As noted previously,[2] the RDF of the random network gives good agreement with those obtained for amorphous Si or Ge. As is the case, the peaks in $G(r)$ for the model (Fig. 3) are expected to be sharper than those shown for amorphous Si since the experimental $G(r)$ for Si includes broadening due to thermal, experimental, and mathematical effects. Significantly, the widths of the second peaks, which depend on bond-angle distortions, are similar when thermal and other broadening effects are removed.[2,4]

That region of the RDF of the model between the second and third major peaks is of special interest since the Si RDF of Moss and Graczyk[4] shows a small relative maximum at an r about twice the value of the maximum of the first peak. Because of the limited size of the model, the statistical fluctuations which are readily evident in Fig. 1 make it difficult to determine whether the model exhibits this behavior. Figure 2, however, suggests that the model may have a similar behavior while the $G(r)$ of Fig. 3, since it includes the term $[\rho(r) - \rho_0]$, magnifies the statistical fluctuations. From Fig. 2 it is clear, however, that the dip between the second and third major maxima will be different than that between the first and second or between the third and fourth.

The coordinates and identification of the first neighbors of the atomic positions comprising the model are available on an individual basis from the authors.

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Elastic Constants in Singlet Ground-State Systems: PrSb and Pr†

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The effect of crystal-field levels on the elastic constants has been measured for the singlet ground-state system PrSb. The results can be accounted for quantitatively. Elastic-constant measurements in double-hexagonal close-packed Pr reveal also strong crystal-field effects.

In rare-earth compounds the ground-state multiplet of the rare-earth ion is split typically of the order of several hundred wave numbers by the crystal field. The effect of these split levels on thermal, magnetic, and electric properties is well documented.[1] In this communication we would like to show the effect of these crystal-field levels on the elastic constants for the case where the lowest level is a singlet state. We show experimental results for two representative samples: PrSb, where the crystal-field effects dominate exchange effects, and double-hexagonal close-packed (dhcp) Pr, where the exchange is not negligible. This is the first time the effect of the crystal-field levels on the elasticity alone has been observed, neglecting complications due to exchange and quadrupole-quadrupole interaction, which can result in magnetic and structural transitions.

A study of this simple situation is worthwhile for the proper understanding of more complicated cases: (1) In cases where the ground-state level is orbitally degenerate, there occurs often a structural transition (the cooperative Jahn-Teller effect) which is accompanied by a softening of a symmetry elastic constant. This effect has been observed now in several cases (e.g., $DyVO_4$, $TbVO_4$, $NiCr_2O_4$).[2] In some cases (DySb, TmCd),

where the excited crystal-field levels are close, the effect of these has to be taken into account for a quantitative interpretation of the experiment.[3] (2) There are indications that for singlet ground-state systems, exhibiting a ferromagnetic ordering,[4] the effect of phonons on the collective excitations may have an important influence.[5] (3) The strain-ion coupling constant deduced from such an experiment is of interest for estimating structural transition temperatures as well as spin-lattice relaxation times.[6] (4) In cases where the crystal-field levels hybridize into electron bands, the strain modulation of the crystal-field levels produces the deformation potential.[7]

For our investigation the simple rocksalt-structure compound PrSb has been chosen, which is known to exhibit a singlet ground-state system with negligible exchange.[4] It was grown by directional solidification in a large temperature gradient in a sealed tantalum crucible. The $Pr^{3+}(^3H_4)$ state splits in the cubic field into the levels (energies in degrees kelvin) Γ_1 (0 K), Γ_4 (73 K), Γ_3 (125 K), Γ_5 (239 K), as determined by neutron-scattering techniques.[4,8] Elastic measurements are shown in Fig. 1 for the $c_{11}-c_{12}$ and c_{44} modes. Also shown for comparison are results for LaSb, which has the same crystal structure as PrSb, but no crystal-field levels for the La^{3+} ion. Plotted are the temperature dependences of the elastic constants relative to the elastic constants at $T=200$ K. For this temperature the absolute elastic constants are (in 10^{11} erg/cc), for PrSb, $c_{11}-c_{12}=11.0$, $c_{44}=2.0$; LaSb, $c_{11}-c_{12}=7.2$, $c_{44}=1.9$. One notices from Fig. 1 a normal behavior from LaSb as expected, i.e., an increase towards lower temperatures and a flattening out below 20 K. In contrast to this behavior the elastic constants for PrSb show pronounced minima at 23 K for $c_{11}-c_{12}$ and at

