**Calorimetry and Inelastic Scattering Studies of the
Vibrational Entropy of Alloy Phases**

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**Progress Report (2000)
(covering work through January, 2001)**

for the

U. S. Department of Energy
Office of Basic Energy Science
Division of Materials Science
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from

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1. Context and Related Issues for DoE BES

This research is on the entropy of materials, particularly alloy phases. It is an experimental effort utilizing inelastic neutron scattering facilities at two DoE facilities: Oak Ridge National Laboratory (HFIR) and Argonne National Laboratory (IPNS), and the NIST Center for Neutron Research. Collaborators in this work include Dr. J. Lee Robertson (ORNL) and Dr. R. J. McQueeney (LANL).

I was one of the three principal investigators on the proposal (4.4 M\$) to build a high intensity chopper spectrometer, HELIOS, at the Los Alamos National Laboratory. This evolved into a proposal for a second-generation instrument, VERTEX, which Rob McQueeney and I presented in December 2000 to the SPSS Enhancement Project Review Committee at LANSCE. Both HELIOS and VERTEX received strongly favorable reviews, but the state of operations at LANSCE makes it premature to develop additional instruments for the Lujan Center. At present I am considering seriously the P.I. role for a 4-5 yr, 12 M\$ chopper spectrometer project at the SNS.

Although the Lujan Center has not been productive as a facility, scientific interactions with McQueeney have been highly successful. One of my graduate students, Michael Manley, is completing his Ph.D. thesis now, and will be a Director's postdoc at LANL in MST-10. Mike's thesis includes a significant success in measuring the phonon DOS of uranium metal (described below [1]), and this will likely extend to phonons in ^{242}Pu . I have recently received a Q clearance, and I hope that Manley, McQueeney, and I will be able to make measurements on phonons in ^{242}Pu under pressure.

2. Completed Research

The free energy change, ΔF , of an alloy phase transformation is:

$$\Delta F = \Delta E - T(\Delta S_{\text{config}} + \Delta S_{\text{vibr}} + \Delta S_{\text{el}} + \Delta S_{\text{cf}}) \quad .$$

The change in configurational entropy, ΔS_{config} , is well-known. Our measurements of the change in vibrational entropy, ΔS_{vibr} , have now attracted considerable attention. Under this DoE grant we seek to understand the origin of the vibrational entropies of various alloy phases. In recent work with f-electron metals we find a large contribution from the electronic entropy, ΔS_{el} , and in the case of cerium metal we were able to quantify the Schottky entropy associated with crystal field level excitations, ΔS_{cf} [2-4].

Figure 1 shows the spectacular softening of the phonon DOS of α -uranium metal from 0 to 913 K [1]. These data, taken by Mike Manley (and me too at LRMECS), cannot be explained by the classical argument involving thermal expansion against the bulk modulus. They require a temperature-dependent change in the interatomic forces.

Interestingly, although the interatomic potential becomes softer with temperature, it remains harmonic.

FIG 1. The phonon DOS of uranium. Data from 300 K and above were obtained from spectra acquired with the Fermi-Chopper Spectrometer (FCS) at the National Institute of Standards and Technology. Data from 300 K and below were measured on the Low Resolution Medium Energy Chopper Spectrometer (LRMECS) at Argonne National Laboratory. The curves labeled DOS_calc, LRMECS_calc and FCS_calc were all calculated from a previous force constant model of Crummett, et al. The 913 K α -uranium DOS is superimposed on all curves above 300 K and the 300 K data is superimposed on all curves below 300 K. The three solid state phases, orthorhombic (α), tetragonal (β) and body centered cubic (γ) are compared at the top.

We measured the phonon DOS of nanocrystalline Ni_3Fe a couple of years ago. These data showed an enhancement in the number of vibrational modes at low energies, and this was suggested to be surface modes localized around the elastic discontinuity of the grain boundaries in the material. These previous data were limited to energies above about 2 meV, however. In a “shot-in-the-dark” experiment we measured the inelastic scattering at energies from 1 to 20 micro-eV at the high flux backscatter spectrometer at NIST. It took

a while for us to interpret these data, but we are now confident that some, although not all, of the low-energy modes in nanocrystalline materials extend to the micro-eV range [5]. These extremely-low energy modes must be a cooperative phenomenon involving the mutual movements of many crystallites in the nanocrystalline material. We also studied relaxations of the atom structures in grain boundaries by small-angle neutron scattering [6].

