid circles: excitation by 647 nm with Zn as pressure marker. Open squares: excitation by 514.5 nm with ruby as pressure marker. The solid line serves as a guide for the eye.

of the E_{2g} mode increases throughout the hcp phase as the pressure rises, and using the equation of state data [6] an average mode Grüneisen parameter $\gamma(E_{2g})$ of approximately 0.4 is derived. Estimates of the pressure dependence of C_{44} have been obtained by using the relation [2, 16, 17]

$$\nu(E_{2g}) = \frac{1}{2\pi}\sqrt{\frac{4\sqrt{3}a^2C_{44}}{mc}}, \tag{1}$$

where a and c are the lattice constants and m the atomic mass. Equation (1) gives reasonable quantitative estimates for C_{44}, provided that the elastic anisotropies are not too large, as is the case for Sc [2]. In figure 3 the pressure shift of C_{44} for various metals is compared.

4. Discussion

The E_{2g} mode exhibits a positive pressure shift throughout the stability field of the hcp phase, which is in contrast to the behaviour in Y and the regular lanthanides, where softening is associated with the transition to the high-pressure Sm-type structure [1]. The transition from hcp to Sm-type results simply in a different stacking sequence of the hexagonal layers (AB for hcp and ABABCBCAC for Sm-type), which can be achieved by a shearing of these planes perpendicular to the c-axis and may require weakening of certain interlayer force constants. Since the E_{2g} mode probes the interlayer bonds—the E_{2g} mode corresponds to vibrations of successive hexagonal planes against each other—the observed softening might be considered as typical for this special phase transition. In this respect the missing softening of the E_{2g} mode in Sc can be considered as being simply the result of the different structural sequence under pressure. Though the E_{2g} mode in hcp Sc shows no frequency decrease in association with the phase transition, the mode Grüneisen parameter is unusually low, with $\gamma(E_{2g}) \approx 0.4$, as compared to normal values which range approximately from 1.3 to 2.3 at room temperature [18]. Similar low or even negative values have also been observed in the

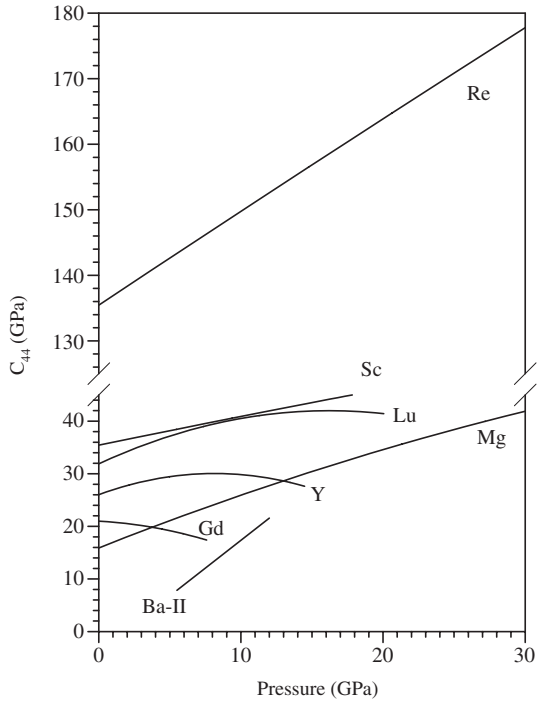

Figure 3. Pressure shift of C_{44} for various metals [2].

Ti-group metals, where it is associated with the hcp $\rightarrow$ ω transition [19], and in Be [20], for which an elastic anomaly, probably related to special features in the electronic structure, has been made responsible. Elastic anisotropies, however, can be ruled out for Sc, as can be noticed from the anisotropy ratios, which are close to 1 for Sc [2].

The low lattice Grüneisen parameter and the softening of longitudinal and transverse acoustic phonons, which are observed for the low-pressure phases of the lanthanides, have been related to s $\rightarrow$ d electron transfer [21] and special aspects of it [22]. Therefore, one would expect similar effects also in Sc, since pressure affects the electronic band structure qualitatively in the same way [5]. Indeed $\gamma(E_{2g})$ for Sc is comparable to the values for Y and Lu near normal pressure prior to the transition to Sm-type [18]. One might expect $\gamma(E_{2g})$ for Sc to go down in the same way on approaching a hypothetical transition to Sm-type, which has been predicted to occur around 24 GPa [5], if the transition to incommensurate tetragonal lattice were not to intervene. From this point of view the behaviour of the E_{2g} mode in Sc is not very different from that in the regular lanthanides, though the high-pressure phase in Sc is different from the Sm-type or related phases. In this respect it is interesting to compare the pressure dependence of the E_{2g} mode of hcp Sc with that of hcp Ba-II, because the high-pressure phases Ba-IV [23] and Sc-II [10] are of the same type, incommensurate host–guest lattices, the only difference being the guest lattices, which are C-face-centred tetragonal and monoclinic in Ba-IV and C-face-centred tetragonal in Sc-II. No softening effects have been observed in Ba-II with $\gamma(E_{2g}) \approx 1.6$–$1.7$ [24].