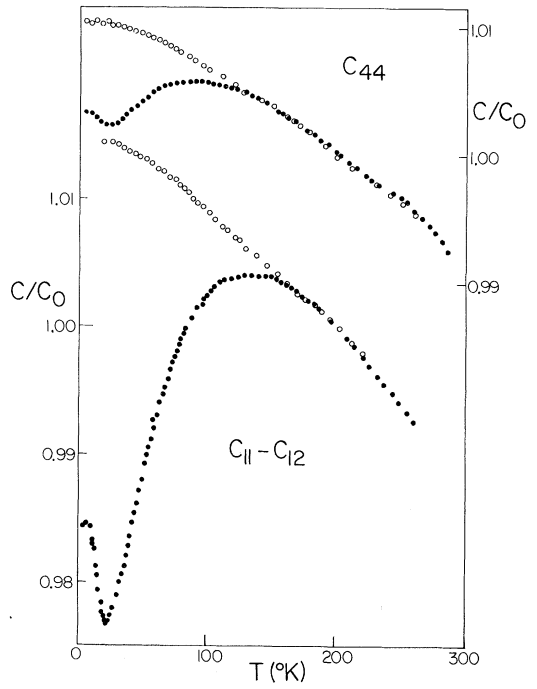

FIG. 1. Elastic constant ratios $c(T)/c(200\text{ K})$ for $c_{11}-c_{12}$ and c_{44}. Full circles, PrSb; open circles, LaSb. For values of $c(200\text{ K})$ see text.

25 K for c_{44}. The depth of these minima is about 3.7% for $c_{11}-c_{12}$ and 0.7% for c_{44}. In both cases the elastic constants at the lowest temperatures (4 K) rise only to a fraction of the normal elastic constant and become temperature independent for $T<8$ K.

A theoretical description of these effects starts by noting that for cubic symmetry $c_{11}-c_{12}$ belongs to the symmetry strains $\epsilon_2=(\frac{1}{2})^{1/2}(\epsilon_{xx}-\epsilon_{yy})$, $\epsilon_3=(\frac{1}{6})^{1/2}(2\epsilon_{zz}-\epsilon_{xx}-\epsilon_{yy})$ which transform under the two-dimensional representation Γ_3; c_{44} belongs to $\epsilon_{xy}, \epsilon_{xz}, \epsilon_{yz}$ (Γ_5); and $c_{11}+c_{12}$ belongs to the volume strain $\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz}$ (Γ_1). Therefore, the strain-ion interaction can be written, in lowest order,

$$
\begin{aligned}
H'(c_{11}-c_{12}) &= -g_2[(c_{11}^0-c_{12}^0)/N]^{1/2}\textstyle\sum_i(\epsilon_2 O_{2i}^2-\epsilon_3 O_{2i}^0),\\
H'(c_{44}) &= -g_3(c_{44}^0/N)^{1/2}\textstyle\sum_i 2\epsilon_{xy}(J_xJ_y+J_yJ_x)_i+\cdots,\\
H'(c_{11}+2c_{12}) &= -g_1[(c_{11}^0+2c_{12}^0)/N]^{1/2}NJ^2(\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz}),
\end{aligned}
\tag{1}
$$

where c_{ij}^0 are the background elastic constants, the $O_2^2=J_x^2-J_y^2$, $O_2^0=2J_z^2-J_x^2-J_y^2$ are the Stevens operators for the rare-earth ion.[9] This interaction Hamiltonian is the same as commonly used for the cooperative Jahn-Teller effect. However, since the singlet ground state is well separated from the excited crystal-field levels, and the matrix elements of H' between Γ_1 and the next Γ_4 are zero, one does not get a structural transition in this case. A rather unexpected result of the neutron-scattering study[8] was that the crystal-field levels listed above for this metallic compound fit a point-charge model very well. Therefore, we can use the wave functions of such a calculation also to determine the strain depen-

