

Stabilization of bcc Co via Epitaxial Growth on GaAs

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A new metastable phase of cobalt—body-centered cubic—has been synthesized by use of molecular-beam epitaxial growth to stabilize the crystal structure. Large ($1 \times 1 \text{ cm}^2$) films have been grown on (110) GaAs and characterized by high-energy electron diffraction, Auger analysis, x-ray diffraction, magnetometry, spin-polarized photoemission, and ferromagnetic resonance. The results indicate a ferromagnetic material very similar to α -Fe both electronically and magnetically, with a metastable lattice constant $a_0 = 2.827 \text{ \AA}$. This technique provides a general approach for the realizing of metastable phases.

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Employing epitaxial growth to induce formation of nonthermodynamic phases of materials is one of the most intriguing aspects of modern thin-film material preparation. The present paper describes the use of molecular-beam epitaxy (MBE) to stabilize a metastable phase of cobalt—bcc.

The existence of metastable phases of the $3d$ transition metals is intimately connected with the occurrence of magnetism in certain elements in this series. Mn, Fe, and Co have crystal structures different from their nonmagnetic isoelectronic $4d, 5d$ counterparts. In addition, the five elements, Cr through Ni, all exhibit compressibilities and atomic volumes which are larger than would be expected if the $3d$ series followed the same trends as the $4d$ and $5d$ series. These anomalies have been attributed to the magnetism of these elements and explained by the itinerant-electron model of magnetism¹: spin polarization occurs when the energy gained by splitting bands offsets the increase in kinetic energy due to the filling of high-kinetic-energy (antibonding) states at the top of the majority spin band. Part of this kinetic energy “cost” can be recovered by a lattice expansion. In the detailed balancing of these energies, phases other than the nonmagnetic equilibrium phases predicted by simple band-filling arguments may be stabilized. The occurrence of magnetism in these elements can be viewed as providing an extra degree of freedom whereby metastable states may exist at only slightly elevated energies.²

The several phases observed in the magnetic elements confirm this view. Fe, Co, and Ni are of particular interest because they are known to form ferromagnetic phases. At ambient pressure Ni is fcc up to its melting point, while Co is hcp to 425°C , above which it is fcc (ferromagnetic) until it melts. In Fe, the ferromagnetic bcc α phase persists up to 910°C where it transforms to fcc γ -Fe (antiferromagnetic). This phase obtains to 1390°C where it transforms to δ -Fe, a nonmagnetic bcc phase, which holds to the melting point of 1534°C . The application of high

pressure can induce the nonmagnetic hcp ϵ phase.

Guidance for obtaining the bcc phase of cobalt was derived from a known property of the $\text{Fe}_x\text{Co}_{1-x}$ alloy system.³ As shown in Fig. 1, that system forms a bcc structure over the range $1.0 \geq x > 0.25$. For $x < 0.25$ one obtains progressively mixed phases of bcc (α) plus fcc (γ), pure γ , γ plus hcp (ϵ), and finally pure ϵ . By simple linear extrapolation of the lattice constant from the bcc phase, one obtains a “predicted” value for the lattice constant of bcc cobalt as indicated in Fig. 1. Its value of 2.819 \AA is only 0.2% less than that of a 2×2 construction upon a GaAs lattice. Since it had already been shown⁴ that bcc α -Fe could be successfully grown as a 2×2 construction upon GaAs with a 1.35% mismatch, the outlook for obtaining bcc cobalt seemed promising.

