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Electronic Properties and the Lattice Instability of Laves-Phase ZrV_2

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Pure, perfect, single-crystal ZrV_2 does not undergo a structural phase transformation but all other sample modifications, including twinned single crystal, do transform (~100 K) from the cubic to a rhombohedral phase. All samples exhibit, in addition, an electronic instability (also ~100 K). An anomaly in the ultrasonic velocity occurs at higher temperatures (~150–180 K) for pure polycrystalline ZrV_2 samples.

Since the discovery of martensitic transformations[1] in the high-T_c superconductors V_3Si and Nb_3Sn, it has become increasingly clear that compounds whose lattice and electronic structures seem to favor superconductivity often exhibit lattice softening and/or structural transformations or, in extreme cases, exhibit a thermodynamic instability of the crystal structure itself.[1-3] In order to elicit the relationship, if any exists, between these instabilities and high-temperature superconductivity, the nature of the lattice transitions themselves has become the focus of much of the current research in this area. Among the most studied examples of materials in which the two phenomena coexist [$A15$, VRu, and MoRe alloys; and $B1$ compounds, e.g., Refs. 1–3] no common characteristics connecting lattice instability and high T_c have emerged, either because of the very different natures of the particular lattice transitions or because the role of sample microstructure in the observed properties has not been unraveled.

ZrV_2, HfV_2, and their pseudobinary alloys ($Hf_xZr_{1-x}V_2$) have the highest superconducting transition temperatures[4] among the cubic Laves-phase compounds ($C15$) and have, in their arc-cast modification, been shown to undergo lattice transformations from the cubic structure to a low-temperature phase of lower symmetry[5,6]: ZrV_2 transforms to a rhombohedral symmetry[6]; HfV_2, to an orthorhombic crystal structure.[5] The similarities between these compounds and the high-T_c $A15$ alloys are striking in that, for those low-temperature transport properties found to be anomalous in the $A15$-structure group, there are analogous abnormalities[7-9] observed for both ZrV_2 and HfV_2. On the other hand, the origins of the structural transformation in the two different symmetry classes are clearly different since the $C15$ transitions are unambiguous first-order transformations[6] and specific heat data[10] indicate no unusually large electron density of states at the Fermi level. Thus, a study of the $C15$ alloy system allows both an intraclass as well as an interclass comparison of materials in which a lattice instability accompanies high-T_c superconductivity.

The ZrV_2 samples used in the present research were grown[11,12] by a variation of a traveling-solvent-zone-melting technique in ultrahigh vacuum, using a vertical-electron-gun-traverse system. All are single-phase cylindrical rods of 3.6 mm diameter, ranging in length from 2 to 12 mm and having dislocation densities[13] $< 10^7/\mathrm{cm}^2$. Since the arc-cast ZrV_2 used in earlier reported studies exhibited a large variation of given electronic properties depending on the metallurgical condition of the sample,[5-10] a number of different modifications of ZrV_2 were grown for the present investigation. All of the experiments discussed here were performed with members of the same set of four samples: a pure perfect single crystal 2 mm long, a pure twinned single crystal 7.23 mm long, a pure multigrained polycrystalline sample 6.32 mm long, and 11.6-mm-long polycrystalline sample containing approximately 1% by volume of Zr inclusions.[14,15]

To determine the existence of phonon softening or an actual structural transformation, these samples were evaluated first by ultrasonic techniques, followed by elastic-neutron-scattering experiments. Resistivity was then measured as a function of temperature to determine the order of the phase transition, followed by T_c and resistive critical-field measurements to observe differences in superconducting parameters as a function of sample type and microstructure.[16]