dence of the energy levels[10]:

$$|E - E^0(\Gamma_j) + \langle \Gamma_j' | H' | \Gamma_j \rangle| = 0, \quad (2)$$

where the $E^0(\Gamma_j)$ are the energies listed above. The elastic constants can be calculated by constructing the free energy from the $E(\Gamma_j, \epsilon)$ and taking the second derivative. The result can be expressed in terms of thermal averages of the derivatives of these energies:

$$\frac{c - c_0}{N} = \left\langle \frac{\partial^2 E}{\partial \epsilon^2} \right\rangle - \beta \left\langle \left(\frac{\partial E}{\partial \epsilon} \right)^2 \right\rangle + \beta \left\langle \frac{\partial E}{\partial \epsilon} \right\rangle^2, \quad (3)$$

where the third term on the right-hand side does not contribute. The result of this calculation is shown in Fig. 2. The bulk modulus does not show any temperature dependence in the approximation of Eq. (1). Clearly the results for $c_{11} - c_{12}$ and c_{44} exhibit the salient features of our experimental results of Fig. 1.

For $c_{11} - c_{12}$ the minimum in the theoretical curve (Fig. 2) occurs at 24 K compared to the experimental 23 K. Furthermore, for temperatures below the minimum the elastic constant, both calculated and measured, rises only a small fraction of the total anomaly and becomes temperature independent for $T < 8$ K. Since the high-temperature tail of the calculated anomaly is still quite appreciable for $T \sim 300$ K, it is difficult to make a complete quantitative comparison for the whole temperature range. Note that the absolute value of the elastic constants quoted above for PrSb and LaSb are only known to about 1% accuracy. From the experimental results of Fig. 1 we estimate a coupling constant $g_2(c_0/N)^{1/2} \sim 10$ meV/ion. It is interesting to note that a point-charge calculation gives 51 meV/ion.

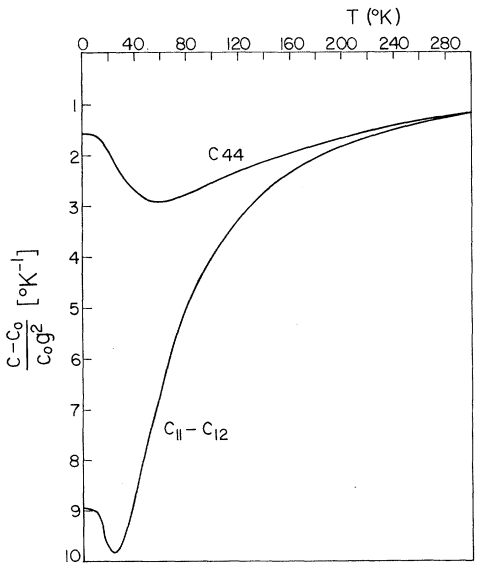

FIG. 2. Calculated elastic constants $(c - c_0)/g^2 c_0$ for $c_{11} - c_{12}$ and c_{44} for PrSb. g is the coupling constant g_2 or g_3. c_0 is the background elastic constant.

For c_{44} the agreement between theory and experiment is less satisfactory. We get a calculated minimum at 60 K compared to the measured one at 25 K. We determined c_{44} from two experiments for (110)- and (100)-axis propagation with identical results, excluding possible errors due to misalignment of the transducers. The magnitude of the elastic anomaly for c_{44} compared to $c_{11} - c_{12}$ is roughly the same both experimentally and theoretically. The measured coupling constant is $g_3(c_0/N)^{1/2} \sim 4$ meV/ion compared to a point-charge estimate of 34 meV/ion. Higher-order terms in the strain for both $c_{11} - c_{12}$ and c_{44} do not give contributions.

We have also measured other elastic modes (c_{11} and $c_{11} + c_{12} + 2c_{44}$) which exhibit similar features as the symmetry modes discussed above. In fact, the size and the temperature dependence of the anomaly agrees quite well with what one expects from calculations based on the three symmetry modes of Eq. (1).