Figure 1 suggests that bcc Co is *almost* a stable phase and a total-energy calculation of the system might yield a local minimum in phase space for bcc Co at the extrapolated lattice constant. This minimum, however, must occur at a higher energy than the energy minimum for the stable hcp phase of Co. In this case,

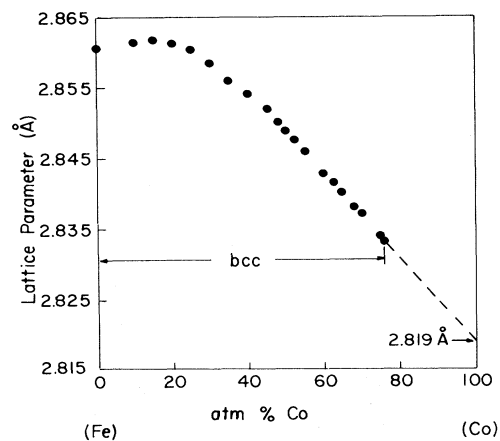


FIG. 1. Lattice constant vs composition for the Fe-Co alloy system (Ref. 3).

the bcc phase of Co is properly termed "metastable." It may be useful to distinguish these structures formed at total-energy minima from those which are forced into some completely nonequilibrium morphology by imbedding them in a foreign matrix. The latter are not properly termed metastable and might better be labeled a "forced structure." The procedure exploited here might be applicable to other systems, serving as a guide for locating the appropriate substrate structure to use for stabilizing the desired phase at its energy minimum. Such an experimental procedure is the natural complement to the total-energy calculations carried out in band theory that predict the lattice constants for the minimum energy of stable and metastable phases. This offers the promise of studying systems which may be both experimentally realized and susceptible to electronic modeling calculations.

The growth was carried out in a PHI Model 400 MBE system using procedures described earlier for growing α -Fe on (110) GaAs.⁴ Auger spectra of the finished films show small ($\approx 2\%$) traces of carbon and oxygen on the surface. The reflection high-energy electron-diffraction (RHEED) patterns obtained during growth are shown in Fig. 2, where they are compared with (110) GaAs and (110) α -Fe. The Co diffraction patterns are seen to have the same symmetry as bcc Fe and the same spacing in all three of the prin-

cipal crystallographic directions on the (110) face. The streak patterns of this 357-Å Co film are not as well developed as those from the 2400-Å Fe film, indicating that the Co is still atomically rough compared to the Fe, but nevertheless single crystal and of the same structure. Above a critical thickness, the bcc structure of Co will no longer hold and the diffraction pattern bifurcates along the [001] and [110] directions, while forming a lattice-work pattern along [111]. X-ray diffraction studies show that thicker films yield both cubic and hexagonal peaks. The cubic peaks show only a $1'$ deviation from the GaAs (220) reflection (using Cu $K\alpha_1$ radiation) indicative of a 0.4×10^{-3} expansion of the d spacing of those planes and a cubic lattice constant of $a_0 = 2.827$ Å. The hexagonal peaks index to yield the published d spacings for hcp Co. The critical thickness depends upon growth conditions, the 357-Å film shown here being the thickest grown without bifurcation. A complete study of the details of growth (flux rate, substrate temperature, and morphology) is underway and shall be reported elsewhere.⁵

The magnetization was measured at room temperature by use of a vibrating sample magnetometer. Specimens were prepared as 5-mm disks and the magnetic field was applied in the plane of the disk. Since the (110) plane contains [001] (0°), [111] (35°), and [110] (90°), the magnetization (M) versus applied field (H) could be obtained readily along each of these axes and the results are displayed in Figure 3. The most obvious features are the following: [001] is an easy axis; [111] is intermediate; and [110] is hard. This is in contrast to the case in α -Fe where [111] is hardest and [110] is intermediate, leading to the reported⁶ first-order spin reorientation which is seen in that material but absent here. This implies a negative value for the cubic anisotropy constant K_1 as opposed to α -Fe where K_1 was positive. Furthermore, the large field needed for saturation along [110] (≈ 2 kOe) indicates that the anisotropy is larger than the value found for K_1 in α -Fe. Available data for the Fe-Co alloy system⁷ indicate that as one moves from Fe to Co, K_1 does indeed go from positive to negative, and by extrapolating to pure bcc Co, as was done in Fig. 1, one would anticipate that $K_1(\text{Co})/K_1(\text{Fe}) \approx -2$. Detailed ferromagnetic resonance measurements, to be reported elsewhere⁸ have confirmed this prediction for the cubic anisotropy constant. A precise measurement of the magnetic moment was obtained by calibration of the magnetometer using a 10^3 -Å film of polycrystalline Ni deposited on a 5-mm disk of the same GaAs substrate material as was used for the Co films. Using a value of $M = 484$ emu/cm³ for the Ni, we obtained $M = 1257 \pm 10$ emu/cm³ for bcc Co. If we use our value for the bcc unit-cell dimension of 2.827 Å, the magnetic moment per atom is $1.53\mu_B$, which is lower than the reported value for hcp Co of 1.714 .⁹