In Y and the regular lanthanides the transition to the high-pressure phase Sm-type involves also weakening of the elastic shear modulus C_{44}. One can notice from figure 3 that no weakening of C_{44} occurs in Sc in the vicinity of the transition to the high-pressure phase unlike for Y and the regular lanthanides. The rise in C_{44} with pressure for Sc is comparable to that of Lu and Y in the low-pressure range 0–5 GPa and by far lower than for Ba-II. For

hexagonal crystals with approximately equal compressibilities of the a- and c-axes the pressure dependence of C_{44} can be expressed by

$$\frac{dC_{44}}{dP} = \frac{C_{44}}{B}\left(2\gamma_i + \frac{1}{3}\right). \tag{2}$$

For most metals, which have no distinct elastic anisotropy, $\frac{C_{44}}{B}$ ranges from 0.4 to 0.6 and 'normal' values for the E_{2g} mode Grüneisen parameter vary approximately from 1.3 to 2.3. Using these numbers one obtains lower and upper bounds for the pressure slope of C_{44}, which are 1.1 and 3, respectively. Re and Mg can be considered as good examples for this normal behaviour; they are also shown in figure 3. Here it is important to note that for Sc the pressure slope $\frac{dC_{44}}{dP} \approx 0.6$ is well below the range of normal behaviour.

Though Sc exhibits no negative pressure shift of the E_{2g} mode and no weakening of elastic modulus C_{44} at the transition to the high-pressure phase like the regular lanthanides including Y, the low mode Grüneisen parameter and the small pressure increase of elastic modulus C_{44} are comparable to those of the regular lanthanides far away from the phase transition, which might be related to s $\rightarrow$ d transition-induced softening. It has been pointed out that the differences between Sc on the one hand and Y and the regular lanthanides on the other hand could be explained by subtle differences in the electronic structure [3]. Unlike Y and the regular lanthanides, Sc has no d shell in the ionic core and the extra core repulsion due to the orthogonality condition is missing for the 3d electrons in Sc, which leads to more strongly localized d electrons. An analogous difference in the electronic core structure has been made responsible for example for the different pressure response of the LO mode of the β-tin structure in Si with respect to that in Ge [25, 26]. With respect to the differences to Ba-II one should note that the elastic modulus C_{44} can be considered as the force constant which governs the E_{2g} mode. Since $\frac{C_{44}}{B}$ is nearly the same for both substances, the difference is made by the pressure slope C'_{44} (0.6 for Sc and 2 for Ba-II), which is linked to the changes in the electronic structure, and one might speculate that the unlike valence electron configuration leads to a different evolution of electronic band structure in both elements, as is evident for example from completion of s $\rightarrow$ d transfer, which requires approximately 40 GPa in Ba [27], but more than 240 GPa in Sc [28].

Recently, Y has been shown to reach superconducting temperatures T_c as high as 17 K under 89 GPa pressure [29]. Theoretical studies suggest that strong electron–phonon coupling occurs at high pressure and ascribe the increase of T_c with pressure to a softening of the lattice [30]. Assuming Sc, which has a factor of two smaller mass, behaving similar to Y, one would expect even higher $T_c = 28$ K instead of the observed 8.1 K at 74 GPa [31], indicating that electron–phonon coupling is not as strong as in Y. Though the structural behaviour of Sc is different from that of Y, and superconductivity has been observed only in Sc-II [32], the by far lower softening effects observed in hcp Sc would be in line with Sc having a much lower T_c than Y.

5. Conclusions

Lattice-dynamical data of hcp Sc at high pressure were obtained using the method of Raman spectroscopy. The E_{2g} mode in hcp Sc shows unusual behaviour under pressure in many respects: in contrast to Y and the regular lanthanides no frequency decrease takes place and the elastic modulus C_{44} does not weaken in the vicinity of the transition to the high-pressure phase; similar to Y and the regular lanthanides, but contrary to Ba-II which has a closely related subsequent high-pressure phase, its mode Grüneisen parameter and the increase of C_{44} under compression is comparably low. The anomalous behaviour of $\gamma(E_{2g})$ and C_{44} in these rare

earth metals seems to be related to special changes in electronic structure, associated with pressure-induced s → d electron transfer. A reason for the different behaviour between Sc on the one hand and Y and the regular lanthanides on the other hand might originate from the differences in the electronic structure of the ionic cores. The different valence electron configuration and a subsequent different evolution of electronic band structure might be the cause for the differences from Ba-II. A final clarification of these questions must be left to future lattice-dynamical calculations, which explicitly investigate the effect of the electronic structure and its pressure-induced changes on the mode frequencies.

Acknowledgments

HO acknowledges financial support by EPSRC under GR/M32597 and by JSPS under L-04519.

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