The ultrasonic technique is a modification of the coherent-pulse-detection scheme devised[17,18] by Williamson and Eden for measuring longitudinal (and shear) sound velocities in liquids (and solids). The carrier (or transducer) frequency used in our experiments was 10 MHz. [The intrinsic or natural resonant frequency of ZrV_2 is approximately 10 kHz.[9]] As shown in Fig. 1, the data for each of the three samples tested show a dramatic change in longitudinal sound velocity (v_l) between 95 and 120 K. There was no appreciable increase in signal attenuation (to within 1 dB/cm) at the critical point for any of these specimens, although an increase is to be expected when a lattice transformation occurs.[9,19] In addition, the character of the sound-velocity behaviors during heating and cooling are distinctly different for the pure polycrystalline material. The usual behavior (observed for the Zr-included sample and the twinned single crystal) is for v_l to decrease monotonically from room temperature to the structural-transformation temperature (T_M). As seen in Fig. 1, however, there is for the pure polycrystal a pronounced cusp in v_l from ~150–180 K. There were no accompanying changes in signal attenuation or transmitted pulse shape over these temperatures. We note that Finlayson, using well-homogenized arc-cast ZrV_2 samples with T_M's slightly above that of this sample, reports[20] large increases in attenuation at approximately this temperature in internal-friction experiments (10 kHz).

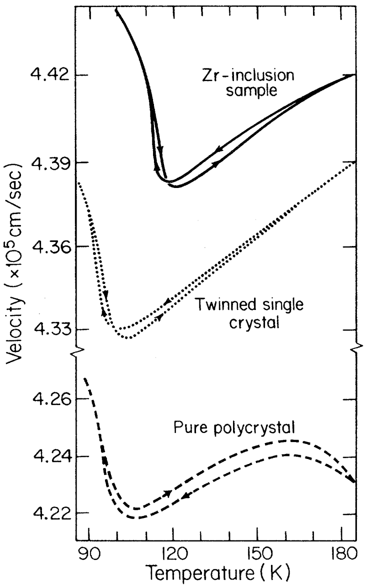

FIG. 1. The logitudinal sound velocity for the different ZrV_2 modifications. (Transducer frequency 10 MHz.) The precision of the relative-velocity measurements is better than the line thickness.

Subsequent to the ultrasonic study, coherent elastic neutron scattering experiments were carried out to confirm the existence of lattice transformations in these samples.[21] The perfect single crystal, which was not investigated ultrasonically because of its short length, shows no lattice transformation down to 10 K; the twinned single-crystal and Zr-included samples, on the other hand, were found to transform in agreement with the ultrasonic results. The Zr-included sample underwent a clear transition between 121 and 115 K, consistent with earlier studies on arc-cast material,[6] but the apparent mosaic spread below T_M increased enough that meaningful low-temperature data could not be obtained.[22] The twinned single crystal showed a transformation of 70% of its volume to a rhombohedral phase[23] between 99 and 87 K; to first order in crystal strain, there is no volume change in this low temperature phase.

Resistivity and resistive T_c were measured using a standard pressure contact (dc) four-point-probe apparatus in a liquid-helium cryostat.[12] The resistivity as a function of temperature was measured from 300 to 4.2 K and the data for a given sample were then normalized to the measured room-temperature resistivity (~ 120 $\mu\Omega$ cm). The normalized curves for all samples are linear with the same slope above 150 K. Below this temperature the curve gradually falls to a minimum, followed by an increase in resistivity to some maximum value beyond which the curve then continues with constant slope to the superconducting transition temperature. The general character of this behavior is shown in Fig. 2(a) for the nontransforming single crystal.[24] In Fig. 2(b) the region of anomalous resistivity, 75–125 K, is shown for the three structurally transforming samples; hysteresis in the heating-cooling data is directly superposed on the anomaly observed for the nontransforming sample. The size of the hysteresis indicates a rather large latent heat of transformation, consistent with earlier measurements on arc-cast material.[10] Taken together, the existence of a latent heat, the volume conservation observed in the neutron experiments, and the decrease and discontinuity of slope in the ultrasonic velocity indicate these transformations are thermodynamically first order, driven, perhaps, by a softening phonon mode, although that is still to be proven.

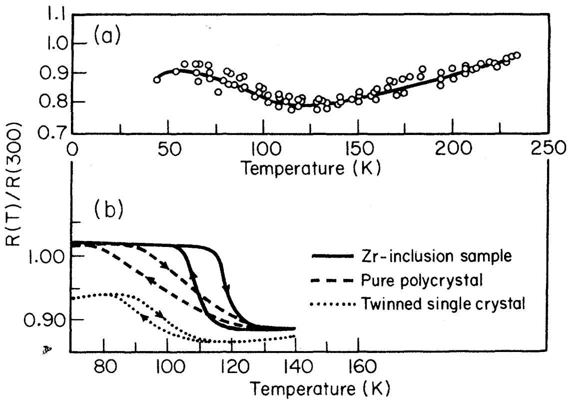

FIG. 2. (a) Normalized resistivity curve for the nontransforming single crystal. Circles represent both cooling and heating data. (b) Resistivity hysteresis for the transforming modifications of ZrV_2. These loops occur superimposed on the nontransforming background shown in (a).