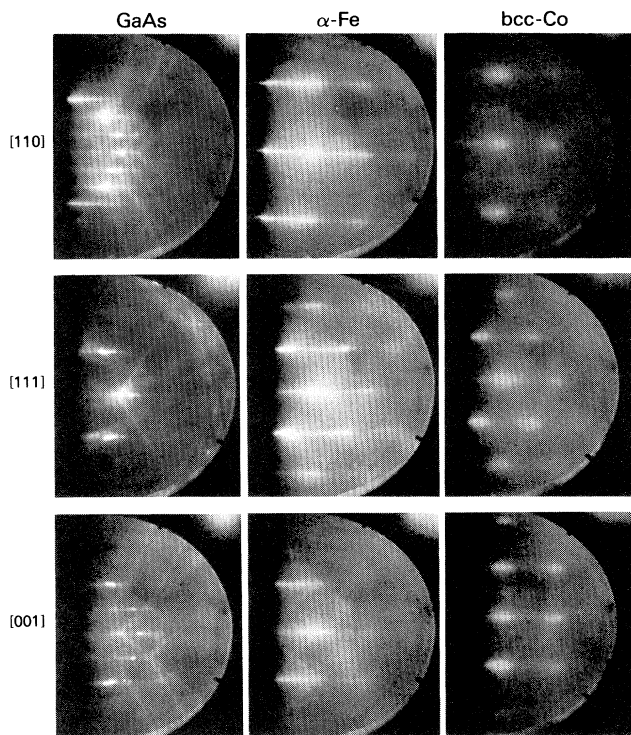


FIG. 2. RHEED patterns of GaAs, α -Fe, and bcc Co obtained along the three principal axes in the (110) plane.

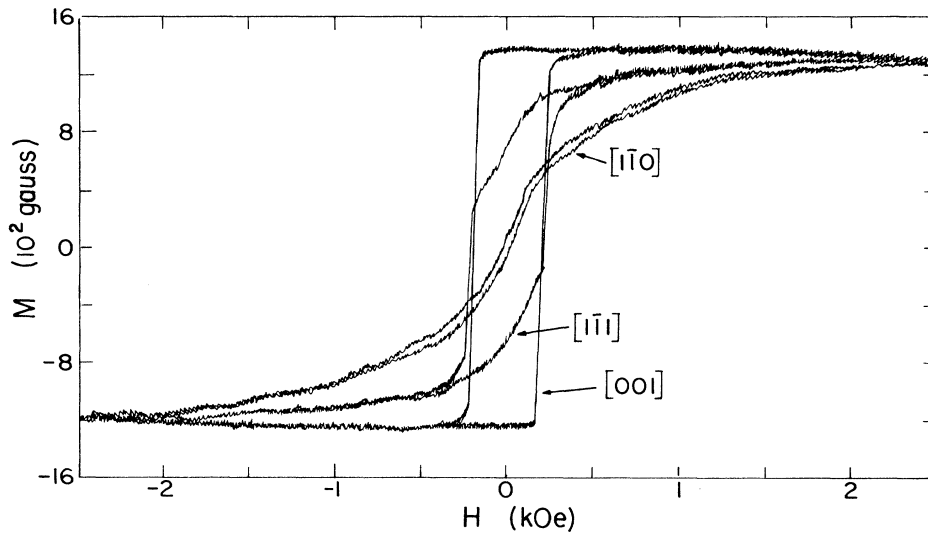


FIG. 3. Magnetization vs applied field along the three principal axes in the (110) plane for a 5-mm disk of bcc Co 357 Å thick on a GaAs substrate. Note the diamagnetism of GaAs at high fields.