Next we show experimental results for dhcp Pr. The crystal we used for these measurements was cut from the same batch as the one used for other experiments.[11] In Fig. 3 we show temperature dependences for two elastic constants: a longitudinal (c_{33}) and shear wave (c_{44}) propagating along the hexagonal c axis. For c_{33} one notices an elastic anomaly below 160 K. Similar to the case of PrSb one notices a minimum of about 5% in c_{33} at about 30 K. Again below 30 K the elastic constant does not regain its full value. The c_{44} mode shows an anomaly of somewhat different nature[12] as shown in Fig. 3.

It is clear that these elastic anomalies can be explained along the same lines as for PrSb. However, because there are two inequivalent sites for the Pr ions, because the crystal-field levels are not very well known (although the ground state is a singlet for both sites), and because exchange interactions are not negligible in this case, we do not try to interpret these results quantitatively.[13]

There remains the interesting question of the existence of a magnetic phase transition in dhcp Pr. Polycrystalline Pr shows a magnetic phase transition at ~25 K; however, in single-crystal Pr, neutron measurements failed to detect any long-range order down to 1.7 K.[13,14] On the oth-

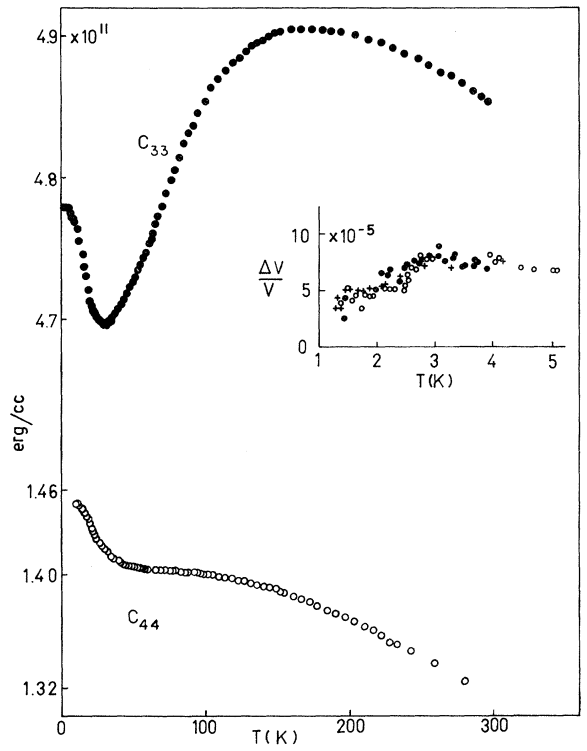

FIG. 3. Temperature dependence of c_{33} and c_{44} for dhcp Pr. The inset gives three runs (three different symbols) for the sound-velocity change $\Delta V/V$ of the c_{33} mode below 5 K.

er hand, hyperfine specific-heat measurements indicate an ordered state in the 100-mK region.[11] In the inset of Fig. 3 we show elastic-constant measurements for the c_{33} mode from 5 down to 1.4 K. Shown are measurements from three different runs. All of them show a very small anomalous decrease below 3 K with a slope of $\Delta V/V \sim 2\times10^{-5}$ per degree. No measurable attenuation change accompanies this small anomaly. While this feeble indication is no clear-cut proof for the existence of an induced magnetic phase transition, it nevertheless suggests an anomaly for $T < 1.4$ K. It should be noted that for singlet ground-state systems undergoing exchange-induced ordering, the anomalies of the thermodynamic quantities at the transition temperatures are appreciably reduced in magnitude.[4]

In conclusion, we have shown for the first time the influence of crystal-field levels on elastic constants in a situation (PrSb) where there are no competing influences due to exchange interactions or softening of elastic modes. These effects can be satisfactorily explained. We also have shown results for a more complicated situation, where these other effects can no longer be neglected (dhcp Pr).

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Note added.—J. D. Greiner, R. J. Schiltz, J. J. Tonnies, F. H. Spedding, and J. F. Smith (to be published) have also measured the elastic constants of dhcp Pr with very similar results.

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