In other work, we used calorimetry to measure the internal strain energy in Pd_3V [7]. The strain energy from anisotropic thermal contractions of grains in the tetragonal tetragonal (DO_{22} -ordered) Pd_3V phase makes a non-negligible contribution to the heat capacity, destabilizing the ordered phase for microstructural reasons. The same type of heat evolution was found in polycrystalline α -uranium, as compared to single crystals, but this work is still in progress.

Finally, Peter Bogdanoff and I measured the change in the phonons above and below the martensitic transformation of the shape-memory alloy NiTi [6]. The evolved heat, measured by calorimetry, was found to be consistent with the change in vibrational entropy. By modeling the lattice dynamics, it appears that the weakness of the transverse component of the first-neighbor force constants in the austenite phase is responsible for the large vibrational entropy of this bcc-like phase. This hypothesis is also consistent with the development of a soft mode in the austenite phase that has been associated with the mechanism of the martensitic transformation.

Graduate Students supported under this grant

Peter Bogdanoff, Materials Science, Ph.D. expected: 2001

Peter won a NDSEG Fellowship, which provided most of his support in his first years.

Michael Manley, Materials Science, Ph.D. expected: 2001

Mike Manley transferred to the Los Alamos Neutron Science Center for inelastic neutron scattering studies on Ce, U, and perhaps Pu metal. His support is derived in part from the DoE Weapons Program.

Alan Yue, Materials Science, Ph.D. expected 2003.

Other personnel supported by this grant in 1998-9 have been:

Prof. Brent Fultz, Professor of Materials Science, Caltech

Funds

Our bookkeeping shows that there will be no carryover of funds into the next year of the grant.

Publications in 2000

Publications in archival journals:

1. M. E. Manley, B. Fultz, R. J. McQueeney, C. Brown, W. L. Hults, J. L. Smith, D. J. Thoma, R. Osborn, and J. L. Robertson, "Large harmonic softening of the phonon density of states of uranium", Phys. Rev. Lett., in press.
2. M. E. Manley, R. J. McQueeney, B. Fultz, G. Kwei, R. Osborn, and P. Bogdanoff, "Vibrational and electronic entropies of γ -cerium and β -cerium measured by inelastic neutron scattering" Philos. Mag., submitted.
3. R. J. McQueeney, M. E. Manley, B. Fultz, G. Kwei, R. Osborn, and P. D. Bogdanoff, "The dynamic magnetic susceptibility in γ -cerium, β -cerium, and low-density cerium alloys", submitted to Phys. Rev. B.
4. M. E. Manley, R. J. McQueeney, J. L. Robertson, B. Fultz, and D. A. Neuman, "Phonon densities of states of γ -cerium and δ -cerium measured by TOF inelastic neutron scattering", Philos. Mag. Lett. 80 (2000) 591-596.
5. A. F. Yue, B. Fultz, R. Dimeo and D. A. Neumann, "Low-energy phonons in nanocrystalline Ni_3Fe ", submitted to Phys. Rev. Lett.
6. H. N. Frase, B. Fultz, J. L. Robertson and S. Spooner, "Structural Relaxation within the Grain Boundaries of Nanocrystalline Ni_3Fe ", Philos. Mag. B 80 (2000) 1545-1554.
7. M. E. Manley, B. Fultz, and L. J. Nagel, "Heat capacity and microstructure of ordered and disordered Pd_3V ", Philos. Mag. B 80 (2000) 1167-1178.
8. P. Bogdanoff and B. Fultz, "The role of phonons in the thermodynamics of the martensitic transformation in NiTi ", Philos. Mag. B, 81, (2001) 299-311.

Papers by students supported under this grant:

9. Peter Bogdanoff, "Vibrational Entropies of Cu-Au Alloys", First Prize Student Poster Competition, Los Alamos Neutron Science Center (LANSCE) Users' Group Meeting, January, 2000.
10. Michael Manley, "Vibrational Softening in α -Uranium", Los Alamos Science, Nov. 26, 2000 (LA-UR-00-4100) p. 202-207.