Finally, a spin-polarized photoemission study of these films yielded an energy-loss spectrum similar to α -Fe except for a shift in the Fermi-level reference energy of approximately 0.8 eV. This is in agreement with band-theory calculations of bcc Co which indicate that to a first approximation the band structure of bcc Co is that of bcc Fe except for a shift in the Fermi level amounting to 0.9 eV, corresponding to the addition of one electron per atom.¹⁰

It should be noted that recent work has been reported¹¹ on sputtered polycrystalline modulated films of cobalt and chromium. For modulation periods < 50 Å, an x-ray diffraction line is observed from planes parallel to the film surface with a d spacing of 1.96 Å. This was attributed to (110) diffraction from oriented grains of a bcc Co structure having a lattice parameter of 2.77 Å. This represents an 11% volume compression from the bcc Cr lattice in which it was imbedded, and a 6% volume compression from the bcc Co lattice found here. This material might be an example of a "forced structure" defined earlier.

In summary, it has been demonstrated that a "missing" metastable phase of one of the elemental magnetic metals can be stabilized conveniently by thin-film epitaxy in specimens that are of large area and in a useful form for a wide variety of experimental investigations. The metastable lattice spacing, magnetic moment, magnetic anisotropy, and principal electronic levels below the Fermi level have been determined. Many interesting studies remain (e.g., fermiology, electronic levels above the Fermi level, electronic transport properties, etc.) The most important aspect of this work, however, is that it suggests a practical approach to realizing other metastable phases. This is

valuable not only for the help it may provide in understanding the variety of magnetic and crystallographic phases formed by materials, but also in preparing artificially synthesized metastable phases with specifically desired properties. In addition, the realization and characterization of the ferromagnetic 3d metals Fe, Co, and Ni in all of the phases (bcc, hcp, and fcc) would be of enormous usefulness in determining the contributions of magnetism to phase stability and in understanding the occurrence of magnetism in these metals.

This Letter represents a preview of a great deal of work to be published more completely as indicated in the references. The author is indebted therefore to those many authors for permission to cite their results, as well as the U. S. Office of Naval Research which supported this work.

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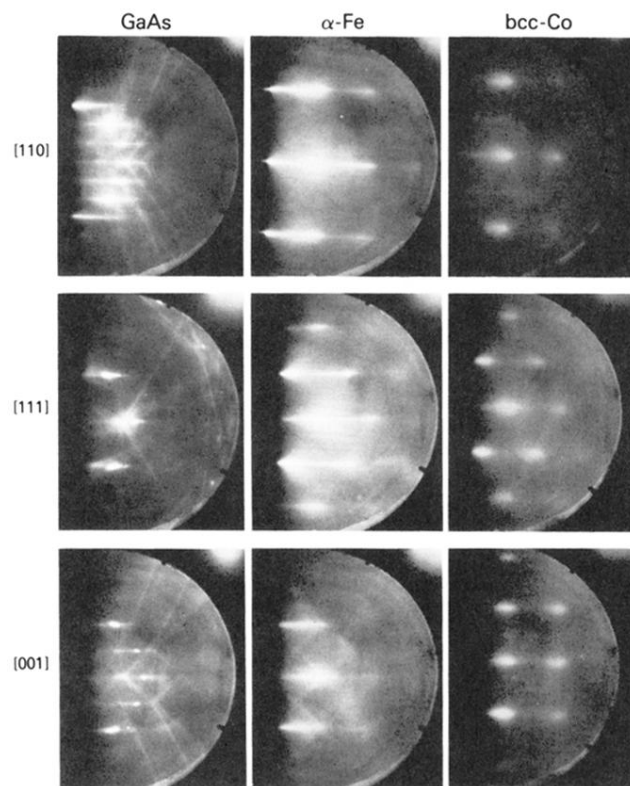


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