The existence of the resistivity anomaly in the nontransforming sample itself, however, indicates that there is also an electronically driven transition at ~ 100–110 K which is independent of the existence of the actual structural transformation. Thus, the lattice transformation is microstructurally induced in imperfectly crystalline samples. This interpretation is also reinforced by a comparison of the ranges over which changes take place in the transport properties versus those seen in the neutron data. For example, the resistivity hysteresis and changes in v_l for the Zr-included sample extend from ~ 127 to 104 K, while the neutron experiment indicates a lattice transition from 121 to 115 K; for the twinned single crystal the changes in transport properties are from ~ 105–84 K and the neutron study indicates onset and completion from 99–88 K for structural effects.

The general character of the temperature-dependent resistivity of all the ZrV_2 modifications studied suggests that there is an electronic instability which, perhaps because of internal-local-stress distributions in imperfectly crystalline samples, causes an unstable softening phonon to condense into the lattice. The behavior of the resistivity, when only the electronic instability is present, is reminiscent of a shifting of electrons in Brillouin zones which overlap the Fermi surface[2] signaling, perhaps, a transition from metallic to covalent behavior.[25]

The picture that emerges from this research highlights the dominant role of microstructure in the observed properties of ZrV_2 and the necessity for obtaining perfect, or nearly perfect, single-crystal samples if intrinsic lattice properties are to be separated from those which may be microstructurally induced.[26] A similar situation exists, we believe, in current research on the $A15$ materials, especially Nb_3Sn and V_3Si, in which the existence or nonexistence of a martensitic lattice transformation seems to be inordinately sample dependent; and, like ZrV_2, both transforming and non-transforming samples have approximately the same superconducting-transition-temperature characteristics. Assuming that an $A15$ study similar to the present one could show that local stresses play a significant role in the observed electronic behavior, as they clearly do in ZrV_2, not only could the static[26] versus dynamic[27] character of the lattice transformation be determined, but also it should then be possible to discriminate between the various theories describing the possible electronic instabilities of the $A15$ structure.[1,28]

The special contribution of G. Shirance who performed the neutron experiments on the Zr-included polycrystal and the perfect-single-crystal samples is gratefully acknowledged by the authors. We would like to thank C. Garland of the M. I. T. Chemistry Department for the use of his ultrasonics equipment, T. R. Finlayson for frank discussions concerning his ongoing research of Laves-phase compounds, D. Moncton and B. Matthias for bringing this problem to our attention, and R. M. Rose for discussions and constant encouragement. This work was supported in part by the U. S. Department of Energy and the National Science Foundation.

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[13] This value is an upper bound; the brittleness of the material precluded obtaining larger areas for observation.

[14] The perfect single crystal has a ⟨211⟩ orientation along the cylinder axis; the twinned-single-crystal orientation is ~13° from ⟨110⟩ toward the ⟨321⟩ direction. The lattice constant for both single crystals is $(7.4458\pm4)\times10^{-4}$ Å.

[15] The properties of arc-cast ZrW_2 will be reported at a later time.

[16] The superconducting parameters for these samples will be published separately. Here it suffices to note that the single crystals both have the same midpoint T_c of 8.72 K; the Zr-included sample has a T_c of 7.6 K; and the polycrystalline material has a broad double-hymped transition extending from 8.73 to 7.73 K.

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[19] W. Rehwald, Adv. Phys. 22, 721 (1973).

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[21] These experiments were carried out at Brookhaven National Laboratory, Upton, New York.

[22] Since information on the low-temperature-phase lattice structure could not be extracted from this Zr-inclusion-sample data, the pure polycrystal was not evaluated with neutrons.

[23] Consistent with the diagonal lattice contraction observed by Moncton (Ref. 6), we observed all four possible rhombohedral domains in the transformed material with an attendant double-scattering background which precludes a definitive statement on whether this transition is, in fact, driven by a softening zone-center optical mode (Ref. 12). The data obtained, however, are consistent with an $R\bar{3}m$ ($D_{3d}{}^5$) space group.

[24] The precision of this measurement is a factor of 3 less than that of the other samples because the 2-mm single crystal had a large cross section relative to the distance between voltage probes (Ref. 12).

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[28]See, e.g., R. N. Bhatt, Phys. Rev. B 17, 2947 (1978).

Charged Particles in Polarizable Fluids

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A molecular-dynamics calculation of the work of introducing a charge in a polarizable fluid leads to about twice the value predicted by the Born continuum model. The screened Coulomb field reaches its macroscopic limit about three molecular diameters from the charge but is larger than the continuum dielectric prediction because of higher-order polarizability corrections. The diffusion coefficient leads to a Stokes radius that corresponds roughly to a singly ionized particle and its solvation shell diffusing as a unit.

Despite the importance of solutions of electrolytes in many physical and particularly biophysical situations it is remarkable that primary reliance for estimating both equilibrium and transport properties of such systems is still based on continuum models.[1,2] Recently several works concerned with ion dynamics in polar fluids have appeared, but these present either continuum models[3] or an heuristic approach[4] to account for relaxation of the solvent as the ion moves through it. In hopes of stimulating the development of molecularly based statistical-mechanical theories for these systems and to check on the accuracy of continuum-model predictions, we present here a molecular-dynamics study of a charged particle in an idealized solvent consisting of point polarizable atoms.

The model is defined by the potential-energy function

$$U=-q\sum_i \vec{p}_i\cdot\frac{\vec{r}_{i0}}{r_{i0}^3} - \sum_{i>j}\vec{p}_i\cdot\overleftrightarrow{T}_{ij}\cdot\vec{p}_j+\sum_i\frac{P_i^2}{2\alpha}+\sum_{i>j}V(r_{ij}). \qquad (1)$$

The first term describes the interaction of the charge, q, of the nonpolarizable particle, 0, with the induced dipoles, $\vec{p}_i$. The second term represents the induced-dipole–induced-dipole interaction via the dipole tensor $\overleftrightarrow{T}=\nabla\nabla(1/r)$. The third term is the potential energy of induced-dipole for formation, where α is the isotropic point polarizability of the solvent particles. Finally, the last term represents the pairwise short-range interaction between all particles including the charged particle. For this the Lennard-Jones 12-6 potential was used with the well depth at $r=2^{1/6}\sigma$ denoted by ϵ_{LJ} to avoid confusion with the dielectric constant ϵ. The induced polarization at particle i is proportional to the instantaneous electric field at i,

$$\vec{p}_i=\alpha\vec{E}_i=\alpha[q(\vec{r}_{i0}/r_{i0}^3)+\textstyle\sum_j\overleftrightarrow{T}_{ij}\cdot\vec{p}_j]. \qquad (2)$$

In the computations the electric field at i is obtained iteratively from Eq. (2) using the value of p_i at the preceding step. If the iteration is started from the polarization due to the pure Coulomb field of the charged particle, the terms in the expansion in powers of α for

$$\vec{E}_i=q\frac{\vec{r}_{i0}}{r_{i0}^3}+\alpha q\sum_{j\neq i}\overleftrightarrow{T}_{ij}\cdot\frac{r_{j0}}{r_{j0}^3}+O(\alpha^2) \qquad (3)$$

can be examined separately.

The linear term in Eq. (3) is correctly given by the dielectric continuum theory when particle i is far from the charged particle. In evaluating the linear term for large distances the dominant contribution to the sum is from screening particles j which at large separations are uncorrelated with either the charged particle or the particle i. Thus,

$$\vec{E}_i=\frac{q\vec{r}_{i0}}{r_{i0}^3}\left[1-\frac{8\pi}{3}\rho\alpha\right]+O(\alpha^2), \qquad (4)$$

independent of the detailed nature of the forces. The term in brackets is the asymptotic value of the screening function $S(r)$ to first order in the polarizability. Continuum theory predicts the screening as the usual $1/\epsilon$, modified by a cavity-field correction because the field is evaluated at the center of a particle. Since a particle in continuum theory is considered as being contained in